



**SYNTHESES AND CHARACTERIZATIONS OF NOVEL
POLYMER MEMBRANE ELECTROLYTES COMPRISING OF
IONICALLY CROSS-LINKED CHITOSAN HYDROGELS FOR
APPLICATION IN SUPERCAPACITORS**

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF DOCTOR OF
PHILOSOPHY

By

DIPANKAR HAZARIKA

PhD/CHE/00548, Dated: 27/10/2021

DEPARTMENT OF CHEMISTRY

SCHOOL OF SCIENCES

NAGALAND UNIVERSITY

LUMAMI-798627

NAGALAND, INDIA

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By

DIPANKAR HAZARIKA

Under the Supervision of

DR. NURUL ALAM CHOUDHURY

Submitted

In partial fulfillment of the requirements for the Degree of
Doctor of Philosophy in Chemistry of Nagaland University

Lumami-798627

Nagaland, India

DEDICATED

To

My Parents

Late Smt. Shikha Rani Hazarika

&

Shri Chakra Hazarika

“Who inspired me to move forward with unwavering determination,
regardless of the obstacles”



नागालैण्ड विश्वविद्यालय NAGALAND UNIVERSITY

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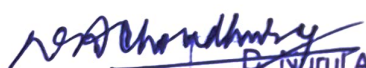
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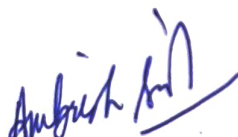
DECLARATION

I, **Mr. Dipankar Hazarika**, bearing registration number **PhD/CHE/00548** with effect from **27/10/2021**, do hereby declare that the contents of the thesis entitled “*Syntheses and Characterizations of Novel Polymer Membrane Electrolytes Comprising of Ionically Cross-Linked Chitosan Hydrogels for Application in Supercapacitors*” is the result of my research on the subject. I also declare that the contents of this thesis did not form basis of the award of any previous degree to me or to the best of my knowledge to anyone else, and that the thesis has not been submitted by me for any research degree in any other University/Institute.

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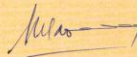
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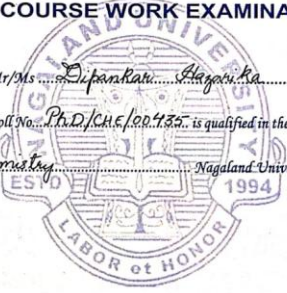
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“No journey of research is ever walked alone; its success is woven together by the efforts of many”

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Dipankar Hazarika

ABBREVIATIONS

Abbreviation	Full Form
AC	Alternating Current
BPC	Black Pearls Carbon
BSK	Bazant-Storey-Kornyshev
CPE	Constant Phase Element
CV	Cyclic Voltammetry
DC	Direct Current
DI	Deionized (water)
DR	Dissolution Ratio
DSC	Differential Scanning Calorimetry
ESs	Electrochemical Supercapacitors
EDLC	Electrical Double Layer Capacitor
EDX	Energy Dispersive X-ray
EIS	Electrochemical Impedance Spectroscopy
ESR	Equivalent Series Resistance
ESSs	Energy Storage Systems
EV	Electric Vehicle
FE-SEM	Field Emission Scanning Electron Microscopy
FT-IR	Fourier Transform Infrared
GCD	Galvanostatic Charge-Discharge
GCCHME	Gradient Cross-linked Chitosan Hydrogel Membrane Electrolyte
GPEs	Gel Polymer Electrolytes
HMEA	Hydrogel Membrane Electrode Assembly
ICCH	Ionically Cross-linked Chitosan Hydrogel
ICCHME	Ionically Cross-linked Chitosan Hydrogel Membrane Electrolyte
KBr	Potassium Bromide
KOH	Potassium Hydroxide

Li-ion	Lithium-ion
LED	Light Emitting Diode
LSV	Linear Sweep Voltammetry
MAB	Metal-Air Battery
Ni-Cd	Nickel-Cadmium
NiMH	Nickel-Metal Hydride
OER	Oxygen Evolution Reaction
ORR	Oxygen Reduction Reaction
PAA	Poly(acrylic acid)
PAAm	Poly(acryl amide)
PCs	Pseudocapacitors
PEO	Poly(ethylene oxide)
PMMA	Poly(methyl methacrylate)
POM	Polarized Optical Microscopy
PVA	Poly(vinyl alcohol)
R_b	Bulk Resistance
R_{ct}	Charge Transfer Resistance
RFB	Redox Flow Battery
R_s	Solution Resistance
SPE	Solid Polymer Electrolyte
SS	Stainless-Steel
SSE	Solid-State Electrolyte
TGA	Thermogravimetric Analysis
UCM	Uncross-linked Chitosan Membrane
VRB	Vanadium Redox Battery
W	Warburg impedance
WU	Water Uptake
WVTR	Water Vapor Transmission Rate
XRD	X-ray Diffraction
ZAB	Zinc-Air Battery
ZnBr	Zinc-Bromine

ABSTRACT

The global energy crisis and the rising penetration of renewable sources demand advanced energy storage technologies that are efficient, sustainable, and environmentally benign. Among the available options, Electrical Double Layer Capacitors (EDLCs) have emerged as highly attractive owing to their fast charge-discharge rates, long cycle life, and high power density. However, the development of suitable solid or quasi-solid electrolytes remains a critical constraint, as conventional synthetic polymers often suffer from toxicity, poor biodegradability, and limited ionic conductivity. In this context, biopolymer-based hydrogel electrolytes offer a promising alternative. This thesis focuses on the design, syntheses, and characterizations of novel ionically cross-linked chitosan hydrogel membrane electrolytes, with systematic exploration of different crosslinking strategies to establish structure-property performance relationships for EDLC applications. All EDLCs in this work were fabricated using Black Pearl Carbon (BPC) as the electrode material.

The first set of membranes, synthesized by isotropic mixing of chitosan with sodium carbonate in aqueous medium achieved an ionic conductivity of 7.89 mS cm^{-1} . A prototype comprising of five such EDLCs successfully powered a red Light Emitting Diode (LED) for 1.83 minutes, confirming their practical viability. Building on this baseline, a gradient carbonate crosslinking method was developed, offering simple and time-efficient preparation. The EDLC comprising of the optimized membrane exhibited a maximum areal capacitance of 299.4 mF cm^{-2} , an energy density of $41.58 \text{ } \mu\text{Wh cm}^{-2}$, and sustained 57,000 cycles at 1 mA cm^{-2} . A five-cell prototype powered a red LED for 95 seconds, demonstrating reliable device integration.

Further enhancement was achieved with potassium oxalate crosslinking, where denser ionic linkages provided superior performance. The oxalated crosslinked membrane exhibited high ionic conductivity of 4.84 mS cm^{-1} , tensile strength of 55 MPa, and electrochemical stability up to 2.1 V. Devices fabricated with oxalate cross-linked membranes delivered capacitances up to $300.80 \text{ mF cm}^{-2}$, an energy density of $42.11 \text{ } \mu\text{Wh cm}^{-2}$, and long cycle life, maintaining stability over 46,000 cycles at 2 mA cm^{-2} and 32,000 cycles at 5 mA cm^{-2} . A prototype device illuminated a red LED for 1.76

minutes. Finally, borax-based dual ionic-covalent crosslinking produced membranes with strong structural resilience, balanced ionic transport with solution resistance around $0.19\ \Omega$, and reliable long-term cycling stability of 30,000 cycles at $5\ \text{mA cm}^{-2}$. These EDLCs achieved maximum areal capacitance of $378\ \text{mF cm}^{-2}$ from initial of $32\ \text{mF cm}^{-2}$, when tested at a high current density of $5\ \text{mA cm}^{-2}$, while a five-cell prototype powered a red LED for 1.5 minutes, validating scalability.

Taken together, the isotropic carbonate crosslinking laid the foundation, while gradient crosslinking highlighted synthesis simplicity. Oxalate crosslinking offered better capacitance and durability, and borax dual crosslinking improved long-term stability. The comparative insights demonstrate that ionically cross-linked chitosan hydrogels form a family of scalable, eco-friendly, and high-performance polymer electrolytes. By successfully integrating them into functional EDLC prototypes capable of powering LEDs, this work bridges materials chemistry with device application and offers a sustainable pathway toward the development of next-generation energy storage systems.

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CHAPTER 1

Introduction

This chapter introduces the global energy demand and the significance of electrochemical energy storage technologies. It discusses various batteries and capacitors, with emphasis on EDLCs and their charge storage mechanisms. The role of electrolytes is highlighted, followed by the emergence of solid-state gel, and hydrogel electrolytes. Special attention is given to biopolymer-based hydrogels, their crosslinking strategies, and ionic crosslinking approaches. The chapter concludes by identifying research gaps, motivation, and objectives of the present study on ionically crosslinked chitosan hydrogel membrane electrolytes for EDLCs.

1.1 Global energy crisis and need for advanced energy storage systems

The global energy landscape is undergoing a profound transformation, yet it remains overshadowed by one of the greatest challenges of the 21st century: the energy crisis [1,2]. This crisis arises from the confluence of rapidly rising global energy demand, continued dependence on finite fossil fuel resources, and the urgent need to mitigate the impacts of climate change [3]. According to the International Energy Agency, global primary energy demand has steadily increased over the past decades, driven by industrialization, urbanization, and population growth [4]. Fossil fuels, coal, oil, and natural gas, still account for the majority of the energy sources, but their extraction and combustion are accelerating resource depletion and producing vast quantities of greenhouse gas emissions [5]. These emissions remain the primary drivers of global warming, which is manifesting in the form of extreme weather events, environmental degradation, and ecological instability. At the same time, heavy reliance on fossil fuel supply chains has created economic and geopolitical vulnerabilities, further highlighting the fragility of existing energy systems [5,6]. In response, the global community is intensifying efforts to transition toward renewable energy sources such as solar, wind, hydropower, and emerging alternatives like green hydrogen. These resources are abundant, widely distributed, and inherently more sustainable, making them indispensable for a low-carbon future [7]. However, their fundamental limitation lies in their intermittency and variability. Solar energy depends on sunlight availability, while wind energy production fluctuates with changing wind patterns [8]. Such irregularities create mismatches between energy supply and demand, undermining grid stability and posing risks to energy reliability. As the penetration of renewables in modern power systems continues to rise, this challenge becomes more critical. Without robust mechanisms to balance fluctuations, renewables alone cannot ensure a consistent and reliable energy supply for growing needs. It is within this context that Energy Storage Systems (ESSs) emerge as a pivotal enabler of the sustainable energy transition. ESSs function as a bridge between intermittent renewable generation and continuous demand by capturing surplus energy during peak production periods and releasing it when generation is low or demand is high [9,10]. In doing so, they enhance grid flexibility, improve system reliability, and allow renewable resources to be utilized more effectively rather than wasted. Beyond

balancing supply and demand, ESSs also contribute to energy security, support disaster resilience, and enable the decentralization of power networks, key features of future energy systems. In this way, ESSs act as the backbone of a sustainable energy infrastructure. They provide the means to stabilize renewable-based grids, strengthen energy security, and reduce dependence on fossil fuels. The global energy transition cannot succeed without parallel advancements in energy storage, which are essential for building a secure, resilient, and low-carbon future.

1.2 Fundamentals of electrochemical storage: energy and power characteristics

Energy storage devices are essential components in modern power systems because of their ability to convert and store electrical energy in chemical form and release it back when required. The performance of these systems is generally characterized by two important parameters: energy density and power density [11,12]. Energy density refers to the total amount of energy stored per unit weight or volume, thereby governing the duration for which a device can supply electricity. Power density, on the other hand, describes the rate at which the stored energy can be delivered, dictating the rapidity of energy response under dynamic conditions [13]. High energy density ensures prolonged operation, whereas high power density ensures fast charge–discharge capability, but these two parameters are usually mutually exclusive in practical devices [14].

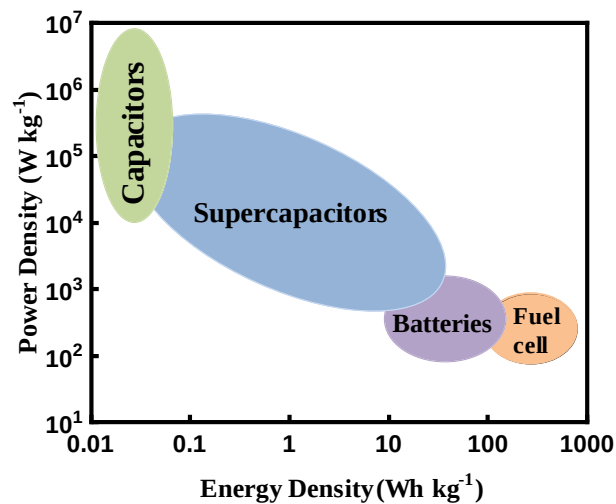


Fig.1.1 Ragone plot showing specific power vs specific energy of energy storage devices [15].

The trade-off between energy and power density is conventionally represented by the Ragone plot as shown in Fig.1.1, which provides a comparative framework for various storage technologies [15]. In this plot, capacitors are positioned in the region of extremely high power density but low energy density, indicating their utility in applications requiring instantaneous power delivery rather than long-term storage. Electrochemical Supercapacitors (ESs) bridge the gap between capacitors and batteries, offering much higher power density than batteries while simultaneously storing more energy than conventional capacitors [16]. Batteries, in contrast, provide higher energy densities than ESs, but their relatively lower power densities limit their effectiveness in short-duration, high-power applications [3]. Fuel cells occupy a different regime in the Ragone plot, exhibiting very high energy densities but relatively low power densities, making them suitable for continuous energy supply rather than for rapid bursts of power [16,17]. The Ragone plot thus highlights the complementary nature of different energy storage technologies and their specific application domains. ESs are suitable for applications demanding rapid power delivery and long cycle life, such as power backup, hybrid electric vehicles (EVs), and load levelling [16,18,19]. Batteries remain the preferred option for portable electronics, grid-scale storage, and electric mobility where sustained energy delivery is critical [3]. Fuel cells serve long-duration applications including transportation and stationary power generation [20]. This clear demarcation emphasizes that no single technology can meet all performance demands simultaneously. Hence, significant research efforts are directed toward the development of hybrid ESSs that integrate multiple technologies to simultaneously exploit high energy density and high power density.

1.3 Battery systems

1.3.1 Lead-Acid Battery

Lead-acid batteries are among the oldest and most extensively used electrochemical storage systems due to their low cost, reliability, and technological maturity [21]. They are employed in diverse applications such as automobiles, uninterruptible power supplies, telecommunication systems, and substation reserve power [22]. Two common types of lead-acid batteries are sealed lead-acid batteries, which are virtually maintenance-free, and flooded lead-acid batteries, which require regular monitoring of

electrolyte levels. The operating principle is based on the electrochemical reaction between lead electrodes and a sulfuric acid-water electrolyte, as illustrated schematically in Fig.1.2 [21]. Key performance parameters of lead-acid batteries include an energy density of $60\text{--}75 \text{ Wh L}^{-1}$, specific energy of $30\text{--}40 \text{ Wh kg}^{-1}$, specific power of around 180 W kg^{-1} , charge-discharge efficiency in the range of $50\text{--}92 \%$, and cycle durability of $500\text{--}800$ cycles. They exhibit a nominal cell voltage of 2.105 V and a self-discharge rate of $3\text{--}20 \%$ per month [22]. The cost of lead-acid batteries remains highly competitive at approximately $\$ 0.17/\text{Wh}$, reinforcing their widespread commercial use [23].

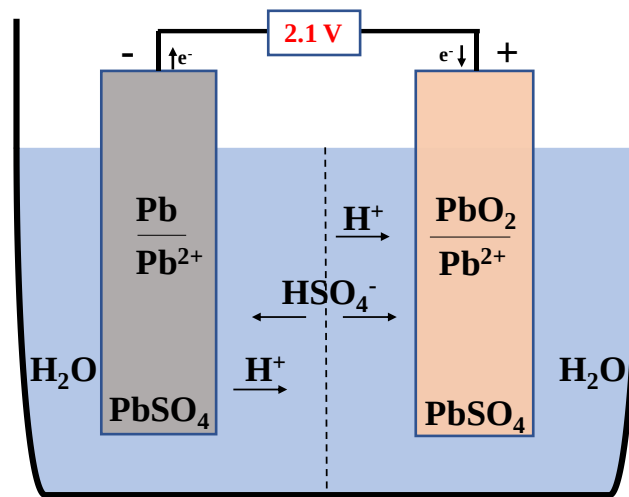


Fig.1.2 Schematic diagram of lead-acid battery [21].

Despite their advantages of low cost, easy availability, and well-established recycling infrastructure, lead-acid batteries face limitations such as short cycle life, relatively low specific energy and power, and high maintenance requirements [24]. Furthermore, their use raises environmental concerns due to lead toxicity, although risks can be mitigated through proper handling, recycling, and disposal practices [25].

1.3.2 Nickel-Cadmium Battery

Nickel-Cadmium (Ni-Cd) batteries are rechargeable systems that utilize nickel hydroxide $[\text{Ni}(\text{OH})_2]$ as the positive electrode, cadmium as the negative electrode, and potassium hydroxide (KOH) as an alkaline electrolyte [26]. The operating principle is based on reversible electrochemical reactions occurring at both electrodes, as shown

schematically in Fig.1.3. At the anode, cadmium is oxidized to cadmium hydroxide, while at the cathode, $\text{NiO}(\text{OH})_2$ is reduced to $\text{Ni}(\text{OH})_2$ during discharge.

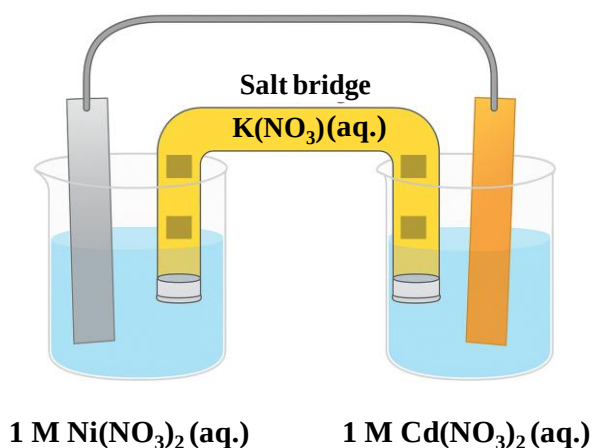


Fig.1.3 Schematic diagram of Ni-Cd battery [26].

Ni-Cd batteries exhibit robust performance over a wide temperature range from -40°C to 70°C , although they are characterized by relatively high self-discharge rates of about 10-20 % per month [26]. Their specific energy lies in the range of $40\text{-}60\text{ Wh kg}^{-1}$, energy density between $50\text{-}150\text{ Wh L}^{-1}$, and specific power of around 150 W kg^{-1} . The charge-discharge efficiency is typically 70-90 %, with a nominal cell voltage of 1.2 V and cycle durability of approximately 2000 cycles [27]. These batteries have found applications in utility and telecommunication backup systems, as well as in consumer electronics. However, the cost of Ni-Cd batteries is relatively high at around \$ 1.50/Wh [27]. Moreover, cadmium is a highly toxic heavy metal, posing significant environmental risks if not properly managed. Recycling and safe disposal facilities are therefore essential to mitigate contamination and ensure sustainable use [28].

1.3.3 Nickel-Metal Hydride Battery

Nickel-Metal Hydride (NiMH) batteries are a class of secondary batteries, where the electrochemical reactions are fully reversible. These batteries employ a metal hydride alloy as the negative electrode (anode), $\text{NiO}(\text{OH})_2$ as the positive electrode (cathode), and KOH as the alkaline electrolyte [29]. The anode consists of metal hydrides, typically alloys incorporating elements such as vanadium, chromium, titanium, or

zinc. The cathode is composed of nickel oxyhydroxide, which participates in redox transformations during cycling, while the KOH electrolyte provides ionic conductivity and mediates charge transport. A schematic representation of a NiMH battery is presented in Fig.1.4, illustrating the electrode-electrolyte configuration and the direction of charge-discharge reactions.

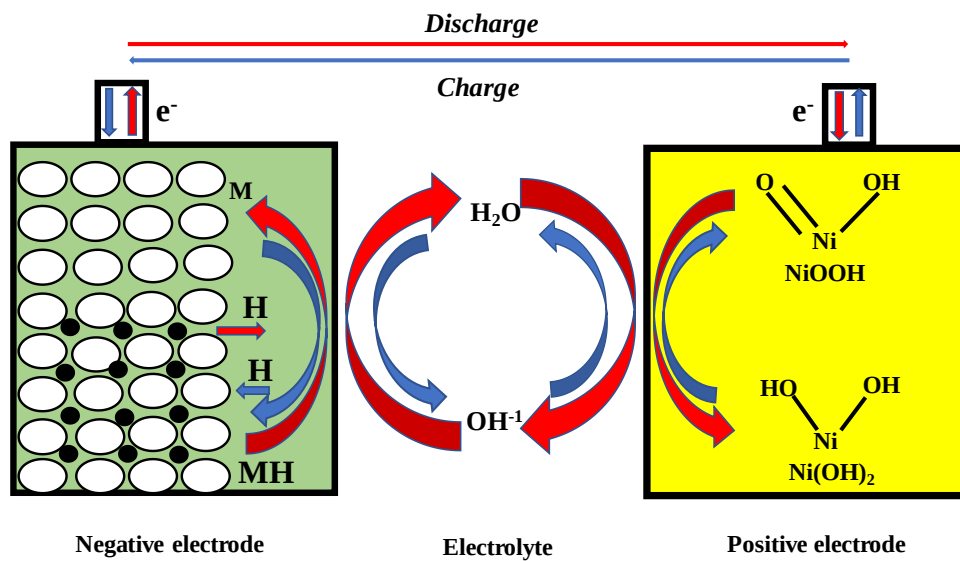


Fig.1.4 Schematic diagram of a NiMH battery [29].

These complementary half-reactions collectively govern the charge and discharge processes, with the overall reaction being highly reversible under normal operating conditions [29,30]. However, at high currents and with repeated deep discharge cycles, the cycle life of NiMH batteries may be reduced. In terms of performance, NiMH batteries typically operate at a nominal cell voltage of 1.2 V, with a specific energy of 60-120 Wh kg⁻¹ and an energy density of 140-300 Wh L⁻¹. They deliver specific power values of 250-1000 W kg⁻¹, a charge/discharge efficiency of ~66 %, and a cycle life ranging from 500 to 1000 cycles. One limitation is their relatively high self-discharge rate (~30 % per month), which reduces long-term energy retention [31]. Economically, the cost of NiMH batteries is approximately \$0.99/Wh [32]. Their strengths include well-established technology, relatively high energy density, and superior cycle life compared to lead-acid batteries. However, disadvantages include higher cost than lead-acid systems and limited long-term potential for cost reduction, particularly with the

growing dominance of Lithium-ion (Li-ion) batteries. As a result, NiMH batteries remain important in consumer electronics, hybrid EVs, and backup power applications in utilities and telecommunications, but are increasingly being replaced in high-performance markets by Li-ion systems due to the latter's superior energy density and cost trajectory [33].

1.3.4 Lithium-ion Battery

Li-ion batteries have become the most dominant energy storage technology, particularly in EVs, due to their high energy density and lightweight design. With rising fuel prices and the urgent need to reduce reliance on fossil fuels, EVs powered by Li-ion batteries provide a sustainable pathway to lowering carbon emissions [34]. Unlike conventional fuels, electrical energy generated from renewable or grid sources can be efficiently stored in Li-ion cells, enabling continuous power delivery over extended driving ranges. The schematic representation of a Li-ion battery is shown in Fig.1.5 [35].

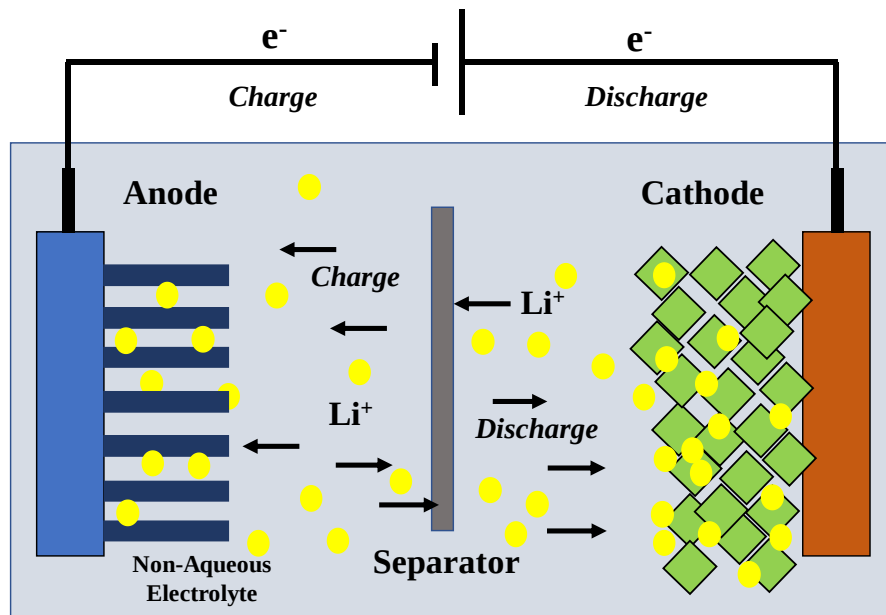


Fig.1.5 Schematic diagram of Li-ion battery [35].

Despite their wide adoption, the major challenge with Li-ion batteries remains cost. While the projected cost was expected to fall to \$ 397/kWh by 2020, this still remains

significantly higher than the target of \$ 150/kWh required for large-scale consumer acceptance [16–19]. Several approaches to reduce costs include developing advanced electrode materials, improving cathode voltage and capacity, and exploring alternative next-generation chemistries such as lithium–air or magnesium-ion systems [16]. Li-ion batteries offer numerous advantages: they are lightweight, exhibit low self-discharge, have no memory effect, and can be fabricated in diverse shapes and sizes for various applications. Furthermore, they are environmentally safer than conventional batteries and contribute to reducing carbon emissions from vehicles [20]. However, certain limitations remain, including capacity fading at high charge levels and elevated temperatures, increasing internal resistance with aging, and relatively high costs of production and integration [34]. Containerized Li-ion battery systems are already in use in large-scale energy storage plants, where multiple modules are connected in series to meet the desired voltage levels [36].

1.3.5 Metal-Air Battery

Metal-Air Battery (MAB) represents a unique class of electrochemical energy storage devices, distinguished by their utilization of oxygen from the atmosphere as the cathodic reactant, rather than storing an internal oxidizing agent. This structural simplicity allows the system to employ only a metallic anode as the active electrode, significantly increasing the theoretical energy density compared to conventional batteries [37]. A typical MAB consists of three main components: a metallic anode, a porous air cathode that facilitates oxygen reduction, and an electrolyte that enables ion transport, as shown in Fig.1.6. During discharge, the metallic anode undergoes oxidation to form metal ions, which subsequently migrate through the electrolyte and react with oxygen at the cathode to produce the corresponding metal oxides or hydroxides. The choice of anode material determines the system, with alkali metals (Li, Na, K), alkaline earth metals (Mg), and transition metals (Fe, Zn) commonly used [38].

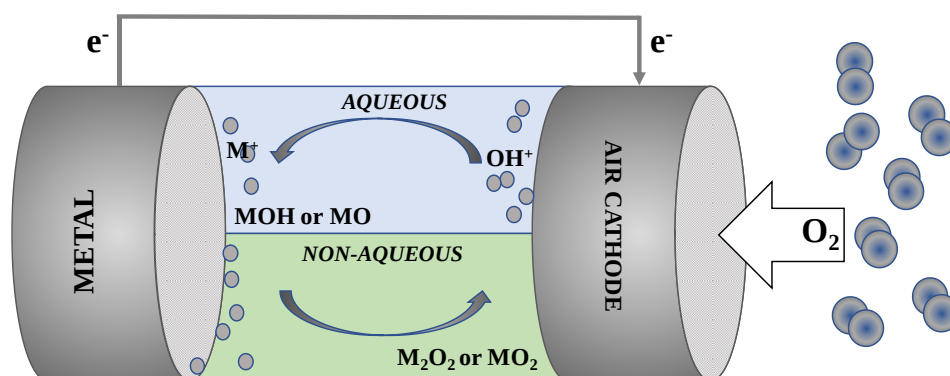


Fig.1.6 Schematic representation of a MAB [37].

Depending on the anode, different electrolytes are employed, ranging from aqueous alkaline solutions (e.g., KOH), to neutral aqueous solutions (e.g., NaCl), or non-aqueous organic electrolytes (e.g., salts of lithium or copper). This flexibility in design enables high theoretical performance, but also introduces challenges related to stability, reversibility, and cycling life [39]. MAB are regarded as one of the most promising next-generation storage technologies due to their exceptionally high theoretical energy density, which can be 3-30 times greater than that of Li-ion batteries. Practical devices have demonstrated specific energies above 500 Wh kg^{-1} and volumetric energy densities exceeding 1000 Wh L^{-1} , typically accompanied by a flat discharge voltage profile [40,41]. Several variants of MABs have been studied extensively, including lithium-air, aluminum-air, silicon-air, sodium-air, and zinc-air systems. Lithium-air systems attract research interest due to their extremely high capacity, while aluminum-air offers cost-effectiveness and safety. However, Zinc-Air Battery (ZAB) is the most technologically mature and widely commercialized, with applications already spanning from medical devices to telecommunications.

Among various MABs, aqueous ZAB stand out as a well-established and promising technology for future energy applications. The concept of ZAB has been known since the late 19th century, and commercial devices were first introduced in the 1930s [42]. The working principle of a ZAB is illustrated in Fig.1.7, where zinc at the anode undergoes oxidation, releasing Zn^{2+} ions into the electrolyte, while oxygen from ambient air is reduced at the porous air cathode.

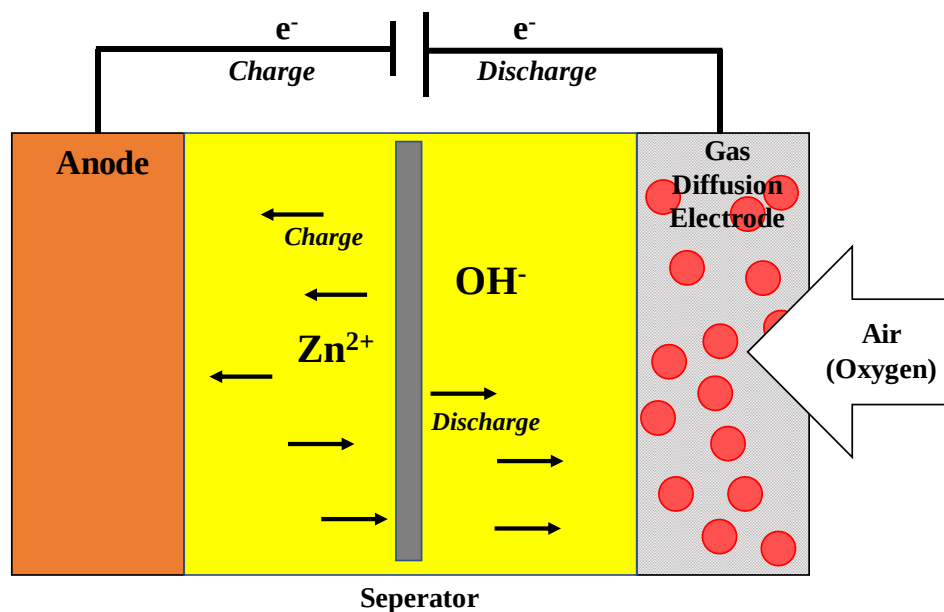


Fig.1.7 Schematic representation of a ZAB [42].

The theoretical energy density of ZAB is 1086 Wh kg^{-1} , nearly five times greater than that of conventional Li-ion batteries, positioning them as a compelling alternative for next-generation energy storage [42]. This exceptionally high energy density makes ZABs particularly attractive for EV applications, where both technical feasibility and economic viability are critical. In practice, primary ZABs are already widely used, particularly in medical devices (e.g., hearing aids) and telecommunication systems, where their high energy density and cost-effectiveness offer clear advantages. However, their power output is typically limited (often below 10 mW in button-cell configurations) due to the sluggish kinetics of the Oxygen Reduction Reaction (ORR) at the air cathode. The efficiency and durability of air catalysts remain one of the key bottlenecks in improving power capability. The development of rechargeable ZAB (secondary ZABs) faces additional challenges. Chief among these are issues of non-uniform zinc dissolution and deposition, leading to dendrite formation, shape change, and poor reversibility during cycling. Furthermore, the lack of efficient and durable bifunctional air catalysts capable of sustaining both ORR and Oxygen Evolution Reaction (OER) processes limits the cycle life of rechargeable ZABs. Despite these challenges, research into advanced catalyst materials (e.g., transition metal oxides, doped carbons, and nanostructured composites) and optimized zinc anode

architectures continues to push ZAB technology closer to practical large-scale adoption. Their relatively low cost, safety, and abundance of zinc offer major advantages over lithium-based systems for future grid storage and electric mobility.

1.3.6 Redox Flow Battery

Redox Flow Batteries (RFBs) are electrochemical storage devices in which two separate liquid electrolytes, containing redox-active species, flow on either side of an ion-selective membrane. The electrolytes are stored in external tanks and circulated through electrochemical cells during charge and discharge operations. The energy capacity of RFBs is determined by the electrolyte volume, while the power capacity is dictated by the size of the cell stack, thus allowing independent scaling of energy and power. The schematic configuration of a typical RFB system is illustrated in Fig.1.8 [43].

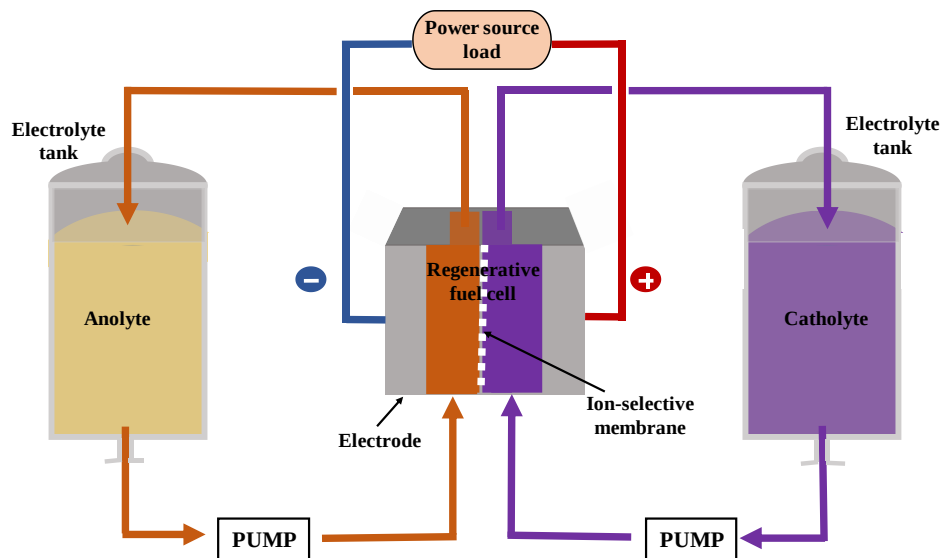


Fig.1.8 Schematic diagram of RFB [43].

Among various RFB types, the Vanadium Redox Battery (VRB) has gained significant attention due to its ability to utilize the same element in different oxidation states, thereby eliminating cross-contamination issues. VRBs find applications in backup power supply, small-scale load levelling, and peak shaving in transmission and distribution networks. The main advantages of VRBs include high energy and power densities, scalability for large-scale applications, ease of upgradability, and independent energy-power sizing. However, limitations such as lack of standardized

sizes, high system cost, and the relatively new stage of technology development hinder their widespread adoption [44]. Another important type is the Zinc-Bromine Battery (ZnBr), which also finds applications in backup power, load levelling, and peak shaving for grid systems. ZnBr batteries exhibit high energy and power densities, scalability for large-scale use, and partially independent energy-power sizing. Nonetheless, disadvantages such as the corrosive and toxic nature of the electrolytes, high maintenance requirements, and early-stage technological maturity present significant challenges for commercialization [44].

1.4 Electrochemical Supercapacitors

ESs represent a class of energy storage devices that employ a wide variety of active electrode materials such as high surface-area carbons, transition metal oxides, nitrides, and electroactive polymers, along with different electrolyte systems (aqueous, organic, or polymer-based) assembled in either symmetric or asymmetric configurations [45]. The inherent versatility in material selection, structural design, and device configuration provides ESs with unique flexibility, allowing them to occupy a wide domain on the Ragone plot, bridging the gap between conventional capacitors, which provide very high power but limited energy density, and rechargeable batteries or fuel cells, which provide high energy densities but are constrained by lower power capability [46]. Their optimized performance depends critically on the interplay between the electrodes, electrolytes, and current collectors. Specifically, the capacitance of the device is largely determined by the electroactive surface area and electrical conductivity of the electrode material, with carbon-based systems and conducting polymers or oxides being most widely utilized due to their high surface area and rapid electrochemical activity [47]. The overall energy density of ESs is governed by the specific capacitance of the electrodes and the electrochemical stability window of the electrolyte. Hence, selecting an appropriate electrolyte becomes essential to extend the operating voltage and, thereby, enhance the stored energy [47]. On the other hand, the power density is primarily constrained by the Equivalent Series Resistance (ESR), which originates from several contributions including: (i) ionic resistance of the electrolyte, (ii) interfacial resistance between the electrode and current collector, (iii) ionic resistance across the separator/electrolyte interface, (iv) diffusion

resistance of ions within micropores, and (v) electronic resistance of the electrode material itself [45,47]. Due to these characteristics, electrochemical capacitors can be clearly differentiated from high-rate rechargeable batteries by several distinctive operational features: (i) extremely fast charge-discharge times on the order of seconds, (ii) nearly linear and symmetric charge-discharge profiles, and (iii) exceptionally long cycle life, often exceeding hundreds of thousands of cycles without significant degradation [48]. Based on the mechanism of charge storage, the nature of electrode materials employed, and their configuration, ESs are generally classified into three categories: EDLCs, Pseudocapacitors (PCs), and Hybrid Capacitors [49]. The three classes differ in their storage mechanism viz., non-Faradaic, Faradaic, or a combination of both and are discussed in detail in the following sections.

1.4.1 Electrical Double Layer Capacitors

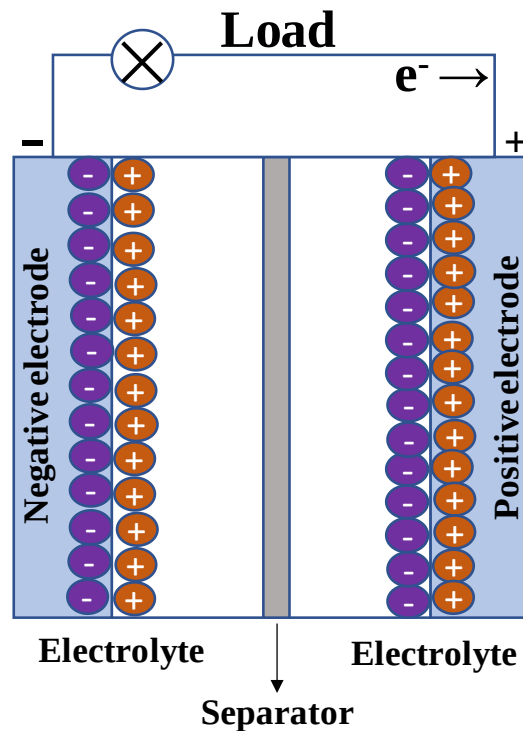


Fig.1.9 Schematic diagram of EDLC [49].

EDLCs consist of two porous electrodes separated by an electrolyte, with a separator preventing electronic contact between them while allowing ionic transport. A current

collector is typically employed to establish electrical connection with the electrode material. The storage of energy in EDLCs arises purely from the electrostatic accumulation of charges at the electrode-electrolyte interface, without any charge transfer reactions across the interface [46,49]. The effective charge separation occurs within a very narrow region defined by the Helmholtz double layer thickness, typically on the order of the diameter of solvated ions at the interface [47]. A schematic illustration of a typical carbon-based EDLC is shown in Fig.1.9. In EDLCs, charge storage occurs through reversible adsorption of electrolyte ions onto high surface-area carbonaceous materials such as activated carbon, carbon aerogels, or carbon nanotubes [40]. The accumulated charges in the double layer are contributed by two components: (i) the compact Helmholtz layer, often containing adsorbed hydrated ions, and (ii) the diffuse layer, consisting of counter-ions extending into the electrolyte. The total capacitance of the double layer can therefore be expressed as the sum of the compact and diffuse layer contributions [47]. Owing to the absence of slow Faradaic reactions, EDLCs are capable of delivering extremely high power density and very long cycle life ($\sim 10^6$ cycles), although with relatively modest energy densities compared to PCs and hybrid systems [48].

1.4.2 Pseudocapacitors

Unlike EDLCs, PCs employ electroactive materials such as transition metal oxides (RuO_2 , MnO_2 , NiO), sulfides, nitrides, or conducting polymers (polypyrrole, polyaniline, etc.), which undergo fast and reversible Faradaic redox processes at the electrode-electrolyte interface [50]. The capacitance in these systems arises not merely from electrostatic ion adsorption but from charge transfer processes associated with redox reactions, electrosorption, or intercalation within the electrode materials [49]. A schematic of the redox-based charge storage in PCs is presented in Fig.1.10.

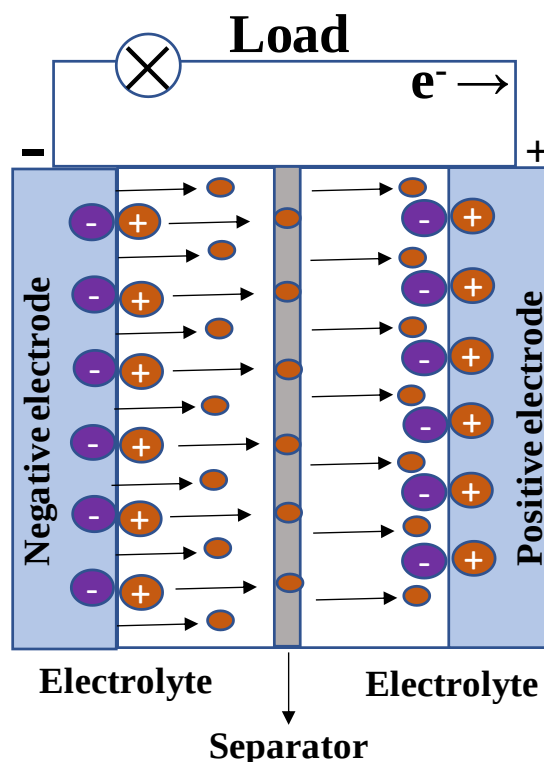


Fig.1.10 Schematic diagram of PC [49].

These Faradaic processes contribute to substantially higher specific capacitances and energy densities compared to EDLCs. For example, pseudocapacitive electrodes typically exhibit specific capacitances in the range of $300\text{--}1000\text{ F g}^{-1}$, whereas EDLCs based on carbon electrodes generally deliver values in the range of $100\text{--}300\text{ F g}^{-1}$ [51]. However, the trade-offs include comparatively lower cycling stability and reduced power density due to kinetic limitations of the redox reactions. Notably, hydrous ruthenium oxide ($\text{RuO}_2 \cdot x\text{H}_2\text{O}$) remains one of the most studied pseudocapacitive materials, though its high cost has encouraged exploration of alternatives such as MnO_2 and conductive polymers [52].

1.4.3 Hybrid Capacitors

Hybrid capacitors are designed to combine the merits of EDLCs and PCs, simultaneously exploiting non-Faradaic double-layer storage and Faradaic redox processes. This hybridization enables them to achieve enhanced energy and power densities while retaining good cycle life. The schematic of a hybrid supercapacitor and

its charge storage behaviour is shown in Fig.1.11. Depending on the configuration, hybrid supercapacitors are categorized into three types: composite-type, asymmetric-type, and battery-type hybrids [53].

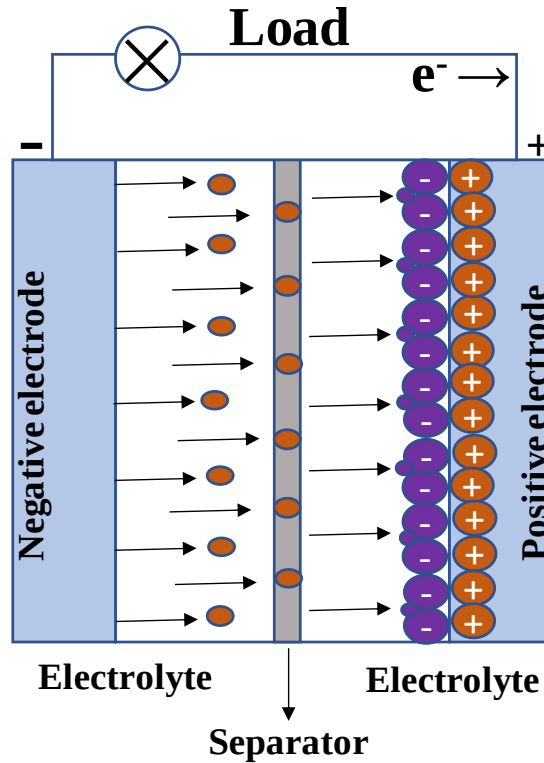


Fig.1.11 Schematic diagram of hybrid capacitor [49].

Composite-type hybrids integrate carbon-based materials with metal oxides or conducting polymers in a single electrode, allowing both electrostatic and Faradaic mechanisms to contribute simultaneously. Here, carbon provides the high surface area and conductivity, while the pseudocapacitive material enhances specific capacitance [54]. Asymmetric-type hybrids couple one EDLC electrode (e.g., activated carbon) with one pseudocapacitive electrode (e.g., conducting polymer), offering complementary characteristics. These devices provide higher energy densities than EDLCs while avoiding the rapid degradation typical of fully pseudocapacitive systems [55]. Battery-type hybrids incorporate one battery-like electrode (e.g., $\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Ni}(\text{OH})_2$, or PbO_2) with one capacitor electrode (e.g., activated carbon). These systems are designed to bridge the performance gap between rechargeable batteries and supercapacitors, though challenges remain regarding stability and scalability [56].

While hybrid capacitors demonstrate great promise in enhancing the performance envelope of electrochemical storage devices, further optimization of electrode materials, electrolyte compatibility, and cost reduction strategies is required to fully realize their technological potential [57].

1.5 Charge storage mechanism of EDLCs

The charge storage behaviour in EDLCs is governed by a series of theoretical models that describe how electrostatic energy is accumulated at the electrode–electrolyte interface. The earliest framework was proposed by Helmholtz in the late 19th century, known as the Helmholtz double layer model [58]. In this representation, ions in the bulk electrolyte remain randomly distributed in the absence of an applied potential. When a potential is introduced, ions migrate toward the oppositely charged electrodes and form a compact layer at the interface, analogous to a parallel-plate capacitor. This Helmholtz layer consists of two sheets of opposite charges separated by the distance corresponding to the solvated ion radius. While this model provides the first explanation of non-Faradaic charge storage, it oversimplifies the interfacial behaviour by neglecting thermal motion and ionic diffusion, which limits its applicability under realistic operating conditions [59].

To improve upon this description, the Gouy-Chapman model was developed. This theory incorporates the role of thermal motion, predicting that counter-ions do not form a rigid layer but instead diffuse into the bulk electrolyte, giving rise to a diffuse double layer. The ion concentration decreases exponentially with distance from the electrode surface, in accordance with the Poisson-Boltzmann equation [58,59]. Although more representative than the Helmholtz model, the Gouy-Chapman framework assumes ions behave as point charges, which leads to inaccuracies at higher electrolyte concentrations where ion size and excluded volume effects become significant.

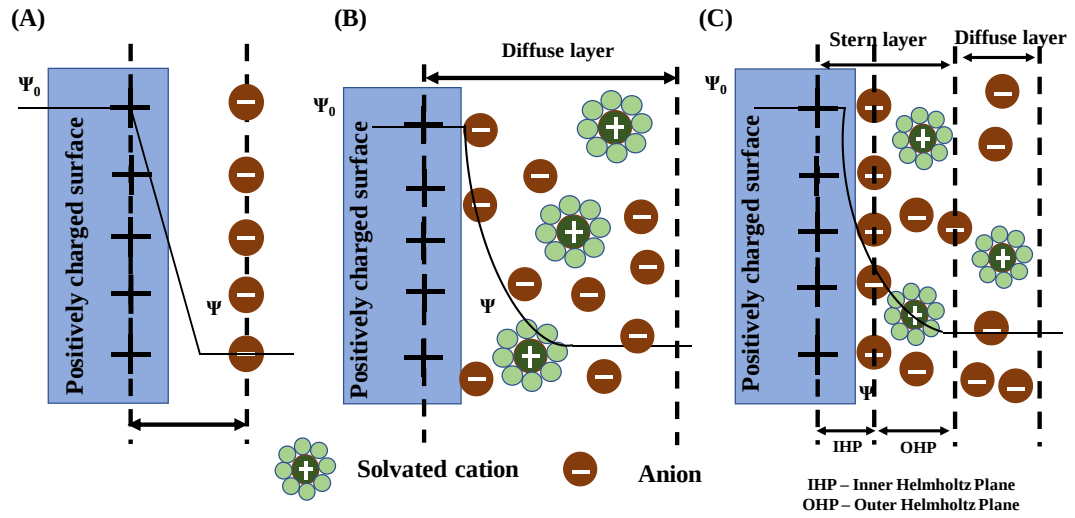


Fig.1.12 The electrical double layer formed at a positively charged electrode in aqueous electrolyte; (A) Helmholtz, (B) Gouy-Chapman, and (C) Stern models [60].

The Stern model was introduced to reconcile these limitations by combining features of both Helmholtz and Gouy-Chapman descriptions. In this approach, the double layer is divided into two distinct regions: (i) a compact layer, often described as the inner Helmholtz plane and outer Helmholtz plane, where ions are specifically or non-specifically adsorbed on the electrode, and (ii) a diffuse layer, extending beyond the outer Helmholtz plane, where ions are distributed in accordance with thermal motion. The total double-layer capacitance (C_{dl}) is therefore treated as the series combination of the compact layer capacitance (C_H) and the diffuse layer capacitance (C_{diff}) [60].

$$\frac{1}{C_{dl}} = \frac{1}{C_H} + \frac{1}{C_{diff}}$$

This composite view provides a more accurate representation of charge storage, particularly in electrolytes of moderate concentration. A schematic illustration of these models is presented in Fig.1.12. The Helmholtz model, as shown in Fig.1.12 (A), depicts a rigid, capacitor-like structure with a linear potential drop (Ψ). The Gouy-Chapman model, as shown in Fig.1.12 (B), introduces an exponential potential decay due to ion diffusion, while the Stern model, as shown in Fig.1.12 (C), incorporates both a compact layer and a diffuse layer, offering a more realistic depiction of

interfacial phenomena. Further advancements have led to the Bazant-Storey-Kornyshev (BSK) model, which extends double-layer theory to highly concentrated electrolytes and ionic liquids [61,62]. At elevated applied potentials, ions pack densely near the electrode surface, giving rise to effects such as ion crowding, over-screening, and even charge inversion. Traditional models fail to capture these behaviors, but the BSK framework accounts for such interactions and provides valuable insights into optimizing EDLC performance under extreme conditions. In summary, while the Helmholtz, Gouy-Chapman, and Stern models offer progressively refined descriptions of the electrical double layer, the BSK model highlights the complex ion-ion correlations that dominate at high concentrations. Together, these frameworks form the theoretical basis for understanding charge storage in EDLCs and guide the development of advanced electrode-electrolyte systems.

1.6 Factors affecting EDLC Performance

The performance of EDLCs is governed by a combination of electrolyte and electrode properties, which directly influence key parameters such as capacitance, resistance ESR, energy and power densities, cycle life, and thermal stability [63]. A schematic overview of these influencing parameters is shown in Fig.1.13, which highlights the interrelationship between electrolyte properties, electrode characteristics, and device-level performance metrics [64]. The electrolyte plays a central role by determining ion transport and electrochemical stability. Ionic conductivity and viscosity of the electrolyte control bulk ion diffusion and directly contribute to the ESR of the device. The electrochemical stability window defines the operating potential window, which has a direct impact on achievable energy and power densities. Furthermore, the ionic strength and ion mobility through the electrode pores are crucial for rapid charge-discharge performance.

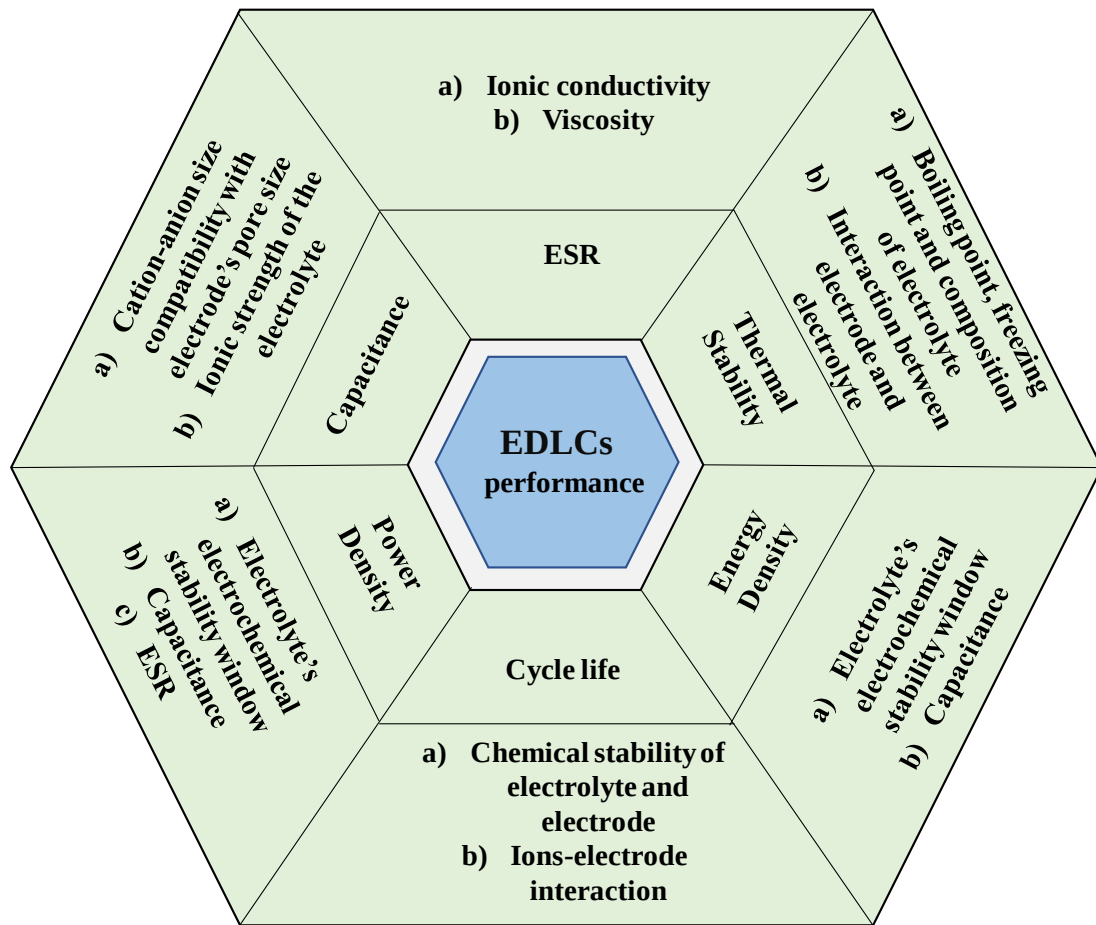


Fig.1.13 Factors affecting the performance of EDLCs [65].

The electrode material denotes the capacitance of the EDLC through parameters such as pore size distribution, accessible surface area, and ion diffusion pathways. High-surface-area carbons with optimized pore architectures facilitate efficient ion adsorption, thereby enhancing capacitance [65]. The absence of Faradaic reactions at the electrode-electrolyte interface ensures long cycle life; however, any undesirable side reactions during charge-discharge may result in heat generation and raise safety concerns. Finally, thermal stability defines the safe operating temperature range of the device. The thermal and chemical compatibility between the electrode and electrolyte are critical for sustained long-term performance, particularly under high current operation.

1.7 Key components of EDLC

As shown in the Fig.1.14, an EDLC consists of four essential components: two porous electrodes, a separator, an electrolyte, and current collectors [66]. The electrodes provide a high surface area for charge accumulation, the electrolyte ensures ionic transport, the separator prevents electrical shorting while enabling ion migration, and current collectors establish electronic conductivity to the external circuit [67]. The performance of EDLCs is thus inherently determined by the design and optimization of these components.

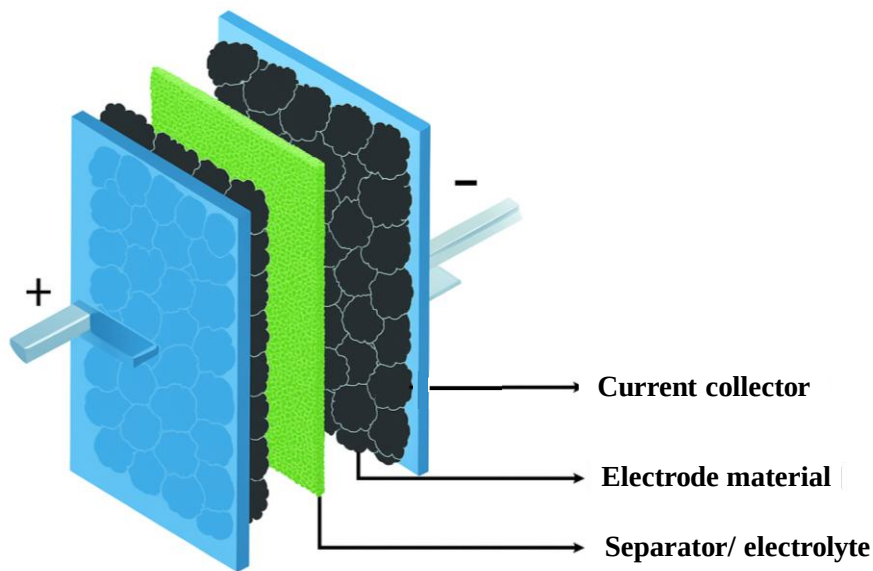


Fig.1.14 Schematic representation of the key components of an EDLC.

1.7.1 Electrodes

Electrodes are the most critical components of EDLCs, as their surface area, pore structure, and conductivity dictate the overall capacitance and energy storage capability [46,56]. Commonly used materials include activated carbon, carbon nanotubes, and graphene, owing to their high surface area, tunable pore size distribution, and electrical conductivity. Activated carbon remains the most widely applied due to its cost-effectiveness and commercial maturity, while advanced nanocarbons offer enhanced power density and specific capacitance [68]. The pore structure of the electrode material is especially significant: micropores (< 2 nm) provide high surface area for ion adsorption, while mesopores (2-50 nm) facilitate ion

transport and reduce resistance [69]. Therefore, a balance between micro and meso porosity is essential for optimizing both energy and power density. Recent research has also explored heteroatom-doped carbons and composite electrodes (carbon with metal oxides or conducting polymers), aiming to improve wettability and enhance charge storage through synergistic mechanisms [70].

1.7.2 Electrolytes

Electrolytes act as the ionic medium in EDLCs, enabling charge compensation between electrodes during charging and discharging. They directly influence key performance metrics such as ionic conductivity, operating voltage window, energy density, and cycle stability of the device [71]. A well-designed electrolyte ensures rapid ion transport with minimal internal resistance, thereby improving both power and energy density. Moreover, the electrochemical stability of the electrolyte determines the safe operating voltage and long-term durability of the capacitor [71]. Advances in electrolyte research have demonstrated that properties such as viscosity, ion mobility, and chemical compatibility with electrode surfaces are crucial for optimizing device performance [72]. In addition, safety concerns associated with volatility and flammability of conventional liquid electrolytes have motivated the development of gel and Solid-State Electrolytes (SSEs), which offer enhanced stability, reduced leakage, and compatibility with flexible devices [73]. Thus, electrolyte synthesis remains one of the most active research areas in EDLC development, as it plays a significant role in improving energy storage capability, safety, and long-term reliability.

1.7.3 Separators and current collectors

The separator is a porous, electrically insulating membrane placed between the two electrodes to prevent short-circuiting, while still allowing ionic transport. Typical separator materials include polypropylene, polyethylene, or cellulose-based membranes, valued for chemical inertness, thermal resistance, and electrolyte wettability [74]. The pore size, porosity, and thickness of the separator directly influence internal resistance and power density. Advanced polymeric designs, such as polyimide-based separators, have been reported to effectively suppress self-discharge

and enhance cycling stability in non-aqueous EDLCs [75]. Current collectors establish the electronic pathway between electrodes and the external circuit. They are typically fabricated from aluminium, Stainless-Steel (SS), or nickel foils, chosen for high conductivity, mechanical stability, and corrosion resistance [76]. Beyond conductivity, their surface characteristics influence adhesion with electrode materials and internal resistance. Recent efforts have focused on lightweight, flexible, and corrosion-resistant coatings on collectors to improve long-term reliability and reduce device cost [77].

1.8 Types of electrolytes for EDLCs

Electrolytes are indispensable in EDLCs as they provide ionic transport, electrochemical stability, and ultimately govern the performance metrics such as energy density, power density, and operational safety. Broadly, electrolytes used in supercapacitors can be classified into several types as shown in Fig.1.15.

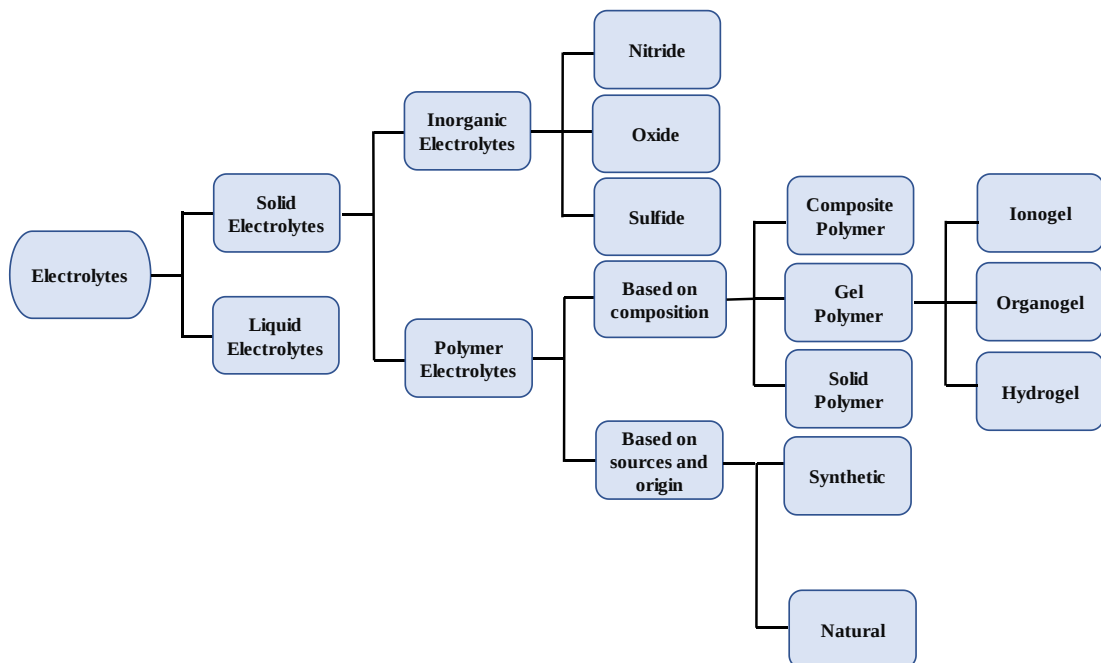


Fig.1.15 Classification of electrolytes.

Liquid electrolytes have been widely used owing to their high ionic conductivity and established electrochemical performance. Aqueous electrolytes such as KOH and H₂SO₄ offer excellent ionic mobility and low resistance, but their operating voltage is

constrained by water decomposition, typically limiting the cell voltage to ~ 1.2 V [78]. Organic electrolytes, based on solvents like acetonitrile or propylene carbonate, extend the voltage window to ~ 2.7 V, enabling higher energy density. However, they present safety challenges such as volatility and flammability, as well as higher costs [79]. Ionic liquids, in contrast, provide wide electrochemical windows (up to 3.5-4.0 V) and intrinsic non-flammability, making them attractive for high-voltage applications. Yet, their high viscosity and expense restrict large-scale deployment [80]. To improve mechanical integrity and safety, SSEs have been developed. These include ceramic electrolytes, known for thermal and electrochemical stability but hindered by brittleness, and Solid Polymer Electrolytes (SPEs), which provide flexibility and ease of processing but suffer from relatively low ionic conductivity [81]. A hybrid approach has been the development of Gel Polymer Electrolytes (GPEs), where liquid electrolytes are immobilized within polymer matrices. GPEs balance ionic conductivity with enhanced safety and have been successfully integrated into flexible EDLCs [82]. Recently, hydrogel electrolytes have emerged as a subclass of GPEs, combining high ionic conductivity with mechanical flexibility. Among them, chitosan-based hydrogels are particularly attractive due to their biocompatibility and sustainability [83]. A detailed discussion on hydrogel electrolytes is presented in Section 1.11. Several studies have demonstrated the potential of chitosan-based hydrogels as electrolytes for high-performance EDLCs. For instance, chitosan-ionic liquid gel electrolytes have shown wide voltage stability and enhanced cycle life [84]. Similarly, chitosan and poly(vinyl alcohol) (PVA) hybrid hydrogels and chitosan-maltodextrin systems doped with ionic liquids have been reported to significantly improve ionic conductivity and device stability [85]. More advanced strategies include in-situ formation of chitosan hydrogels in water-in-salt electrolytes, enabling high-voltage operation in all-solid-state supercapacitors [86]. Thus, while conventional aqueous, organic, and ionic liquid electrolytes have laid the foundation for EDLC development, the emergence of biopolymer-based hydrogel electrolytes, particularly chitosan hydrogels offer a sustainable, safe, and flexible pathway for the next generation of high-performance electrochemical capacitors.

1.9 Emergence of solid-state electrolytes in EDLCs

The emergence of SSEs represents a crucial step in addressing the inherent drawbacks of liquid electrolytes in EDLCs. Conventional liquid electrolytes, while providing high ionic conductivity, suffer from volatility, leakage, corrosion, and narrow operating voltage windows, all of which compromise device safety and long-term stability. In contrast, SSEs offer enhanced safety, improved electrochemical stability, and better compatibility with flexible and miniaturized device architectures, making them particularly attractive for next-generation supercapacitors [64,87,88]. Over the past two decades, SSEs research has diversified into several categories, including composite polymer electrolytes, GPEs, and hydrogels, each offering a balance between ionic conductivity, mechanical robustness, and electrochemical stability [89]. The evolution of these electrolytes reflects the demand for safer, flexible, and environmentally sustainable EDLCs capable of powering portable, wearable, and implantable electronic devices [85].

1.10 Gel polymer electrolytes

The limitations of conventional liquid electrolytes, such as leakage, flammability, and poor mechanical stability, have driven the development of GPEs. First introduced by Feuillade and Perche in 1975 [90], GPEs entrap liquid electrolytes within polymer hosts, thus combining the high ionic conductivity of liquids with the mechanical stability of solids. Since then, GPEs have evolved significantly, finding widespread applications in solid-state EDLCs and lithium-based devices. Typically, GPEs are fabricated by entrapping liquid electrolytes-aqueous, organic, or ionic liquids, within a polymeric host such as PVA, poly(ethylene oxide) (PEO), or poly(methyl methacrylate) (PMMA). This results in a quasi-solid framework where the liquid phase enables ion conduction while the polymer matrix provides dimensional stability [91]. Beyond their safety advantages, GPEs are particularly attractive for flexible and printable energy storage devices, as demonstrated in studies on disposable EDLCs that maintain capacitance even under bending or folding conditions. Ionic-liquid-based GPEs further extend the operating voltage to 2.5-3.0 V, significantly enhancing energy density [92]. Despite these advantages, challenges remain: GPEs often exhibit moderate ionic conductivities (lower than pure liquid electrolytes) and may suffer from

reduced stability under prolonged cycling or elevated temperatures. These limitations have fuelled the transition toward hydrogel electrolytes, which offer a higher degree of ionic transport and mechanical flexibility [87].

1.11 Hydrogel electrolytes

Hydrogel electrolytes have gained prominence as a new generation of SSEs that combine the ionic conductivity of liquids with the structural integrity and flexibility of soft solids. Hydrogels are three-dimensional, cross-linked polymer networks capable of retaining large volumes of aqueous electrolyte, thereby offering continuous ionic pathways with conductivity levels approaching those of liquid systems [80]. An AI generated schematic representation of hydrogel is shown in Fig.1.16.

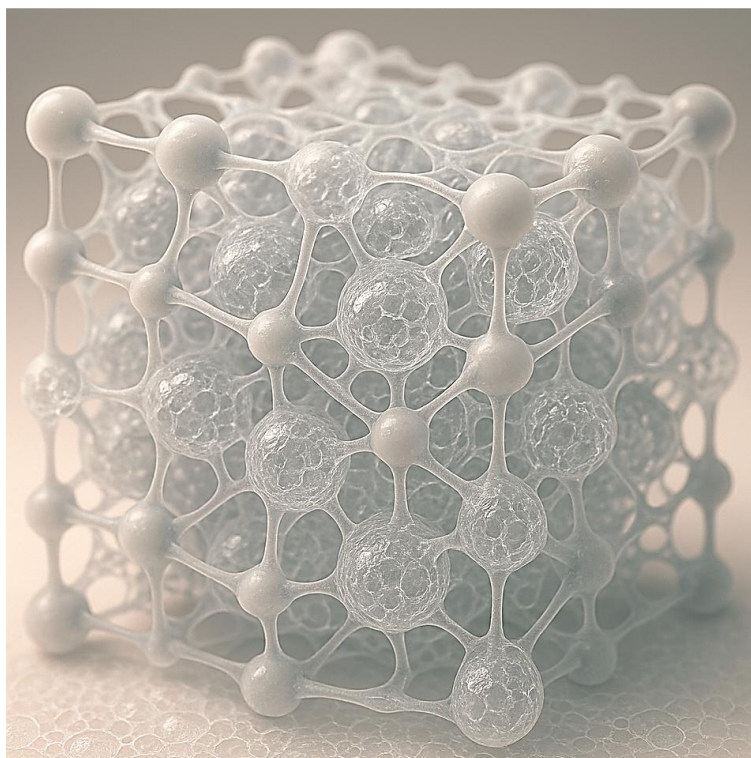


Fig.1.16 An AI generated hydrogel schematic.

Their intrinsic softness and water-rich structure make them particularly suitable for flexible, stretchable, and wearable EDLCs. Moreover, the tunability of hydrogels enables the incorporation of dynamic bonds or functional groups, imparting properties such as self-healing, toughness, and adaptability under mechanical stress [93]. Recent

studies highlight the ability of hydrogel electrolytes to maintain stable capacitance under repeated deformation, demonstrating their potential for powering wearable electronics [94]. Furthermore, hydrogel-based systems can mitigate safety issues associated with organic liquid electrolytes, offering non-flammability and reduced leakage risks. However, challenges such as dehydration during extended use and mechanical brittleness under certain conditions still require innovative material design strategies. Efforts have increasingly focused on natural polymers, such as chitosan and cellulose, to create hydrogel electrolytes that are both environmentally sustainable and electrochemically robust [95]. Given their tunability and safety, hydrogels derived from natural biopolymers are increasingly being explored, as discussed in Section 1.12.

1.12 Biopolymer-based hydrogel electrolytes: properties and importance

Biopolymer-based hydrogels represent a transformative step in the design of green and sustainable electrolytes for EDLCs. Derived from biodegradable resources such as chitosan, cellulose, gelatin, and starch, these hydrogels offer advantages of biodegradability, non-toxicity, and natural abundance, making them well-aligned with the principles of sustainable energy storage [96]. Among these, chitosan has received particular attention owing to its unique cationic nature, film-forming capability, and presence of amine and hydroxyl groups that facilitate ionic conduction and crosslinking. Chitosan-based hydrogels have been cross-linked using ionic species, genipin, or other chemical agents to achieve improved ionic conductivity, mechanical strength, and electrochemical stability [97]. These modifications enhance not only the electrolyte's safety but also its suitability for long-term cycling in EDLCs. Beyond sustainability, biopolymer hydrogels offer the possibility of multifunctionality. For instance, hybrid chitosan-cellulose hydrogels prepared via ionic liquid processing exhibited both high conductivity and superior environmental compatibility, reinforcing the notion that biopolymers can outperform synthetic systems in flexible supercapacitors [52,80]. The importance of biopolymer hydrogels lies not only in their green chemistry credentials but also in their ability to open new design pathways for safe, flexible, and scalable EDLC technologies.

1.13 Preparation strategies for hydrogel electrolytes

Hydrogel synthesis is a multidisciplinary effort at the interface of polymer chemistry, materials science, and electrochemistry, with the primary aim of designing polymeric networks that can exhibit desired mechanical robustness, ionic conductivity, and electrochemical stability. In the context of EDLCs, hydrogels serve as versatile electrolyte media due to their high water content, soft and flexible structure, and tunable ionic pathways. However, the intrinsic mechanical weakness of many natural polymers and the limited ionic conductivity of some synthetic counterparts necessitate strategies for creating cross-linked hydrogel systems. Crosslinking enhances the dimensional stability, ionic transport, and durability of hydrogels by stabilizing the polymer chains into a three-dimensional network structure. Broadly, hydrogel crosslinking approaches can be categorized into physical crosslinking and chemical crosslinking. Physical crosslinking exploits reversible, non-covalent interactions, while chemical crosslinking relies on the formation of covalent or irreversible linkages between polymer chains. Fig.1.17 depicts the chemical and physical crosslinkings of hydrogels. Both approaches significantly influence the electrochemical performance of hydrogel electrolytes, determining factors such as ionic mobility, mechanical integrity, cycling durability, and thermal stability in EDLCs.

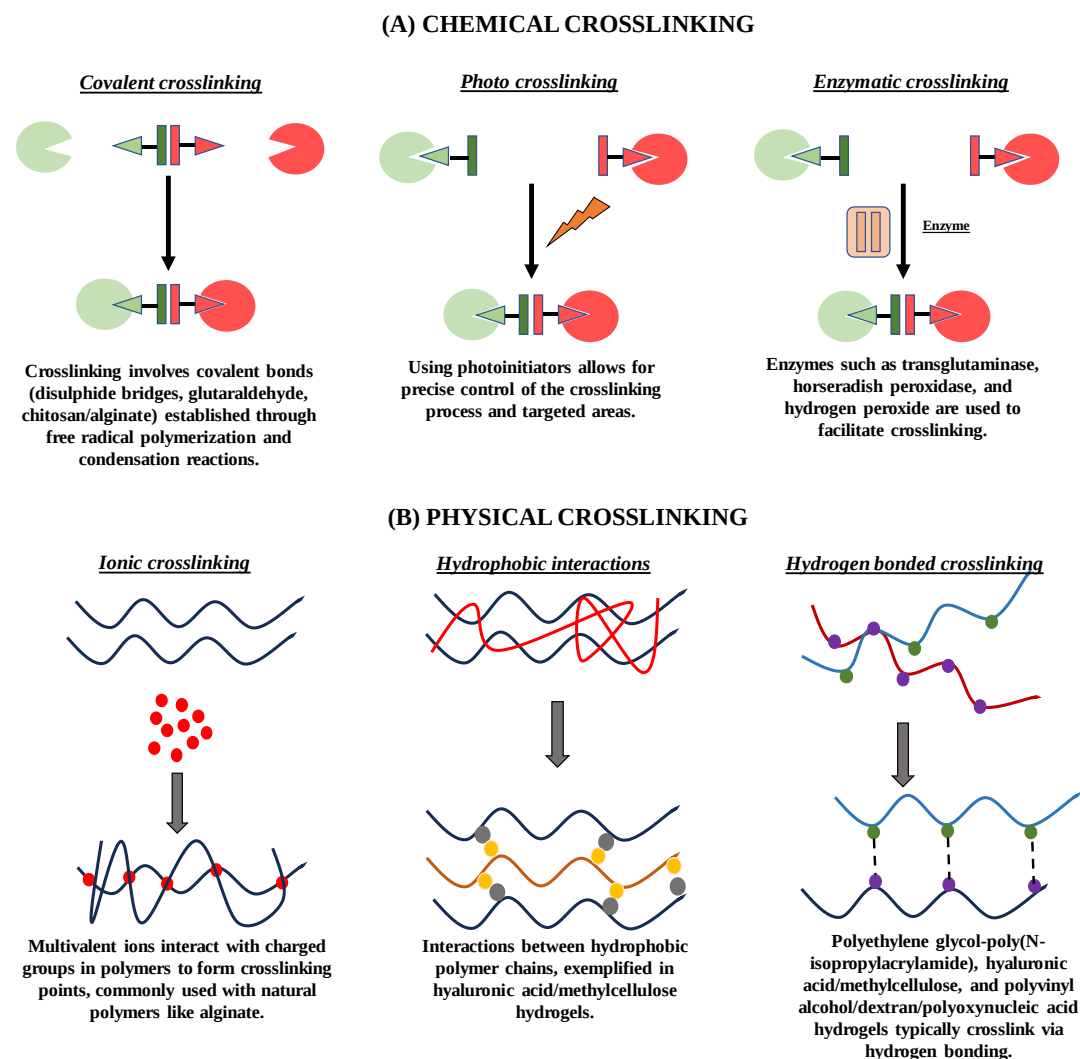


Fig.1.17 Schematic diagram of hydrogel crosslinking methods: (A) Classification and principles of chemical crosslinking in hydrogels; (B) Classification and principles of physical crosslinking in hydrogels. The small balls represent different atoms or ions involved in crosslinking. The grey arrows represent crosslinking reactions. Red and green arrows represent electrostatic forces [98].

1.13.1 Chemical crosslinking

Chemical crosslinking forms permanent covalent bonds between polymer chains, yielding hydrogels with improved mechanical durability, chemical resistance, and long-term stability. Although chemical crosslinking often requires reagents or initiators, it allows for precise control over hydrogel structure, porosity, and ionic transport properties, which is critical in designing high-performance EDLC

electrolytes. Covalent crosslinking uses multifunctional crosslinkers such as glutaraldehyde, epichlorohydrin, genipin, sodium periodate, and isocyanates to react with functional groups (-OH, -NH₂, -COOH) on polymer backbones [99]. These reactions create rigid and stable networks that resist dissolution and mechanical degradation. In the case of hydrogel electrolytes, covalently cross-linked matrices ensure long-term structural stability during repeated charge-discharge cycles, which is essential for achieving high cyclic durability comparable to commercial supercapacitors [100]. Photo crosslinking employs ultraviolet or visible light to activate photoinitiators or photo-reactive moieties within the polymer structure, inducing covalent bond formation. This method provides spatial and temporal control over the gelation process, making it useful for tailoring microstructures and achieving thin, uniform hydrogel membranes. In energy storage applications, photo cross-linked hydrogels have been explored to design patterned or layered electrolytes with enhanced ion transport properties [101]. Enzyme catalyzed crosslinking represents a biologically inspired approach, where enzymes such as transglutaminase or horseradish peroxidase facilitate specific crosslinking reactions under mild conditions. This method is highly selective and avoids harsh chemicals, producing biocompatible and environmentally sustainable hydrogels. For EDLCs, enzyme cross-linked hydrogels can offer flexible, stable, and eco-friendly electrolyte alternatives, although their adoption in energy storage is still at an early research stage compared to biomedical applications [102].

1.13.2 Physical crosslinking

Physical crosslinking involves reversible and dynamic associations such as ionic interactions, hydrogen bonding, hydrophobic associations, or temperature-induced structural rearrangements. These methods are attractive because they often avoid the use of toxic crosslinking agents and proceed under mild conditions, making them ideal for developing safer and environmentally friendly hydrogel electrolytes. Ionic crosslinking is one of the most widely used strategies in the preparation of hydrogel electrolytes. It relies on electrostatic attractions between oppositely charged ions or functional groups present in the polymer backbone. For example, cationic polymers such as chitosan can be cross-linked using multivalent anions like sulfate, phosphate,

citrate, or carbonate, resulting in stable ionic junctions between polymer chains. Similarly, alginate-based systems can be cross-linked using multivalent cations (Ca^{2+} , Al^{3+} , Zr^{4+}), leading to mechanically strengthened networks [103]. The advantages of ionic crosslinking include simplicity, absence of harsh reagents, and tunability of mechanical and electrochemical properties. In EDLCs, ionic crosslinking enhances both ionic conductivity and hydrogel robustness, providing an ideal balance between electrolyte stability and charge transport [103,104]. Another form of physical crosslinking involves self-assembly of polymer chains via non-covalent interactions, including hydrogen bonding, hydrophobic interactions, and supramolecular host-guest interactions. Hydrogen bonding plays a key role in stabilizing physically cross-linked hydrogels, while hydrophobic associations can drive the aggregation of non-polar polymer segments, resulting in gelation [105]. In electrochemical systems, such interactions can create hydrogels with tunable porosity and ionic pathways, which are advantageous for optimizing electrolyte uptake and retention [106]. The freeze-thaw process represents a classical physical crosslinking approach, widely employed for polymers such as PVA. During the freezing stage, water crystallization induces polymer chain aggregation and phase separation, while subsequent thawing maintains physically entangled regions stabilized by hydrogen bonding. Multiple freeze-thaw cycles produce hydrogels with enhanced mechanical strength, elasticity, and internal porosity. [107,108]. For EDLC applications, freeze-thaw hydrogels can act as flexible electrolytes with high ionic conductivity and superior cycling stability due to the presence of interconnected water-filled channels.

1.14 Ionic crosslinking: a strategy for biopolymer-based hydrogel electrolytes

Ionic crosslinking has become one of the most versatile strategies for fabricating hydrogel electrolytes from natural and synthetic polymers, as it combines structural reinforcement with high ionic mobility and environmental safety. The principle of ionic crosslinking is based on the electrostatic interaction between polymer functional groups (such as carboxyl, hydroxyl, or amine groups) and multivalent ionic crosslinkers. Depending on the polymer's chemistry, a wide variety of anionic and cationic crosslinkers have been employed, including carbonate [109,110], citrate [111], sulphate [112], glutaraldehyde [113], tripolyphosphate [114], and genipin [97]

etc. These ions form reversible ionic bridges that stabilize the polymeric network without the need for covalent agents, which are often toxic and irreversible [109,115,116]. The choice of ionic crosslinker significantly influences the physicochemical properties of the hydrogel. For example, sulfate crosslinkers create highly stable networks with enhanced water retention and mechanical durability, making them attractive for electrochemical and biomedical devices [117], phosphate crosslinkers (e.g., sodium tripolyphosphate) interact strongly with protonated amino groups in cationic polymers like chitosan, yielding dense networks with superior ionic conductivity and improved swelling stability [118], citrate crosslinkers, containing multiple carboxyl groups, impart flexibility and biocompatibility, and have been extensively explored in biomedical hydrogels for tissue engineering and wound dressings [111]. Similarly, carbonate-based crosslinkers are used to enhance ionic pathways and buffering capacity, beneficial for sustained ionic transport in electrochemical devices [110]. The versatility of ionic crosslinkers therefore allows tailoring hydrogels for specific applications, ranging from high mechanical integrity to ultrafast ion diffusion. Biopolymer-based hydrogels have found widespread use across multiple domains due to their inherent renewability, biodegradability, and non-toxic nature. In biomedicine, alginate, gelatin, and chitosan hydrogels cross-linked with calcium, phosphate, or sulfate ions are widely employed in wound healing, drug delivery, and tissue scaffolding because they provide controlled swelling and biocompatibility [119]. In environmental engineering, ionically cross-linked hydrogels derived from cellulose or starch are applied in wastewater treatment for heavy metal adsorption, where ionic bridges not only stabilize the structure but also enhance adsorption efficiency [120]. Similarly, in sensor technologies, cross-linked biopolymers provide stable ion conducting matrices for flexible strain sensors and bioelectronic interfaces [121]. These applications demonstrate that ionic crosslinking not only improves mechanical stability but also tailors ionic transport and biocompatibility.

In the energy storage field, ionic crosslinking has enabled the transition from flammable organic electrolytes to solid-state hydrogel-based systems. Hydrogels fabricated from alginate, cellulose, and chitosan have been cross-linked with

multivalent ions to yield mechanically robust electrolytes with ionic conductivities in the range of 10^{-3} - 10^{-2} S cm⁻¹, sufficient for EDLCs and flexible supercapacitors [64,88,115]. Chitosan has emerged as the most promising candidate for EDLC hydrogel electrolytes, owing to its unique cationic nature, abundance, and inherent proton conductivity [115]. The amino groups of chitosan readily protonate under acidic to neutral conditions, enabling strong ionic interactions with multivalent anions such as sulfate, phosphate, citrate, or carbonate. These interactions generate dense yet flexible networks that enhance both mechanical integrity and ionic transport. Importantly, ionic crosslinking creates interconnected water-rich ionic channels that mimic the transport efficiency of liquid electrolytes while maintaining the safety and dimensional stability of solids. For example, sulfate cross-linked chitosan hydrogels have been demonstrated to deliver stable capacitances and excellent long-term cycling behavior due to their reduced interfacial resistance [112]. Similarly, phosphate-cross-linked membranes extend the electrochemical stability window and enable operation at higher voltages, a critical factor for increasing the energy density of EDLCs.

Ionic crosslinking provides an eco-friendly, tunable, and highly effective strategy for preparing biopolymer-based hydrogel electrolytes. Its adaptability across different ionic crosslinkers and polymers underpins applications ranging from biomedicine to energy storage. In the context of EDLCs, chitosan stands out as a biopolymer matrix that balances mechanical stability, ionic conductivity, and environmental sustainability, making it an ideal foundation for designing next-generation, safe, and high-performance hydrogel electrolytes.

1.15 Research gaps and motivation

The development of hydrogel electrolytes has gained substantial momentum in recent years as a means to replace conventional liquid and organic electrolytes in EDLCs. Hydrogels offer inherent advantages such as high water content, ionic conductivity, and mechanical flexibility, which are particularly suitable for next-generation flexible and sustainable energy storage devices. Nevertheless, the majority of reported hydrogel electrolytes are based on synthetic polymers such as PVA, PEO, and poly acrylamide, often modified with redox-active dopants (e.g., hydroquinone, iodides) or

inorganic fillers (e.g., metal oxides, carbon nanotubes) to enhance conductivity and capacitance. While these hybrid strategies can improve electrochemical performance, they introduce several limitations: higher cost, environmental concerns related to synthetic polymers and toxic dopants, and reduced sustainability due to the complex, non-biodegradable components.

A further limitation is related to cyclic stability and scalability. Commercial EDLCs are capable of achieving high life cycles with minimal capacitance fading, while most reported hydrogel electrolytes degrade within thousands of cycles due to structural fatigue, electrolyte evaporation, or loss of electrode-electrolyte interfacial contact. Similarly, although redox-active additives can temporarily increase specific capacitance, they often result in poor long-term durability due to irreversible side reactions. This gap in electrochemical stability under realistic cycling conditions remains a major obstacle for hydrogel electrolytes to be adopted in commercial devices. Another critical challenge lies in the choice of crosslinking agents. Conventional chemical crosslinkers such as glutaraldehyde and formaldehyde, though effective in stabilizing hydrogel networks, are toxic, costly, and environmentally hazardous, making them less attractive for green and sustainable applications. To address these concerns, ionic crosslinking with multivalent anions such as sulfate, carbonate, phosphate, and citrate has emerged as a promising strategy. These ions not only establish stable ionic bridges between polymer chains but also provide low-cost, eco-friendly, and tunable routes for optimizing hydrogel properties. However, systematic studies comparing different ionic crosslinkers in terms of conductivity, structural integrity, and electrochemical performance are still scarce, leaving a significant knowledge gap.

In this context, biopolymers represent a sustainable and renewable alternative to synthetic polymers. Among them, chitosan, derived from chitin, is particularly attractive due to its biocompatibility, biodegradability, and functional amine groups, which can readily interact with multivalent anions for ionic crosslinking. Unlike synthetic hydrogels that require external fillers and dopants, chitosan itself provides functional groups for ionic transport and interfacial bonding, making it an ideal

candidate for eco-friendly hydrogel electrolytes. Despite this potential, the use of chitosan-based hydrogels in EDLCs remains underexplored, particularly in the context of green, low-cost ionic crosslinkers. The motivation of this work, therefore, is to address these research gaps by systematically developing and optimizing chitosan-based hydrogel electrolytes cross-linked with low-cost ionic agents. Instead of relying on synthetic polymers, toxic dopants, or expensive fillers, this study explores ionically cross-linked chitosan networks as a sustainable alternative, focusing on the roles of different ionic crosslinkers in tuning conductivity, electrochemical stability, and mechanical integrity. A comprehensive suite of structural, electrochemical, and mechanical characterizations was performed to evaluate these materials against the benchmarks required for EDLC applications. By doing so, this work aims not only to improve the performance of hydrogel electrolytes but also to contribute toward the development of scalable, environmentally benign, and cost-effective energy storage technologies that align with global sustainability goals.

1.16 Objectives of the work

The present research is focused on the development of low-cost, biopolymer-based, ionically cross-linked chitosan hydrogel membrane electrolytes as sustainable and safe alternatives for EDLCs. By systematically exploring ionic crosslinking strategies with green and economical crosslinkers, the work aims to design hydrogel electrolytes that combine high ionic conductivity, robust mechanical integrity, and long-term electrochemical stability, thereby addressing existing challenges in hydrogel-based supercapacitor systems. The ultimate goal is to fabricate solid-state EDLCs with competitive performance in terms of cyclic stability and energy/power density, comparable to commercial supercapacitors.

The specific objectives of this thesis are outlined below:

- **Preparation and optimization** of ionically cross-linked chitosan hydrogel membranes using a series of low-cost and easily available ionic crosslinkers (e.g., sodium carbonate, potassium oxalate, and borax), evaluating their influence on hydrogel formation, membrane formation, and stability.

- **Comprehensive physicochemical and structural characterization** through techniques such as Fourier-Transform Infrared Spectroscopy (FTIR), Field Emission Scanning Electron Microscopy (FE-SEM), Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), X-ray Diffraction (XRD), Water Uptake (WU), Dissolution Ratio (DR), and Water Vapour Transmission Rate (WVTR) to understand crosslinking efficiency and material morphology.
- **Mechanical and transport property evaluation** of the membranes, including tensile strength, elongation at break, ionic conductivity, dielectric studies, diffusion coefficient and ionic mobility analysis to establish the balance between flexibility, durability, and charge transport pathways.
- **Electrochemical characterization** using Cyclic Voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS), and Galvanostatic Charge-Discharge (GCD), with emphasis on specific capacitance, capacitance retention, energy density, and power density.
- **Cycling stability and testing of prototype powering red LED bulbs** employing the optimized chitosan-based hydrogel membrane electrolytes, thereby evaluating their device-level performance and potential for renewable and environmentally friendly energy storage technologies.

This work does not attempt large-scale commercial device fabrication but rather emphasizes fundamental materials development and systematic performance evaluation of chitosan-based hydrogel electrolytes. Through this approach, the study seeks to contribute to the advancement of sustainable and biodegradable ESSs, demonstrating the potential of ionically cross-linked chitosan hydrogels as next-generation electrolytes for EDLCs.

1.17 References

- [1] C. Popescu, S.A. Apostu, I.G. Rădulescu, J.D. Mureșan, A.G. Brezoi, Energizing the Now: Navigating the Critical Landscape of Today's Energy Challenges—An In-Depth Review, *Energies* (Basel) 17 (2024) 675. <https://doi.org/10.3390/en17030675>.
- [2] K.V.G. Raghavendra, R. Vinoth, K. Zeb, C.V.V. Muralee Gopi, S. Sambasivam, M.R. Kummara, I.M. Obaidat, H.J. Kim, An intuitive review of supercapacitors with recent progress and novel device applications, *J Energy Storage* 31 (2020) 101652. <https://doi.org/10.1016/j.est.2020.101652>.
- [3] K. Aanchal, V. Sharma, Urvashi, Green Battery: Sustainable Way of Energy Storage, in: *Electrocatalytic Materials*, Springer Nature Switzerland, Cham, 2024: pp. 619–636. https://doi.org/10.1007/978-3-031-65902-7_20.
- [4] S. Ghasemian, A. Faridzad, P. Abbaszadeh, A. Taklif, A. Ghasemi, R. Hafezi, An overview of global energy scenarios by 2040: identifying the driving forces using cross-impact analysis method, *International Journal of Environmental Science and Technology* 21 (2024) 7749–7772. <https://doi.org/10.1007/s13762-020-02738-5>.
- [5] J. Wang, W. Azam, Natural resource scarcity, fossil fuel energy consumption, and total greenhouse gas emissions in top emitting countries, *Geoscience Frontiers* 15 (2024) 101757. <https://doi.org/10.1016/j.gsf.2023.101757>.
- [6] S. Kumar, U. Chatterjee, A. David Raj, K.R. Sooryamol, Global Warming and Climate Crisis/Extreme Events, in: 2023: pp. 3–18. https://doi.org/10.1007/978-3-031-44397-8_1.
- [7] X. Li, C.J. Raorane, C. Xia, Y. Wu, T.K.N. Tran, T. Khademi, Latest approaches on green hydrogen as a potential source of renewable energy towards sustainable energy: Spotlighting of recent innovations, challenges, and future insights, *Fuel* 334 (2023) 126684. <https://doi.org/10.1016/j.fuel.2022.126684>.

-
- [8] I. Graabak, M. Korpås, Variability Characteristics of European Wind and Solar Power Resources—A Review, *Energies* (Basel) 9 (2016) 449. <https://doi.org/10.3390/en9060449>.
- [9] M. Yekini Suberu, M. Wazir Mustafa, N. Bashir, Energy storage systems for renewable energy power sector integration and mitigation of intermittency, *Renewable and Sustainable Energy Reviews* 35 (2014) 499–514. <https://doi.org/10.1016/j.rser.2014.04.009>.
- [10] L. Bridier, D. Hernández-Torres, M. David, P. Lauret, A heuristic approach for optimal sizing of ESS coupled with intermittent renewable sources systems, *Renew Energy* 91 (2016) 155–165. <https://doi.org/10.1016/j.renene.2016.01.021>.
- [11] H. Jafarizadeh, M. Soltani, J. Nathwani, A Novel Analysis of Energy Density Considerations and Its Impacts on the Cost of Electrical Energy Storage (EES) Plants, *Energies* (Basel) 16 (2023) 3330. <https://doi.org/10.3390/en16083330>.
- [12] G. Smdani, M.R. Islam, A.N. Ahmad Yahaya, S.I. Bin Safie, PERFORMANCE EVALUATION OF ADVANCED ENERGY STORAGE SYSTEMS: A REVIEW, *Energy & Environment* 34 (2023) 1094–1141. <https://doi.org/10.1177/0958305X221074729>.
- [13] J. Sun, Y. Li, Research on Improving Energy Storage Density and Efficiency of Dielectric Ceramic Ferroelectric Materials Based on BaTiO₃ Doping with Multiple Elements, *Journal of Composites Science* 7 (2023) 233. <https://doi.org/10.3390/jcs7060233>.
- [14] C. Choi, D.S. Ashby, D.M. Butts, R.H. DeBlock, Q. Wei, J. Lau, B. Dunn, Achieving high energy density and high power density with pseudocapacitive materials, *Nat Rev Mater* 5 (2019) 5–19. <https://doi.org/10.1038/s41578-019-0142-z>.
- [15] J. Woods, A. Mahvi, A. Goyal, E. Kozubal, A. Odukomaiya, R. Jackson, Rate capability and Ragone plots for phase change thermal energy storage, *Nat Energy* 6 (2021) 295–302. <https://doi.org/10.1038/s41560-021-00778-w>.

-
- [16] D.P. Dubal, O. Ayyad, V. Ruiz, P. Gómez-Romero, Hybrid energy storage: the merging of battery and supercapacitor chemistries, *Chem Soc Rev* 44 (2015) 1777–1790. <https://doi.org/10.1039/C4CS00266K>.
- [17] S.M. Benoy, M. Pandey, D. Bhattacharjya, B.K. Saikia, Recent trends in supercapacitor-battery hybrid energy storage devices based on carbon materials, *J Energy Storage* 52 (2022) 104938. <https://doi.org/10.1016/j.est.2022.104938>.
- [18] G. Zhou, L. Yang, W. Li, C. Chen, Q. Liu, A Regenerable Hydrogel Electrolyte for Flexible Supercapacitors, *IScience* 23 (2020) 101502. <https://doi.org/10.1016/j.isci.2020.101502>.
- [19] J. Zhang, M. Gu, X. Chen, Supercapacitors for renewable energy applications: A review, *Micro and Nano Engineering* 21 (2023) 100229. <https://doi.org/10.1016/j.mne.2023.100229>.
- [20] N.A. Choudhury, Y. Sahai, R.G. Buchheit, Polyvinyl Alcohol Chemical Hydrogel Electrode Binder for Direct Borohydride Fuel Cells, *J Electrochem Soc* 158 (2011) B712. <https://doi.org/10.1149/1.3581021>.
- [21] R. Ye, D. Henkensmeier, S.J. Yoon, Z. Huang, D.K. Kim, Z. Chang, S. Kim, R. Chen, Redox Flow Batteries for Energy Storage: A Technology Review, *Journal of Electrochemical Energy Conversion and Storage* 15 (2018). <https://doi.org/10.1115/1.4037248>.
- [22] S. Reddy Salkuti, C. Mook Jung, Comparative analysis of storage techniques for a grid with renewable energy sources, *International Journal of Engineering & Technology* 7 (2018) 970. <https://doi.org/10.14419/ijet.v7i3.12728>.
- [23] E. Chemali, M. Preindl, P. Malysz, A. Emadi, Electrochemical and Electrostatic Energy Storage and Management Systems for Electric Drive Vehicles: State-of-the-Art Review and Future Trends, *IEEE J Emerg Sel Top Power Electron* 4 (2016) 1117–1134. <https://doi.org/10.1109/JESTPE.2016.2566583>.
- [24] S.R. Salkuti, Electrochemical batteries for smart grid applications, *International Journal of Electrical and Computer Engineering (IJECE)* 11 (2021) 1849. <https://doi.org/10.11591/ijece.v11i3.pp1849-1856>.

- [25] Electrochemical Energy Storage for Renewable Sources and Grid Balancing, Elsevier, 2015. <https://doi.org/10.1016/C2012-0-01253-7>.
- [26] M.C. Such, C. Hill, Battery energy storage and wind energy integrated into the Smart Grid, in: 2012 IEEE PES Innovative Smart Grid Technologies (ISGT), IEEE, 2012: pp. 1–4. <https://doi.org/10.1109/ISGT.2012.6175772>.
- [27] K. Zaghib, A. Mauger, C.M. Julien, Rechargeable lithium batteries for energy storage in smart grids, in: Rechargeable Lithium Batteries, Elsevier, 2015: pp. 319–351. <https://doi.org/10.1016/B978-1-78242-090-3.00012-2>.
- [28] S.R. Salkuti, Electrochemical batteries for smart grid applications, International Journal of Electrical and Computer Engineering (IJECE) 11 (2021) 1849. <https://doi.org/10.11591/ijece.v11i3.pp1849-1856>.
- [29] M. Sufyan, N.A. Rahim, M.M. Aman, C.K. Tan, S.R.S. Raihan, Sizing and applications of battery energy storage technologies in smart grid system: A review, Journal of Renewable and Sustainable Energy 11 (2019). <https://doi.org/10.1063/1.5063866>.
- [30] T.M. Gür, Review of electrical energy storage technologies, materials and systems: challenges and prospects for large-scale grid storage, Energy Environ Sci 11 (2018) 2696–2767. <https://doi.org/10.1039/C8EE01419A>.
- [31] L. YAO, B. YANG, H. CUI, J. ZHUANG, J. YE, J. XUE, Challenges and progresses of energy storage technology and its application in power systems, Journal of Modern Power Systems and Clean Energy 4 (2016) 519–528. <https://doi.org/10.1007/s40565-016-0248-x>.
- [32] S.R. Salkuti, Large scale electricity storage technology options for smart grid, International Journal of Engineering & Technology 7 (2018) 635. <https://doi.org/10.14419/ijet.v7i2.11395>.
- [33] M.C. Kocer, C. Cengiz, M. Gezer, D. Gunes, M.A. Cinar, B. Albayaci, A. Onen, Assessment of Battery Storage Technologies for a Turkish Power Network, Sustainability 11 (2019) 3669. <https://doi.org/10.3390/su11133669>.

-
- [34] N. Nasajpour-Esfahani, H. Garmestani, M. Bagheritabar, D.J. Jasim, D. Toghraie, S. Dadkhah, H. Firoozeh, Comprehensive review of lithium-ion battery materials and development challenges, *Renewable and Sustainable Energy Reviews* 203 (2024) 114783. <https://doi.org/10.1016/j.rser.2024.114783>.
- [35] J.W. Fergus, Recent developments in cathode materials for lithium ion batteries, *J Power Sources* 195 (2010) 939–954. <https://doi.org/10.1016/j.jpowsour.2009.08.089>.
- [36] D.P. Abraham, M.M. Furczon, S.-H. Kang, D.W. Dees, A.N. Jansen, Effect of electrolyte composition on initial cycling and impedance characteristics of lithium-ion cells, *J Power Sources* 180 (2008) 612–620. <https://doi.org/10.1016/j.jpowsour.2008.02.047>.
- [37] B. Chen, D.Y.C. Leung, J. Xuan, H. Wang, A mixed-pH dual-electrolyte microfluidic aluminum–air cell with high performance, *Appl Energy* 185 (2017) 1303–1308. <https://doi.org/10.1016/j.apenergy.2015.10.029>.
- [38] H.D. Gesser, Electrochemistry, Batteries and Fuel Cells, in: *Applied Chemistry: A Textbook for Engineers and Technologists*, Springer US, Boston, MA, 2002: pp. 159–190. https://doi.org/10.1007/978-1-4615-0531-0_9.
- [39] Y. Li, J. Lu, Metal–Air Batteries: Will They Be the Future Electrochemical Energy Storage Device of Choice?, *ACS Energy Lett* 2 (2017) 1370–1377. <https://doi.org/10.1021/acsenergylett.7b00119>.
- [40] C. Liu, Z.G. Neale, G. Cao, Understanding electrochemical potentials of cathode materials in rechargeable batteries, *Materials Today* 19 (2016) 109–123. <https://doi.org/10.1016/j.mattod.2015.10.009>.
- [41] K.-M. Mangold, Book review, *J Power Sources* 196 (2011) 4871–4872. <https://doi.org/10.1016/j.jpowsour.2011.01.040>.
- [42] Y. Li, H. Dai, Recent advances in zinc–air batteries, *Chem. Soc. Rev.* 43 (2014) 5257–5275. <https://doi.org/10.1039/C4CS00015C>.

-
- [43] Y.K. Zeng, T.S. Zhao, X.L. Zhou, L. Wei, H.R. Jiang, A low-cost iron-cadmium redox flow battery for large-scale energy storage, *J Power Sources* 330 (2016) 55–60. <https://doi.org/10.1016/j.jpowsour.2016.08.107>.
- [44] M. Rychcik, M. Skyllas-Kazacos, Characteristics of a new all-vanadium redox flow battery, *J Power Sources* 22 (1988) 59–67. [https://doi.org/10.1016/0378-7753\(88\)80005-3](https://doi.org/10.1016/0378-7753(88)80005-3).
- [45] F. Wang, X. Wu, X. Yuan, Z. Liu, Y. Zhang, L. Fu, Y. Zhu, Q. Zhou, Y. Wu, W. Huang, Latest advances in supercapacitors: from new electrode materials to novel device designs, *Chem Soc Rev* 46 (2017) 6816–6854. <https://doi.org/10.1039/C7CS00205J>.
- [46] L.L. Zhang, R. Zhou, X.S. Zhao, Graphene-based materials as supercapacitor electrodes, *J Mater Chem* 20 (2010) 5983. <https://doi.org/10.1039/c000417k>.
- [47] A. González, E. Goikolea, J.A. Barrena, R. Mysyk, Review on supercapacitors: Technologies and materials, *Renewable and Sustainable Energy Reviews* 58 (2016) 1189–1206. <https://doi.org/10.1016/j.rser.2015.12.249>.
- [48] Y. Kumar, S. Rawal, B. Joshi, S.A. Hashmi, Background, fundamental understanding and progress in electrochemical capacitors, *Journal of Solid State Electrochemistry* 23 (2019) 667–692. <https://doi.org/10.1007/s10008-018-4160-3>.
- [49] R. Burt, G. Birkett, X.S. Zhao, A review of molecular modelling of electric double layer capacitors, *Physical Chemistry Chemical Physics* 16 (2014) 6519. <https://doi.org/10.1039/c3cp55186e>.
- [50] L. Ji, P. Meduri, V. Agubra, X. Xiao, M. Alcoutlabi, Graphene-Based Nanocomposites for Energy Storage, *Adv Energy Mater* 6 (2016). <https://doi.org/10.1002/aenm.201502159>.
- [51] V.V.N. Obreja, On the performance of supercapacitors with electrodes based on carbon nanotubes and carbon activated material—A review, *Physica E Low Dimens Syst Nanostruct* 40 (2008) 2596–2605. <https://doi.org/10.1016/j.physe.2007.09.044>.

-
- [52] D. Kasprzak, M. Galiński, Chitin as a universal and sustainable electrode binder for electrochemical capacitors, *J Power Sources* 553 (2023) 232300. <https://doi.org/10.1016/j.jpowsour.2022.232300>.
- [53] K. Jurewicz, S. Delpeux, V. Bertagna, F. Béguin, E. Frackowiak, Supercapacitors from nanotubes/polypyrrole composites, *Chem Phys Lett* 347 (2001) 36–40. [https://doi.org/10.1016/S0009-2614\(01\)01037-5](https://doi.org/10.1016/S0009-2614(01)01037-5).
- [54] C. Arbizzani, New trends in electrochemical supercapacitors, *J Power Sources* 100 (2001) 164–170. [https://doi.org/10.1016/S0378-7753\(01\)00892-8](https://doi.org/10.1016/S0378-7753(01)00892-8).
- [55] A. Laforgue, P. Simon, J.F. Fauvarque, M. Mastragostino, F. Soavi, J.F. Sarrau, P. Lailler, M. Conte, E. Rossi, S. Saguatti, Activated Carbon/Conducting Polymer Hybrid Supercapacitors, *J Electrochem Soc* 150 (2003) A645. <https://doi.org/10.1149/1.1566411>.
- [56] M. Mastragostino, Conducting polymers as electrode materials in supercapacitors, *Solid State Ion* 148 (2002) 493–498. [https://doi.org/10.1016/S0167-2738\(02\)00093-0](https://doi.org/10.1016/S0167-2738(02)00093-0).
- [57] H. Li, L. Cheng, Y. Xia, A Hybrid Electrochemical Supercapacitor Based on a 5 V Li-Ion Battery Cathode and Active Carbon, *Electrochemical and Solid-State Letters* 8 (2005) A433. <https://doi.org/10.1149/1.1960007>.
- [58] A. González, E. Goikolea, J.A. Barrena, R. Mysyk, Review on supercapacitors: Technologies and materials, *Renewable and Sustainable Energy Reviews* 58 (2016) 1189–1206. <https://doi.org/10.1016/j.rser.2015.12.249>.
- [59] W. Raza, F. Ali, N. Raza, Y. Luo, K.-H. Kim, J. Yang, S. Kumar, A. Mehmood, E.E. Kwon, Recent advancements in supercapacitor technology, *Nano Energy* 52 (2018) 441–473. <https://doi.org/10.1016/j.nanoen.2018.08.013>.
- [60] S.A. Hashmi, N. Yadav, M.K. Singh, Polymer Electrolytes for Supercapacitor and Challenges, in: *Polymer Electrolytes*, Wiley, 2020: pp. 231–297. <https://doi.org/10.1002/9783527805457.ch9>.

-
- [61] J. Wu, Understanding the Electric Double-Layer Structure, Capacitance, and Charging Dynamics, *Chem Rev* 122 (2022) 10821–10859. <https://doi.org/10.1021/acs.chemrev.2c00097>.
- [62] Y. Lee, J. Cho, Y. Lee, W.B. Lee, Y. Jho, Electric double layer in ionic liquids: A result of interplay between coupling effects and phase demixing, *Phys Rev Res* 6 (2024) 033026. <https://doi.org/10.1103/PhysRevResearch.6.033026>.
- [63] Y. Lee, J. Cho, Y. Lee, W.B. Lee, Y. Jho, Electric double layer in ionic liquids: A result of interplay between coupling effects and phase demixing, *Phys Rev Res* 6 (2024) 033026. <https://doi.org/10.1103/PhysRevResearch.6.033026>.
- [64] R.T. Abdulwahid, S.B. Aziz, M.F.Z. Kadir, Environmentally friendly plasticized electrolyte based on chitosan (CS): Potato starch (PS) polymers for EDLC application: Steps toward the greener energy storage devices derived from biopolymers, *J Energy Storage* 67 (2023) 107636. <https://doi.org/10.1016/j.est.2023.107636>.
- [65] U. Mahanta, IONIC LIQUIDS AND DEEP EUTECTIC SOLVENTS AS ELECTROLYTES FOR ENERGY EFFICIENT ELECTRICAL DOUBLE LAYER CAPACITOR Submitted in Partial Fulfilment of the Requirements for the Degree of DOCTOR OF PHILOSOPHY, 2021.
- [66] P. Phogat, S. Sharma, R. Jha, S. Singh, Electrochemical Capacitors: EDLCs and Pseudocapacitors, in: 2024: pp. 225–255. https://doi.org/10.1007/978-981-96-0527-9_6.
- [67] S. Shiraishi, Electric Double Layer Capacitors, in: *Carbon Alloys*, Elsevier, 2003: pp. 447–457. <https://doi.org/10.1016/B978-008044163-4/50027-9>.
- [68] P. Sharma, T.S. Bhatti, A review on electrochemical double-layer capacitors, *Energy Convers Manag* 51 (2010) 2901–2912. <https://doi.org/10.1016/j.enconman.2010.06.031>.
- [69] A. Lewandowski, M. Galinski, Practical and theoretical limits for electrochemical double-layer capacitors, *J Power Sources* 173 (2007) 822–828. <https://doi.org/10.1016/j.jpowsour.2007.05.062>.

-
- [70] R. Burt, G. Birkett, X.S. Zhao, A review of molecular modelling of electric double layer capacitors, *Physical Chemistry Chemical Physics* 16 (2014) 6519. <https://doi.org/10.1039/c3cp55186e>.
- [71] K.S. Ngai, S. Ramesh, K. Ramesh, J.C. Juan, A review of polymer electrolytes: fundamental, approaches and applications, *Ionics (Kiel)* 22 (2016) 1259–1279. <https://doi.org/10.1007/s11581-016-1756-4>.
- [72] T. Zhao, Q. Xin, G. Yang, S. Liang, J. Lin, Utilizing carboxymethyl cellulose sodium/sodium lignosulfonate hydrogel to build efficient electrolyte/electrode interfaces for multifunctional high-performance supercapacitors, *Int J Biol Macromol* 314 (2025) 144273. <https://doi.org/10.1016/j.ijbiomac.2025.144273>.
- [73] J. Sun, Y. Deng, J. Jiang, Y. Hu, Q. Cui, Z. Lou, Y. Hou, F. Teng, Cationic effects on solid polymer electrolyte-gated organic transistors, *Org Electron* 106 (2022) 106529. <https://doi.org/10.1016/j.orgel.2022.106529>.
- [74] K. Tõnurist, T. Thomberg, A. Jänes, T. Romann, V. Sammelselg, E. Lust, Influence of separator properties on electrochemical performance of electrical double-layer capacitors, *Journal of Electroanalytical Chemistry* 689 (2013) 8–20. <https://doi.org/10.1016/j.jelechem.2012.11.024>.
- [75] K. Tõnurist, T. Thomberg, A. Jänes, T. Romann, V. Sammelselg, E. Lust, Influence of separator properties on electrochemical performance of electrical double-layer capacitors, *Journal of Electroanalytical Chemistry* 689 (2013) 8–20. <https://doi.org/10.1016/j.jelechem.2012.11.024>.
- [76] A. Abdisattar, M. Yeleuov, C. Daulbayev, K. Askaruly, A. Tolynbekov, A. Taurbekov, N. Prikhodko, Recent advances and challenges of current collectors for supercapacitors, *Electrochem Commun* 142 (2022) 107373. <https://doi.org/10.1016/j.elecom.2022.107373>.
- [77] C. Schütter, S. Pohlmann, A. Balducci, Industrial Requirements of Materials for Electrical Double Layer Capacitors: Impact on Current and Future Applications, *Adv Energy Mater* 9 (2019). <https://doi.org/10.1002/aenm.201900334>.

-
- [78] S. Ranganatha, Aqueous Redox-Active Electrolytes, in: *Electroceraamics for High Performance Supercapacitors*, Wiley, 2023: pp. 233–253. <https://doi.org/10.1002/9781394167166.ch10>.
- [79] M. Li, R.P. Hicks, Z. Chen, C. Luo, J. Guo, C. Wang, Y. Xu, Electrolytes in Organic Batteries, *Chem Rev* 123 (2023) 1712–1773. <https://doi.org/10.1021/acs.chemrev.2c00374>.
- [80] D. Kasprzak, M. Galiński, Chitin and chitin-cellulose composite hydrogels prepared by ionic liquid-based process as the novel electrolytes for electrochemical capacitors, *Journal of Solid State Electrochemistry* 25 (2021) 2549–2563. <https://doi.org/10.1007/s10008-021-05036-3>.
- [81] G. Behzadi Pour, H. Nazarpour Fard, L. Fekri Aval, A Comparison of the Electrical Properties of Gel Polymer Electrolyte-Based Supercapacitors: A Review of Advances in Electrolyte Materials, *Gels* 10 (2024) 803. <https://doi.org/10.3390/gels10120803>.
- [82] L.T. Khoon, M.-L.W. Fui, N.H. Hassan, M.S. Su'ait, R. Vedarajan, N. Matsumi, M. Bin Kassim, L.K. Shyuan, A. Ahmad, In situ sol–gel preparation of ZrO₂ in nano-composite polymer electrolyte of PVDF-HFP/MG49 for lithium-ion polymer battery, *J Solgel Sci Technol* 90 (2019) 665–675. <https://doi.org/10.1007/s10971-019-04936-1>.
- [83] J.L. Shamshina, P. Berton, Renewable Biopolymers Combined with Ionic Liquids for the Next Generation of Supercapacitor Materials, *Int J Mol Sci* 24 (2023) 7866. <https://doi.org/10.3390/ijms24097866>.
- [84] M. Yamagata, K. Soeda, S. Ikebe, S. Yamazaki, M. Ishikawa, Chitosan-based gel electrolyte containing an ionic liquid for high-performance nonaqueous supercapacitors, *Electrochim Acta* 100 (2013) 275–280. <https://doi.org/10.1016/j.electacta.2012.05.073>.
- [85] A.S. Mohamed, A.S.F.M. Asnawi, M.F. Shukur, J. Matmin, M.F.Z. Kadir, Y.M. Yusof, The Development of Chitosan-Maltodextrin Polymer Electrolyte with the Addition of Ionic Liquid for Electrochemical Double Layer Capacitor (EDLC)

- Application, Int J Electrochem Sci 17 (2022) 22034. <https://doi.org/10.20964/2022.03.30>.
- [86] H. Wang, Y. Deng, J. Qiu, J. Wu, K. Zhang, J. Shao, L. Yan, In Situ Formation of “Dimethyl Sulfoxide/Water-in-Salt”-Based Chitosan Hydrogel Electrolyte for Advanced All-Solid-State Supercapacitors, ChemSusChem 14 (2021) 632–641. <https://doi.org/10.1002/cssc.202002236>.
- [87] S.B. Aziz, O.Gh. Abdullah, D.M. Aziz, M.B. Ahmed, R.T. Abdulwahid, Energy Storage Performance of Plasticized PVA-Based Electrolyte: Electrical and Electrochemical Properties, ACS Appl Electron Mater 6 (2024) 7763–7780. <https://doi.org/10.1021/acsaelm.4c01040>.
- [88] R.T. Abdulwahid, S.B. Aziz, M.F.Z. Kadir, Environmentally friendly plasticized electrolyte based on chitosan (CS): Potato starch (PS) polymers for EDLC application: Steps toward the greener energy storage devices derived from biopolymers, J Energy Storage 67 (2023) 107636. <https://doi.org/10.1016/j.est.2023.107636>.
- [89] A. Jain, K. Mahata, Onkarnath, S. Banerjee, Biopolymer Derived Gel Polymer Electrolytes: Current Status and Future Perspectives, Macromol Rapid Commun (2025). <https://doi.org/10.1002/marc.202500472>.
- [90] G. Feuilleade, Ph. Perche, Ion-conductive macromolecular gels and membranes for solid lithium cells, J Appl Electrochem 5 (1975) 63–69. <https://doi.org/10.1007/BF00625960>.
- [91] M.-L. Seol, I. Nam, E. Sadatian, N. Dutta, J.-W. Han, M. Meyyappan, Printable Gel Polymer Electrolytes for Solid-State Printed Supercapacitors, Materials 14 (2021) 316. <https://doi.org/10.3390/ma14020316>.
- [92] M. Tripathi, S.K. Tripathi, Electrical studies on ionic liquid-based gel polymer electrolyte for its application in EDLCs, Ionics (Kiel) 23 (2017) 2735–2746. <https://doi.org/10.1007/s11581-017-2051-8>.
- [93] M. Hina, S. Bashir, K. Kamran, J. Iqbal, S. Ramesh, K. Ramesh, Fabrication of aqueous solid-state symmetric supercapacitors based on self-healable poly

- (acrylamide)/PEDOT:PSS composite hydrogel electrolytes, *Mater Chem Phys* 273 (2021) 125125. <https://doi.org/10.1016/j.matchemphys.2021.125125>.
- [94] J. Ding, Y. Yang, J. Poisson, Y. He, H. Zhang, Y. Zhang, Y. Bao, S. Chen, Y.M. Chen, K. Zhang, Recent Advances in Biopolymer-Based Hydrogel Electrolytes for Flexible Supercapacitors, *ACS Energy Lett* 9 (2024) 1803–1825. <https://doi.org/10.1021/acsenerylett.3c02567>.
- [95] H. Yang, Y. Liu, L. Kong, L. Kang, F. Ran, Biopolymer-based carboxylated chitosan hydrogel film crosslinked by HCl as gel polymer electrolyte for all-solid-state supercapacitors, *J Power Sources* 426 (2019) 47–54. <https://doi.org/10.1016/j.jpowsour.2019.04.023>.
- [96] N. Patra, P. Ramesh, V. Donthu, A. Ahmad, Biopolymer-based composites for sustainable energy storage: recent developments and future outlook, *Journal of Materials Science: Materials in Engineering* 19 (2024) 34. <https://doi.org/10.1186/s40712-024-00181-9>.
- [97] K. Nowacki, M. Galiński, A genipin-crosslinked chitosan hydrogel as a quasi-solid-state electrolyte for sustainable electrochemical capacitors, *Sustain Energy Fuels* 9 (2025) 3624–3634. <https://doi.org/10.1039/D5SE00223K>.
- [98] X. Gan, X. Wang, Y. Huang, G. Li, H. Kang, Applications of Hydrogels in Osteoarthritis Treatment, *Biomedicines* 12 (2024) 923. <https://doi.org/10.3390/biomedicines12040923>.
- [99] R. Li, C. Zhou, J. Chen, H. Luo, R. Li, D. Chen, X. Zou, W. Wang, Synergistic osteogenic and angiogenic effects of KP and QK peptides incorporated with an injectable and self-healing hydrogel for efficient bone regeneration, *Bioact Mater* 18 (2022) 267–283. <https://doi.org/10.1016/j.bioactmat.2022.02.011>.
- [100] G.-W. Oh, S.-C. Kim, T.-H. Kim, W.-K. Jung, Characterization of an oxidized alginate-gelatin hydrogel incorporating a COS-salicylic acid conjugate for wound healing, *Carbohydr Polym* 252 (2021) 117145. <https://doi.org/10.1016/j.carbpol.2020.117145>.

-
- [101] Z. Chen, Z. Lv, Y. Zhuang, Q. Saiding, W. Yang, W. Xiong, Z. Zhang, H. Chen, W. Cui, Y. Zhang, Mechanical Signal-Tailored Hydrogel Microspheres Recruit and Train Stem Cells for Precise Differentiation, *Advanced Materials* 35 (2023). <https://doi.org/10.1002/adma.202300180>.
- [102] P. Li, Y. Zhong, X. Wang, J. Hao, Enzyme-Regulated Healable Polymeric Hydrogels, *ACS Cent Sci* 6 (2020) 1507–1522. <https://doi.org/10.1021/acscentsci.0c00768>.
- [103] D. Ji, J.M. Park, M.S. Oh, T.L. Nguyen, H. Shin, J.S. Kim, D. Kim, H.S. Park, J. Kim, Superstrong, superstiff, and conductive alginate hydrogels, *Nat Commun* 13 (2022) 3019. <https://doi.org/10.1038/s41467-022-30691-z>.
- [104] Y. Huang, S. Qian, J. Zhou, W. Chen, T. Liu, S. Yang, S. Long, X. Li, Achieving Swollen yet Strengthened Hydrogels by Reorganizing Multiphase Network Structure, *Adv Funct Mater* 33 (2023). <https://doi.org/10.1002/adfm.202213549>.
- [105] V.G. Muir, J.A. Burdick, Chemically Modified Biopolymers for the Formation of Biomedical Hydrogels, *Chem Rev* 121 (2021) 10908–10949. <https://doi.org/10.1021/acs.chemrev.0c00923>.
- [106] Y. Yang, X. Zhao, S. Wang, Y. Zhang, A. Yang, Y. Cheng, X. Chen, Ultra-durable cell-free bioactive hydrogel with fast shape memory and on-demand drug release for cartilage regeneration, *Nat Commun* 14 (2023) 7771. <https://doi.org/10.1038/s41467-023-43334-8>.
- [107] G. Chen, T. Li, C. Chen, W. Kong, M. Jiao, B. Jiang, Q. Xia, Z. Liang, Y. Liu, S. He, L. Hu, Scalable Wood Hydrogel Membrane with Nanoscale Channels, *ACS Nano* 15 (2021) 11244–11252. <https://doi.org/10.1021/acsnano.0c10117>.
- [108] L. Lei, R. Cong, Y. Ni, X. Cui, X. Wang, H. Ren, Z. Wang, M. Liu, J. Tu, L. Jiang, Dual-Functional Injectable Hydrogel for Osteoarthritis Treatments, *Adv Healthc Mater* 13 (2024). <https://doi.org/10.1002/adhm.202302551>.
- [109] D. Hazarika, D. Kamei, N. Shijoh, N.A. Choudhury, An ionically cross-linked chitosan hydrogel membrane electrolyte for long-lived electrical double layer

- capacitors, J Power Sources 629 (2025) 236037. <https://doi.org/10.1016/j.jpowsour.2024.236037>.
- [110] J. Qian, X. Wang, J. Shu, C. Su, J. Gong, Z. Xu, J. Jin, J. Shi, A Novel Complex of Chitosan–Sodium Carbonate and Its Properties, *Mar Drugs* 16 (2018) 416. <https://doi.org/10.3390/md16110416>.
- [111] N. Zhang, H. Zhang, R. Li, Y. Xing, Preparation and adsorption properties of citrate-crosslinked chitosan salt microspheres by microwave assisted method, *Int J Biol Macromol* 152 (2020) 1146–1156. <https://doi.org/10.1016/j.ijbiomac.2019.10.203>.
- [112] C. Jeyaseelan, N. Chaudhary, R. Jugade, Sulphate-Crosslinked Chitosan as an Adsorbent for the Removal of Congo Red Dye From Aqueous Solution, *Air, Soil and Water Research* 11 (2018). <https://doi.org/10.1177/1178622118811680>.
- [113] M.M. Beppu, R.S. Vieira, C.G. Aimoli, C.C. Santana, Crosslinking of chitosan membranes using glutaraldehyde: Effect on ion permeability and water absorption, *J Memb Sci* 301 (2007) 126–130. <https://doi.org/10.1016/j.memsci.2007.06.015>.
- [114] C.-Y. Yang, C.-H. Hsu, M.-L. Tsai, Effect of crosslinked condition on characteristics of chitosan/tripolyphosphate/genipin beads and their application in the selective adsorption of phytic acid from soybean whey, *Carbohydr Polym* 86 (2011) 659–665. <https://doi.org/10.1016/j.carbpol.2011.05.004>.
- [115] N.A. Choudhury, J. Ma, Y. Sahai, High performance and eco-friendly chitosan hydrogel membrane electrolytes for direct borohydride fuel cells, *J Power Sources* 210 (2012) 358–365. <https://doi.org/10.1016/j.jpowsour.2012.03.013>.
- [116] N.A. Choudhury, P.W.C. Northrop, A.C. Crothers, S. Jain, V.R. Subramanian, Chitosan hydrogel-based electrode binder and electrolyte membrane for EDLCs: experimental studies and model validation, *J Appl Electrochem* 42 (2012) 935–943. <https://doi.org/10.1007/s10800-012-0469-2>.
- [117] H.V.T. Nguyen, S. Lee, K. Kwak, K.-K. Lee, Bis(oxalate)borate-containing electrolytes for high voltage electric double-layer capacitors: A comparative

study, *Electrochim Acta* 321 (2019) 134649.
<https://doi.org/10.1016/j.electacta.2019.134649>.

- [118] J. Ma, Y. Sahai, R.G. Buchheit, Evaluation of multivalent phosphate cross-linked chitosan biopolymer membrane for direct borohydride fuel cells, *J Power Sources* 202 (2012) 18–27. <https://doi.org/10.1016/j.jpowsour.2011.11.003>.
- [119] A.C. Calkin, P. Tontonoz, Transcriptional integration of metabolism by the nuclear sterol-activated receptors LXR and FXR, *Nat Rev Mol Cell Biol* 13 (2012) 213–224. <https://doi.org/10.1038/nrm3312>.
- [120] F. Persano, C. Malitesta, E. Mazzotta, Cellulose-Based Hydrogels for Wastewater Treatment: A Focus on Metal Ions Removal, *Polymers (Basel)* 16 (2024) 1292. <https://doi.org/10.3390/polym16091292>.
- [121] X. Dai, L.-B. Huang, Y. Du, J. Han, J. Kong, Self-healing flexible strain sensors based on dynamically cross-linked conductive nanocomposites, *Composites Communications* 24 (2021) 100654. <https://doi.org/10.1016/j.coco.2021.100654>.

CHAPTER 2

An Ionically Cross-linked Chitosan Hydrogel Membrane Electrolyte for Long-lived Electrical Double Layer Capacitors

This chapter presents the synthesis, characterizations of ICCHMEs for application as electrolyte cum separator in EDLCs. ICCHMEs were fabricated by ionic crosslinking of chitosan with sodium carbonate, and their physicochemical properties such as WU, dissolution stability, crystallinity, and mechanical strength were examined. Structural and morphological features of the membranes were analyzed using FTIR, XRD, FE-SEM, and EDX. Electrochemical techniques, including transference number measurement, LSV, CV, EIS, and GCD were employed to evaluate conductivity, transport parameters, electrochemical stability window, capacitance, resistance, and energy storage behavior of the EDLCs utilizing ICCHMEs.

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2.1 Introduction

Coal, petroleum oil, and natural gas fulfill much of our expanding energy needs. Due to the limited availability of conventional fuels and their detrimental impact on the environment and human health, there has been substantial development in renewable energy sources such as fuel cells, solar photovoltaic cells, and hydrogen generation. All renewable energy sources, including wind and sun, are intermittent [1–3]. To use renewable energy sources for sustainable development, considerable R&D is needed in electrochemical energy storage technologies like ESs and rechargeable batteries [4]. ESs are divided into EDLCs and PCs by charge-storage mechanism [5–7]. PCs store electrical energy by rapid chemical reactions such as under-potential deposition, intercalation, and redox processes, which occur at or close to a solid electrode surface at the suitable electrode potential. On the other hand, EDLCs create electrical double layers at interfaces between the electrode and electrolyte [3,8,9]. High-surface-area electrode materials such as activated carbons, xerogel carbons, and carbon nanotubes are used in EDLCs. However, PCs use redox-active electrodes such as transition metal oxides and conducting polymers [9]. EDLCs are used in hybrid energy devices of EVs, utility load levelling, diesel locomotive heavy-load starting assist, medical and military purposes [10]. EDLCs feature faster charge-discharge rates, long cycle life, and better power density than rechargeable batteries [9].

The efficiency of EDLCs is reliant upon the characteristics of the electrode materials, electrolyte materials, and the interfaces between the electrodes and electrolytes. Electrolytes have a crucial role in managing the maximum operating voltage, ion transfer efficiency, energy density, and safety concerns [11,12]. EDLCs utilize both non-aqueous and aqueous electrolytes, which can be either solid or liquid type [2]. Liquid electrolytes have concerns such as leakage, corrosion, decreased flexibility, and packaging issues. Solid electrolytes provide the benefits of being leakage-free, compact, and reliable [13,14]. EDLCs that use solid electrolytes have lower capacitive capabilities due to several disadvantages. These include a smaller contact surface between the electrolyte and electrode, limited availability of ions to the electrode, and reduced ionic conductivity compared to liquid electrolytes [15,16]. A particular type of solid electrolytes is polymer electrolytes, and it is made up of electrolytic dopants

that are dissolved in the matrix of polymers. They are typically utilized as thin membranes [6,12,17]. GPEs are the predominant choice for EDLCs among various types of polymer electrolytes. GPEs consist of a polymer network that absorbs a liquid component known as plasticizer [13,14]. GPEs provide several desirable characteristics, including high ionic conductivity, minimal volatility, mild reactivity, and acceptable operational safety [18]. They have excellent chemical, electrochemical, mechanical, and structural stabilities. GPEs are being considered as a promising solution for solving the challenges posed by both liquid electrolytes and solid-state polymer electrolytes. As a result, they have garnered significant interest from the researcher community [17,18]. GPEs are categorized into three types based on the liquid component: HPEs, which contain water as their plasticizer [6,12], ionogel electrolytes employ ionic liquids as the plasticizer [19], while organogel utilize organic liquids as the plasticizer [2].

Hydrogels are 3D semi-solid polymer matrices that possess the capacity to hold a significant quantity of water or a biological fluid. The formation of hydrogels involves cross-linking among polymer chains, which occurs through a physical, chemical, or ionic interaction. Physical crosslinking involves the presence of hydrogen bonding, ionic complexation, physical domain junctions, and, hydrophobic interaction. Chemical crosslinking involves the formation of covalent bonds between polymer chains using a crosslinking agent having low molecular weight. Ionic crosslinking relies on the interaction of charged groups within the polymer chains or between polymer chains and ions in the surrounding environment [20]. Crosslinking creates a three-dimensional network within the hydrogel, thereby crucial for their structural integrity, controlled swelling, tenable properties, enhanced mechanical strength, and long-term stability [21]. Hydrogels containing dissolved electrolytes exhibit high ionic conductivities and thus can be utilized as SSEs [22]. Hydrogels may comprise of either natural polymers [23] or synthetic polymers [24]. Synthetic polymers, including PVA, PEO and poly(acrylic acid) (PAA), were utilized as polymeric hosts [25]. The utilization of synthetic polymer-based matrices gives rise to environmental concerns and challenges regarding their biodegradability. Furthermore, the manufacturing procedure necessitates a series of intricate procedures and entails safety hazards as

well as exorbitant fabrication expenses. These factors impede the utilization of such polymers. In contrast, natural polymers are both environmentally friendly and renewable. Because of biodegradability, hydrogel electrolytes comprising of natural polymers are of sustainable nature. Biopolymers have attracted a significant attention due to their environmentally benign attributes and hence, great potential to replace synthetic polymers derived from fossil fuels that are major contributors to environmental degradation and climate change [26]. In recent years, bioplastics comprising of both bio-based and petroleum-derived biodegradable polymers have emerged as a critical area of focus. These polymers are primarily sourced from plant (vegetable), animal, and synthetic origins. Their adoption is increasing rapidly, with annual growth rates reported between 10 to 20 % [27,28]. Because of their ability to offer superior mechanical, thermal, and electrical properties while minimizing ecological impact, biopolymers have been extensively investigated for use in energy storage devices, such as ESs and batteries. Due to their inherent porosity, activation properties, and heteroatom incorporation, carbon-based electrode materials derived from biomass have been found to be particularly effective in enhancing supercapacitor performances such as specific capacitance [29,30]. The incorporation of nanofillers, such as graphene, carbon nanotubes, and metallic nanoparticles, has significantly improved the mechanical strength, electrical conductivity, and barrier properties of biopolymer composites, making them highly suitable for applications in energy storage and consumer electronics [31,32]. The biopolymers can be processed for their utilization as thin film electrolytes) in energy devices. This type of electrolytes offers critical advantages, viz. enhanced thermal stability, wide electrochemically stable potential windows, and leak-proof nature [33,34]. These properties are essential for developing solid-state ESSs for commercial applications. Recent studies have demonstrated the viability of biopolymer-based electrolytes in competing with their synthetic counterparts, while concomitantly reducing environmental impact and enabling application flexibility in emerging technologies such as wearable electronics and EV [35,36]. The advancements in this field underscore the potential of biopolymers to play a pivotal role in the future of energy storage. Since the beginning of the twenty-first century, researchers have been exploring the possibility of using

natural polysaccharides (such as, chitosan, and alginate) and poly(amino acid) (such as collagen and gelatin) to produce multifunctional hydrogel electrolytes [37].

Chitosan, a biopolymer derived from chitin, is found abundantly in crustacean exoskeletons of shrimp, crabs, cell walls of fungi, and other shellfish [38,39]. Upon dissolution in acidic solutions, chitosan forms a positively charged polymer, exhibiting unique gelation properties [40,41]. The resulting hydrogels possess greater network rigidity and mechanical strength, attributing to their potential usages in diverse fields viz. drug delivery systems [42], wound healing [43], and tissue engineering scaffolds [44]. Chitosan can form hydrogels either by chemical crosslinking or ionic crosslinking. Qu et al. [45] prepared a chitosan-based hydrogel electrolyte using a triple chemical cross-linking method for application in supercapacitors. In another work, Dai et al. [46] reported chemically cross-linked chitosan and guar gum hydrogels for water treatment and energy storage applications. Several other works on chemically cross-linked chitosan hydrogel electrolytes were also reported [47–55]. Choudhury et al. [56] prepared an ionically cross-linked chitosan hydrogel membrane electrolyte using Na_2SO_4 as the ionic crosslinker and successfully used it in direct borohydride fuel cell. Fazdallah et al. [57] reported a low-cost ionically cross-linked chitosan and oxalic acid positive ion conducting membrane for application in fuel cells. Zaidi et al. [58] reported an ionically cross-linked chitosan-reinforced gelatin composite hydrogel electrolyte for supercapacitor application. Lin et al. [59] reported a carboxylated chitosan-based hydrogel electrolyte prepared using Na_2SO_4 as ionic crosslinker and used it for supercapacitor application. Ionic crosslinking of chitosan with Na_2CO_3 has been reported in literature [60]. To the best of our knowledge, however, its preparation in the form of a membrane and application as an electrolyte has not been explored yet. Towards filling this research gap and in continuation of our ongoing research works in this field [15,16,56,61,62], we herein report a polymer hydrogel membrane electrolyte prepared by ionic crosslinking of chitosan with Na_2CO_3 crosslinker for application as a semi-solid electrolyte in an EDLC. The challenge posed by evolution of carbon dioxide bubbles in preparing a smooth membrane has been successfully met by a meticulous optimization procedure. Significantly, the EDLC has been found to exhibit a very low solution-resistance and a long cycle life.

2.2 Materials and methods

2.2.1 Materials

Chitosan (Loba Chemie Pvt. Ltd., CAS No.: 9012-76-4, degree of deacetylation of 75 %, anhydrous sodium carbonate (Na_2CO_3 , AR, Molychem India; CAS.: 497-19-8), glacial acetic acid (CH_3COOH , 90-100 %, Merck), Black pearl Carbon (BPC), Black pearls 2000, CABOT), PVA (Loba Chemie Pvt. Ltd CAS: 9002-89-5, and ethanol (absolute, 99.9 %).

2.2.2 Preparation of chitosan aqueous solution

A typical preparation of 100 mL of 2 % (w/v) aq. chitosan solution involved dissolution of 2 g of chitosan in 100 mL of 2 % (v/v) aqueous acetic acid by stirring for 24 hours at ambient temperature, then stirring again for another 2 hours at 93°C using water bath.

2.2.3 Preparation of Ionically Cross-linked Chitosan Hydrogel

For the preparation of a standard Ionically Cross-linked Chitosan Hydrogel (ICCH), 10 mL of 2 % (w/v) aq. solution of chitosan was mixed with a certain volume of Na_2CO_3 crosslinker solution of a given concentration in a 25 mL beaker with constant stirring. This mixing produced a huge number of bubbles due to the formation of CO_2 . The bubbles were eliminated with a glass rod during the mixing. After continuous mixing, a viscous solution formed, which finally transformed into the ICCH.

2.2.4 Preparation of Ionically Cross-linked Chitosan Hydrogel Membrane Electrolytes

A typical process involved mixing 10 mL of a 2 % (w/v) chitosan solution with 2 mL of 0.5 M (w/v) Na_2CO_3 solution in a 25 mL beaker. A large number of small bubbles formed due to the production of CO_2 , which were eliminated using a glass rod. Continued mixing at high RPM converted the mixed solution into a highly viscous solution, which was transferred to a Petri plate (Sterile ETO & 90 × 15 mm² dimension) and kept at room temperature for 48 hours to finish the cross-linking process between chitosan and carbonate, and to thoroughly dry. The ICCHME was then immersed in crosslinker solution for 30 minutes for extra crosslinking. The

crosslinker solution that had been utilized was thereafter removed. Resulting extra cross-linked ICCHME was then meticulously rinsed with DI water multiple times and stored in DI water for future use.

2.2.5 FT-IR spectroscopic studies

A Perkin Elmer FT-IR spectrometer (Model: Spectrum Two, Serial No.: 104140) was utilized to collect the FTIR spectra of chitosan powder, Na_2CO_3 , and the ICCHME. The wave numbers ranging from 4000 to 400 cm^{-1} were examined. The samples used for ICCHME experiments were circular membranes with a diameter of 1.3 cm. To conduct study on chitosan and Na_2CO_3 powder, a pellet was obtained by subjecting the samples to a hydraulic press with a weight of 255 kg cm^{-2} after they had been mixed with potassium bromide (KBr) powder.

2.2.6 WU studies

WU measurement was performed on ICCHMEs cut into $6 \times 6 \text{ cm}^2$ pieces. The ICCHMEs were kept in DI water in a Petri dish to thoroughly absorb water in their polymeric networks. After wiping their surfaces with soft tissue paper to remove free water, hydrated membranes were weighed (W_h). The ICCHME pieces were dried in an oven for 48 h at 45 °C to evaporate absorbed water. ICCHMEs were weighed every 12 h until a stable dry weight (W_d) was attained to assure complete evaporation. The percentage WU values were evaluated from their wet and dry weights using the formula given below [15,63,64].

$$\text{WU (\%)} = \left(\frac{W_h - W_d}{W_d} \right) \times 100 \quad (1)$$

2.2.7 DR studies

To determine DR (%), the ICCHME was initially sliced into $2 \times 2 \text{ cm}^2$ segments. The wet weights of these segments were recorded. To conduct the dissolution study under an accelerated environment, the ICCHME samples were subjected to boiling in DI water for a duration of 1 to 6 hours. After boiling, ICCHME samples were dried for 48 h at 34°C in an oven, and their final dry weights were then noted. The following formula was used to determine DR (%) [63,65].

$$DR (\%) = \left(\frac{W_1 - W_2}{W_1} \right) \times 100 \quad (2)$$

In Eq. (2), W_1 is the initial wet weight before boiling process and W_2 is the final dry weight of ICCHME sample after boiling and drying procedure.

2.2.8 WVTR studies

The Wet Cup method of ASTM E 96-95 [66] was employed for the measurement of WVTR of the extra cross-linked ICCHME. A Petri dish with 30 mL of DI water was covered with the ICCHME having an area of $4.29 \times 10^{-3} \text{ m}^2$. To stop water vapor from leaking, the side of ICCHME was securely glued to the Petri dish wall using adhesive tape (Cello tape; Premier 42). Noting the initial weight, the whole system was placed in an oven at 34°C and its weight was noted at the interval of 12 h. The WVTR of the ICCHME was obtained by using the given formula [67,68].

$$WVTR = \frac{G}{t \times A} \quad (3)$$

WVTR as evaluated by Eq. (3) has the unit of $\text{g m}^{-2} \text{ h}^{-1}$, where G is quantity of water loss in grams (g), t is duration in hours (h), and A is surface area of ICCHME exposed in transmission of water vapor (m^2).

2.2.9 FE-SEM and EDX studies

Surface as well as cross-sectional topographies of the ICCHME were assessed by a FE-SEM (make: ZEISS Sigma) operating at a voltage of 5 kV. Before being subjected to FE-SEM analyses, the ICCHME samples were gold-plated. The elemental composition of the ICCHME was analyzed using EDX equipment that is connected to the microscope.

2.2.10 Mechanical strength studies

Uncross-linked chitosan membrane (UCM) and ICCHME samples were subjected to mechanical testing using an INSTRON UNIVERSAL TESTING MACHINE E-3000,

US. The experiments were carried out at a stretching velocity of 1 mm/min, enabling accurate assessment of mechanical characteristics.

2.2.11 XRD studies

XRD patterns of the pure Na_2CO_3 salt, UCM, and ICCHME were obtained by employing Ni-filtered Cu radiation at 30 kV and 30 mA as the X-ray source through an X-ray diffractometer (Model: D8 Advance; Bruker, Germany). The diffraction patterns were documented at a rate of $1^\circ (2\theta)$ per minute and with a step of $0.1^\circ (2\theta)$ across a range of diffraction angles $2\theta = 5^\circ$ to 65° .

Deconvolution of the XRD patterns for both the UCM and ICCHME was done by using OriginPro 2022 software. The areas under the crystalline peaks (A_c) and amorphous peaks (A_a) were calculated on the basis of assumption of Gaussian peak functions. To determine the degree of crystallinity (X_c), the following equation was used [69,70].

$$X_c = \left[\frac{A_c}{A_c + A_a} \right] \times 100 \% \quad (4)$$

2.2.12 Ionic conductivity studies

The ionic conductivity of the ICCHME with varying crosslinker concentration were analyzed to evaluating their performance for supercapacitors. A Hydrogel Membrane Electrode Assembly (HMEA) was utilized to determine the ionic conductivity. The ICCHMEs with a thickness of 0.06 mm and a geometric size of 1 cm^2 was placed between two blocking electrodes of SS. Each electrode has a 1 cm^2 flat zone and a 2.5 cm long thin tail section. As seen in Fig. 4(A), the HMEA was securely inserted into a Teflon holder with three screws fastened by Teflon tape. Using filter papers, the surface water of ICCHME was removed before the HMEA was assembled for ionic conductivity measurements. We used emery sheets (Nokila Coated Abrasives, Aloxide Cloth R/G) to induce surface roughness on the SS-blocking electrodes. Screws were used to tighten the Teflon holders so that the ICCHME and SS electrodes made good contact. To measure ionic conductivity of the ICCHME, EIS was measured with a potential amplitude of 5 mVrms in frequency range between 1 MHz to 0.1 Hz. The

bulk resistance (R_b) was evaluated from the Nyquist plot [71], was used to measure the ionic conductivity employing the following equation [62,71].

$$\sigma = \frac{L}{A \times R_b} \quad (5)$$

In equation (5), L is the membrane thickness, and A denotes area of the ICCHME.

2.2.13 Determination of ion transport parameters

The EIS approach was used to determine the transport parameters that are achieved from the Nyquist plot. The following equations illustrate how the diffusion coefficient (D), mobility (μ), and number density (n) of ions form the mathematical foundation of an impedance plot [72]. D is determined from the following Eq. [73].

$$D = \left(\frac{(k \epsilon_0 \epsilon_r A)^2}{\tau} \right) \quad (6)$$

In Eq. (6), k is the reciprocal of the constant phase element (CPE), τ is the reciprocal of angular frequency (ω), which is related to the frequency (f) by the equation $\omega = 2\pi f$. A is the area of the membrane, ϵ_0 is the permittivity of free space ($8.85 \times 10^{-12} \text{ Fm}^{-1}$), and the dielectric constant (ϵ_r) is expressed by the equation $\epsilon_r = \frac{Z_i}{\omega C_0 (Z_r^2 + Z_i^2)}$; where Z_i is imaginary part and Z_r consists of real part of the Nyquist plot. C_0 is the vacuum capacitance, which can be expressed by the equation $C_0 = \frac{\epsilon_0 A}{d}$. Furthermore, the ion mobility μ can be expressed using equation (7) [73].

$$\mu = \left(\frac{eD}{k_B T} \right) \quad (7)$$

In Eq. (7), T is the absolute temperature, k_B is the Boltzmann constant ($1.38 \times 10^{-23} \text{ JK}^{-1}$), and e is the electric charge ($1.602 \times 10^{-19} \text{ C}$).

Finally, the ion number density n for the ICCHME can be calculated using the equation (8) [73].

$$n = \left(\frac{\sigma k_B T \tau}{(e k \epsilon_0 \epsilon_r A)^2} \right) \quad (8)$$

In Eq. (8), σ represents the ionic conductivity of the ICCHME and the other parameters have their usual meanings as described above.

2.2.14 Transference number measurement

The ionic transference number was determined using the Direct Current (DC) polarization technique, which involved application of a constant DC voltage of 1 V across the electrodes of an electrochemical cell comprising of the ICCHME sandwiched between two SS blocking electrodes and monitoring the resultant current as a function of time until it stabilized to a steady value. The initial current (I_0) represents the combined contributions of both ionic and electronic currents. As the current decays over time, it reaches a steady-state current (I_{ss}), which solely represents electronic current. The transference number for ions (t_{ion}) was evaluated using the following equation [69,74].

$$t_{ion} = \frac{I_0 - I_{ss}}{I_0} \quad (9)$$

As evident from Eq. (9), t_{ion} represents the fraction of the current carried by ions, which provides an insight into the ionic transport mechanism, and the relative contributions of cations and anions to the overall conductivity.

The cationic transference number is a vital metric for understanding electrolyte performance. Accurate assessment of ionic conductivity requires measuring this type of parameters. A common approach to determine cationic transference number combines DC polarization with Alternating Current (AC) impedance spectroscopy is known as the Bruce-Vincent method. AC impedance is performed before and after the DC polarization to account for interfacial resistances. Using these measurements, the cationic transference number (t_{cation}) is evaluated by the following equation [75–77].

$$t_{cation} = \frac{I_{ss} (\Delta V - I_0 R_0)}{I_0 (\Delta V - I_{ss} R_{ss})} \quad (10)$$

In Eq. (10), ΔV is the potential applied, R_0 is the resistance before polarization, and R_{SS} is the resistance after polarization.

2.2.15 Linear Sweep Voltammetry study

The breakdown voltage of the ICCHME was evaluated by assessing its electrochemical stability using Linear Sweep Voltammetry (LSV) study, which was carried on an electrochemical cell comprising of the ICCHME sandwiched between two SS blocking electrodes at a scan rate of 5 mVs^{-1} using a Multi Autolab potentiostat (Metrohm, Netherlands, Model M204, Serial No.: MAC90429) connected to a 10A Booster (BST70872).

2.2.16 Electrochemical characterizations of ICCHME

All electrochemical analyses, except the cycle life tests, were done with a Multi Autolab (Metrohm, Netherlands, M204, Serial No.: MAC90429) along with a 10A Booster (BST70872). Cycle life tests were performed using an 8 Channels Battery Analyzer (Make: MTI Corporation, USA; Model: BST8-MA (10 mA)). Solid-state EDLC was built with HMEA including ICCHME as electrolyte-cum-separator and BPC as electrode for supercapacitor performance investigations. An electrode ink was prepared by dispersing BPC and PVA binder in ethanol at a ratio of 80:20 (w/w) as reported by us previously [61]. In a standard procedure, 0.1 g of BPC and 1 mL of ethanol were mixed for approximately 1 hour in a glass vial using a magnetic stirrer to obtain a suspension. Then, a 0.83 mL portion of a 3% (w/v) aqueous PVA solution was added to the suspension in small drops. Afterwards, 0.83 mL of glutaraldehyde (25 %) was added dropwise into the suspension. Finally, a solution of concentrated sulfuric acid was added dropwise to the above mixture to act as a catalyst. After that, the suspension was stirred in an ultrasonic water bath for approximately 3 hours. It was then agitated on a magnetic stirrer for 48 hours to achieve a fine ink. In the electrode formulation, PVA serves as a hydrophilic polymeric binder that ensures uniform dispersion of the carbon particles and strong adhesion to the stainless-steel current collector. Glutaraldehyde acts as a chemical crosslinker for PVA under acidic conditions, forming a stable crosslinked network that enhances electrode cohesion and suppresses binder dissolution during electrolyte contact. The crosslinked PVA matrix

improves interfacial stability at the electrode-electrolyte interface by promoting effective wetting while limiting excessive swelling, thereby facilitating efficient ion transport and contributing to the observed electrochemical stability of the EDLC devices. The electrode ink was coated on the surface of the SS current collectors using a paintbrush to achieve an electrode loading of 1 mg cm^{-2} . The electrodes made from BPC were utilized to create HMEA for symmetrical solid-state EDLC. To create a specific HMEA, an ICCHME was utilized as an electrolyte as well as a separator. The ICCHME was sandwiched between two BPC-coated electrodes. The HMEA was properly sealed with Teflon tape and fitted firmly into a Teflon holder that was furnished with three screws, as shown in Fig.2.4 (A) [16,71]. To prevent any potential water leakage from the ICCHME, a Parafilm (Bemis Laboratory Film) was positioned over the Teflon holder.

The symmetrical solid-state EDLC was tested for electrochemical characterization using CV, GCD plots, as well as EIS. The CVs were measured within the voltage range of 0 to 1V, using various scan rates ranging from 5 to 1000 mV s^{-1} . The GCD plots were obtained within the voltage range of 0 to 1V, with different constant current densities ranging from 1 to 20 mA cm^{-2} . The EIS plots were recorded within a frequency of 1 MHz to 0.1 Hz, having perturbation of $5 \text{ mV}_{\text{rms}}$ [78]. The frequency sweep was performed from higher to lower frequencies with a total of 50 data points within the specified frequency range. All measurements carried out in the current study were performed at ambient conditions of temperature and pressure.

The cycling stability of the EDLC was investigated by analyzing GCD plots under two different constant current densities of 2 and 5 mA cm^{-2} . The areal capacitance C_A (mF cm^{-2}), energy density E ($\mu\text{Wh cm}^{-2}$), as well as the power density P (mW cm^{-2}) of the EDLC were calculated by analyzing from GCD plots using equations (11), (12), and (13), respectively [79–81].

$$C_A = 2 \times \frac{I \times t_d}{A \times \Delta V} \quad (11)$$

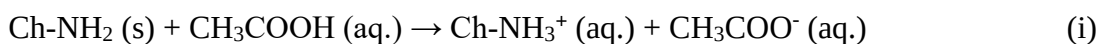
$$E = \frac{1}{2} \times \frac{1000}{3600} C_A \times (\Delta V)^2 \quad (12)$$

$$P = \frac{E}{t_d} \times 3600 \quad (13)$$

In these equations, I (mA) is the current density, t_d (seconds) is the time of discharge post IR drop, A is the geometrical area (cm²) of the electrode, and ΔV is the potential window (V).

2.3 Results and discussion

The structure of chitosan [38] is illustrated in Fig.2.1 (A), revealing that it does not contain any ionizable functional group but contains amino groups (-NH₂) in its structure. Because of the absence of any ionizable functional groups, chitosan is insoluble in water [15]. However, it dissolves in aqueous solutions of weak acids such as formic acid, acetic acid, citric acid, and lactic acid due to the protonation of its amino groups by the acid [82]. The protonation converts the -NH₂ groups into positively charged ammonium (-NH₃⁺) groups [15,38] as illustrated by reaction (i), thereby disrupting the intermolecular interactions and increasing the solubility of chitosan in the acidic medium. The ionic attraction between positively charged (-NH₃⁺) groups of the chitosan chain and negatively charged oxygen atoms of carbonate anion (CO₃²⁻) crosslinker results in the formation of a stable cross-linked chitosan network that gives rise to the hydrogel. This interaction is schematically shown in Fig.2.1 (B)



Protons from acetic acid, which was used for the protonation of chitosan and its consequent dissolution in water, convert sodium carbonate into carbonic acid (H₂CO₃) as shown in reaction (ii) by ion exchange reaction. H₂CO₃ is unstable in the presence of water [83] and, hence, undergoes dehydration to liberate CO₂ in the form of bubbles as shown in reaction (iii). As soon as the aqueous solution of Na₂CO₃ was added to the

aqueous acidic solution of chitosan during the synthesis of ICCH/ICCHME, a lot of bubbles formed. With meticulous stirring, the bubbles could be eliminated and the ionic crosslinking of chitosan took place concomitantly and the solution turned into a semi-solid hydrogel. The different stages of the elimination of CO₂ bubbles and the concomitant synthesis of ICCH are shown in Fig.2.1 (C) (i-iv). An image of the final ICCH in an inverted beaker is shown in Fig.2.1 (C) (v), which demonstrates a stable hydrogel structure within the beaker.

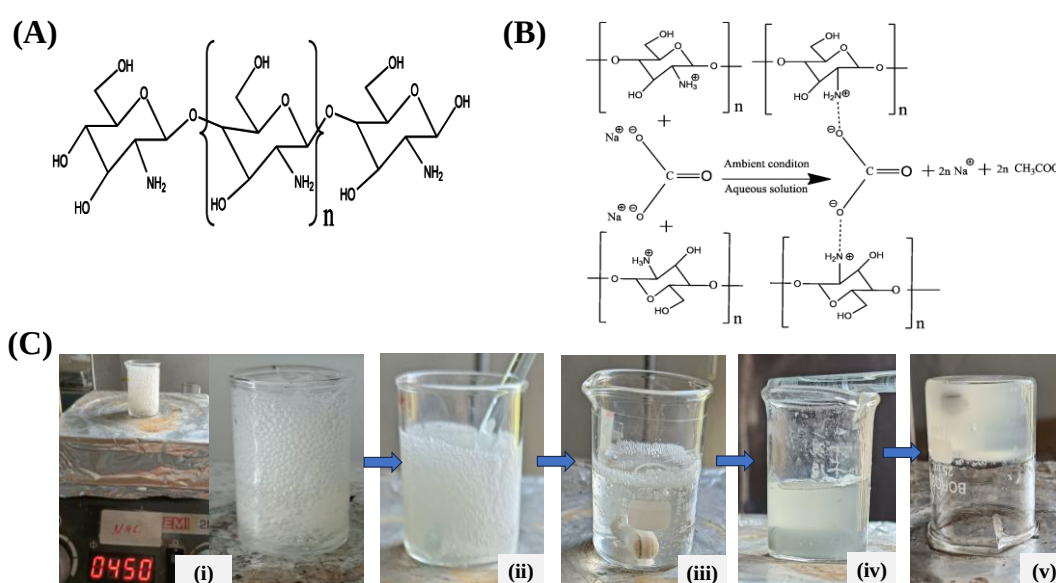


Fig.2.1 (A) Chemical structure of chitosan; (B) Schematic diagram of the ionic cross-linking reaction between protonated chitosan and Na₂CO₃; (C) Images showing different stages ((i)-(iv)) of the preparation of ICCH and concomitant elimination of CO₂ bubbles. Image (v) shows the ICCH in an inverted beaker.

The optimization process for the synthesis of ICCH using 2 % (w/v) chitosan dissolved in 2 % (v/v) aqueous glacial acetic acid solution and different concentrations as well as volumes of aqueous solutions of Na₂CO₃ crosslinker is summarized in Table 2.1. For a chitosan solution of a given concentration, the time taken for formation of ICCH decreases with increase of both the concentration and volume of the crosslinker solution. For a given concentration of crosslinker, time for formation of ICCH decreases with increase in volume of the crosslinker. Elimination of the bubbles

formed during the preparation of ICCH depends on the time of mixing and the concentration as well as volume of the crosslinker. ICCH could not be prepared while using low concentration and volume of the crosslinker even after mixing the contents for a long time. On the other hand, when very high concentration and volume of crosslinker was used, ICCH did form but it eliminated. For the preparation of ICCHME, 2 mL of 0.5 M Na_2CO_3 was found to be optimum. This optimum condition enough time for excellent mixing and elimination of all the bubbles. Also, for all the concentrations and volumes of crosslinkers that allowed formation of good quality ICCH, the process of ICCH formation started immediately after addition of the crosslinker to form islands of hydrogel beads. These hydrogel beads upon further stirring resulted in the formation of ICCH. Due to the immediate formation of Hydrogel beads, casting of the mixed solution to a membrane form was not possible.

Table 2.1: Summary of the optimization process for synthesis of ICCH using different concentrations and volumes of Na_2CO_3 crosslinker in 10 mL of chitosan acidic aqueous solution.

Na_2CO_3 concentration (M)	Volume of Na_2CO_3 (mL)	Observation of ICCH formation
0.5	1	ICCH did not form despite mixing for a long time (typically, a few days). All bubbles were eliminated after 300 min. of mixing.
	2	ICCH did not form despite mixing for a long time (typically, a few days). All bubbles were eliminated after 260 min. of mixing.
	3	Very weak ICCH with bubbles trapped inside formed after mixing for 210 min.
	4	Weak ICCH with bubbles trapped inside formed after mixing for 180 min.

1.0	1	ICCH did not form despite mixing for a long time (typically, a few days). Bubbles were not eliminated.
	2	ICCH did not form despite mixing for a long time (typically, a few days). Bubbles were not eliminated.
	3	ICCH formed after mixing for 170 min. with elimination of all the bubbles.
	4	ICCH formed with bubbles trapped inside after mixing for 90 min. Water seeped out of the ICCH.
1.5	1	Weak ICCH with bubbles trapped inside formed after mixing for 80 min.
	2	ICCH with bubbles trapped inside formed after mixing for 65 min.
	3	ICCH formed after mixing for 55 min. with elimination all the bubbles.
	4	ICCH with bubbles trapped inside formed after mixing for 25 min. Water seeped out of the ICCH.
2.0	1	Weak ICCH with bubbles trapped inside formed after mixing for 75 min.
	2	ICCH formed after mixing for 55 min. with elimination all the bubbles.
	3	ICCH formed after mixing for 35 min. with elimination all the bubbles.
	4	ICCH with bubbles trapped inside formed after mixing for 20 min. Water seeped out of the ICCH.
2.5	1	Weak ICCH with bubbles trapped inside formed after mixing for 50 min.

	2	ICCH formed after mixing for 35 min. with elimination all the bubbles.
	3	ICCH formed after mixing for 15 min. with elimination all the bubbles.
	4	ICCH with bubbles trapped inside formed after mixing for 10 min. Water seeped out of the ICCH.
3.0	1	ICCH formed after mixing for 20 min. with elimination all the bubbles.
	2	ICCH with bubbles trapped inside formed after mixing for 16 min. Water seeped out of the ICCH.
	3	ICCH with bubbles trapped inside formed after mixing for 10 min. Water seeped out of the ICCH.
	4	ICCH with bubbles trapped inside formed after mixing for 5 min. Water seeped out of the ICCH.

Fig.2.2 (A) presents an image of the ICCHME, which is a transparent, colorless, and mechanically strong flexible thin film with a thickness of approx. 60 μm . A schematic diagram of the three-dimensional hydrogel network is given in Fig.2.2 (B), which shows the ionic linkages between two chitosan chains formed by the ionic attraction between $-\text{NH}_3^+$ groups of chitosan and $-\text{O}^-$ ions of carbonate crosslinker. The crosslinking creates an organized and interconnected network, thereby resulting in a strong and stable hydrogel structure. The pores in the ICCHME seen in Fig.2.2 (B), are believed to be produced by the evolution of CO_2 during hydrogel formation. The formation of pores in the ICCHME is similar to the formation of pores in bakery items such as bread and cake by the evolution of CO_2 during the baking process using baking powder (i.e. NaHCO_3) by the leavening process. The pores are produced due to the evolution of CO_2 generated through the reaction between NaHCO_3 and water in the baking mixture. Similarly, the evolution of CO_2 resulting from the dehydration of

H_2CO_3 gives rise to the formation of pores within the mass of the ICCHME. The porous structure in the ICCHME aids in the transportation of ions during its usages as solid electrolyte in EDLCs.

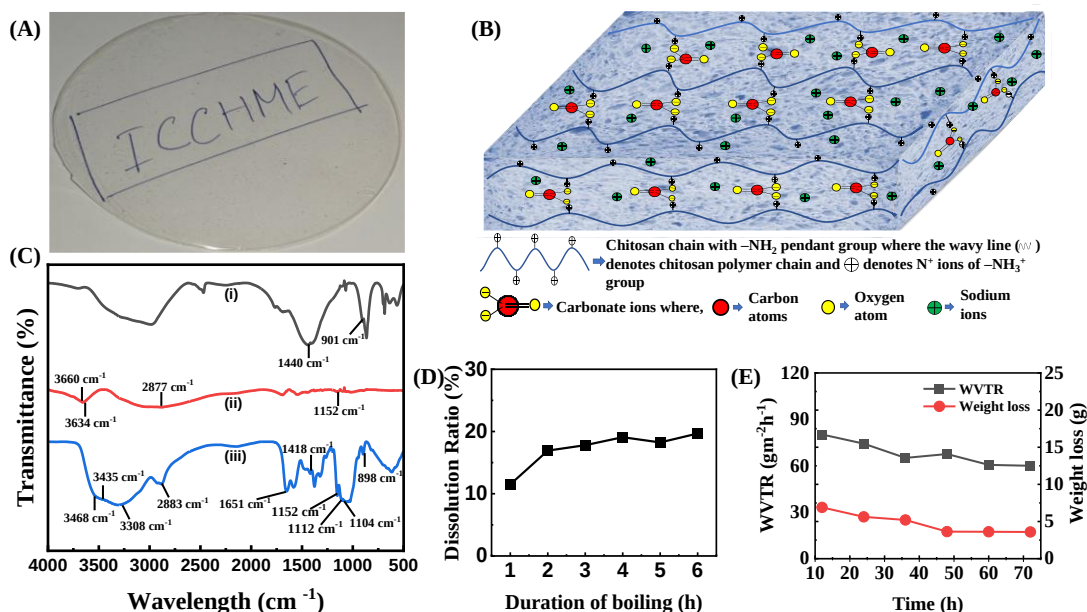


Fig.2.2 (A) An image of the ICCHME cast on a Petri dish; (B) Schematic diagram of the 3D hydrogel structure of the ICCHME; (C) FTIR spectra of Na_2CO_3 powder (i) chitosan powder (ii), and ICCHME (iii); (D) DR (%) of ICCHME as a function of boiling time; (E) Plots of WVTR and the related weight loss of ICCHME as a function time.

The FTIR spectra of ICCHME, chitosan powder, and Na_2CO_3 powder are given in Fig.2.2 (C). Assignment of the various FTIR spectroscopic bands observed in Fig.2.2 (C) to different functional groups associated with each of the materials is presented in Table 2.2. In the FTIR spectral analysis of the ICCHME, distinctive bands emerge, providing substantial evidence of successful crosslinking.

Table 2.2: FTIR spectroscopic bands observed for ICCHME, chitosan powder, and Na_2CO_3 powder.

Band position (cm^{-1}) observed for		

Chitosan powder	Na ₂ CO ₃ powder	ICCHME	Functional groups with their modes of vibration	Compound class/Functional groups
3660		3468	O-H Stretching	Hydrogen bonded
3634	-	3435, 3308	N-H Stretching	Primary amine
2877		2883	C-H Stretching	Alkanes
-	1440 901	1418 898 1112, 1104	CO ₃ ²⁻ stretching CO ₃ ²⁻ bending antisymmetric stretching	Carbonate ion
		1651	antisymmetric deformation	Primary amine
1152,	-	1152	C-O-C stretching	Glycosidic bond

The obtained FTIR spectra are depicted in Fig.2.2 (C). In pure chitosan powder, the amino group and hydroxyl group produced intramolecular and intermolecular H-bonds, resulting in the NH stretching vibration and OH stretching vibration at 3634 cm⁻¹ and 3600 cm⁻¹, respectively. The ICCHME spectrum exhibits a shift of the absorption peak at 3468 cm⁻¹ and a formation of intense sharp peaks at 3435 cm⁻¹ and 3308 cm⁻¹. This suggests the disruption of hydrogen bonds between the amino and hydroxyl groups, resulting in noticeable stretching vibrations of OH or NH. Both chitosan powder and ICCHME show CH stretching vibrations at 2877 cm⁻¹ and 2883 cm⁻¹, respectively. The ICCHME showed extra peaks compared to chitosan powder, which correspond to the distinctive signals of the carbonate group (-CO₃²⁻): 1418 cm⁻¹ and 898 cm⁻¹. The prominent absorption peaks observed at these two locations are indicative of carbonate signals [60]. The spectrum of ICCHME exhibited two absorption bands. The first band at 1651 cm⁻¹, can be assigned to the antisymmetric deformation of N-H vibrations in the NH₃⁺ ion. The second band, which is divided into

two peaks at 1112 and 1104 cm^{-1} , corresponds to the antisymmetric vibrations caused by stretching of carbonate groups. This confirms the presence of ionic crosslinks between the carbonate anions and NH_3^+ groups of chitosan [84].

The WU of ICCHME is 226 %. This high-WU value may be due to the synergistic effect of multiple factors related to the structure of the ICCHME, as discussed below. Chitosan has six-membered rings its polymer backbone and polar functional groups including $-\text{NH}_2$, $-\text{OH}$, and C-O-C . Due to this chitosan generates H-bonds with water and retains water within its rings [85,86]. Secondly, the porous structure within the ICCHME enhances its WU capacity by providing ample pathways for water penetration. In this bulk cross-linked ICCHME, the crosslinker is situated inside the 3D hydrogel network, due to this, there is more of polymer-free region that is occupied by water. This explains the larger WU of ICCHME.

DR (%) indicates the percentage of polymer inside a hydrogel dissolves within a solvent after a specific immersion period, relative to its entire polymer content [87]. The DR assessment of ICCHMEs in deionized water, exposed to an aggravated method of boiling for 6 hours, resulted in a DR of 18.24 %, as shown in Fig.2.2 (D). A similar value of DR was observed for gelatin chemical hydrogel membrane electrolytes recently reported by our group [61]. This result indicates that the membrane has a moderate amount of solubility or dispersibility under the provided timeframe and severe conditions.

The WVTR measures how fast vapor passes through a membrane at certain values of temperature and humidity [66]. In this investigation, we utilized WVTR to indirectly assess how porous the ICCHME material is. Fig.2.2 (E) presents the variations of WVTR and the related loss of weight of water during the entire duration of WVTR study with time. The WVTR and water lost weight during WVTR study have been found to be $60 \text{ gm}^{-2} \text{ h}^{-1}$ and 3.1 g, respectively. In the similar work done by Núñez et al. [88], the WVTR values recorded for chitosan/glyoxal and chitosan/sorbitol were 59 and $54 \text{ gm}^{-2} \text{ h}^{-1}$, respectively. Htay et al. [89] also reported an approximately similar WVTR of $50.3 \text{ gm}^{-2} \text{ h}^{-1}$ for the synthetic polymer polycaprolactone for application in

tissue engineering. Impressively, the ICCHME could hold water in the petri dish kept inside an oven at 34 °C for 72 h.

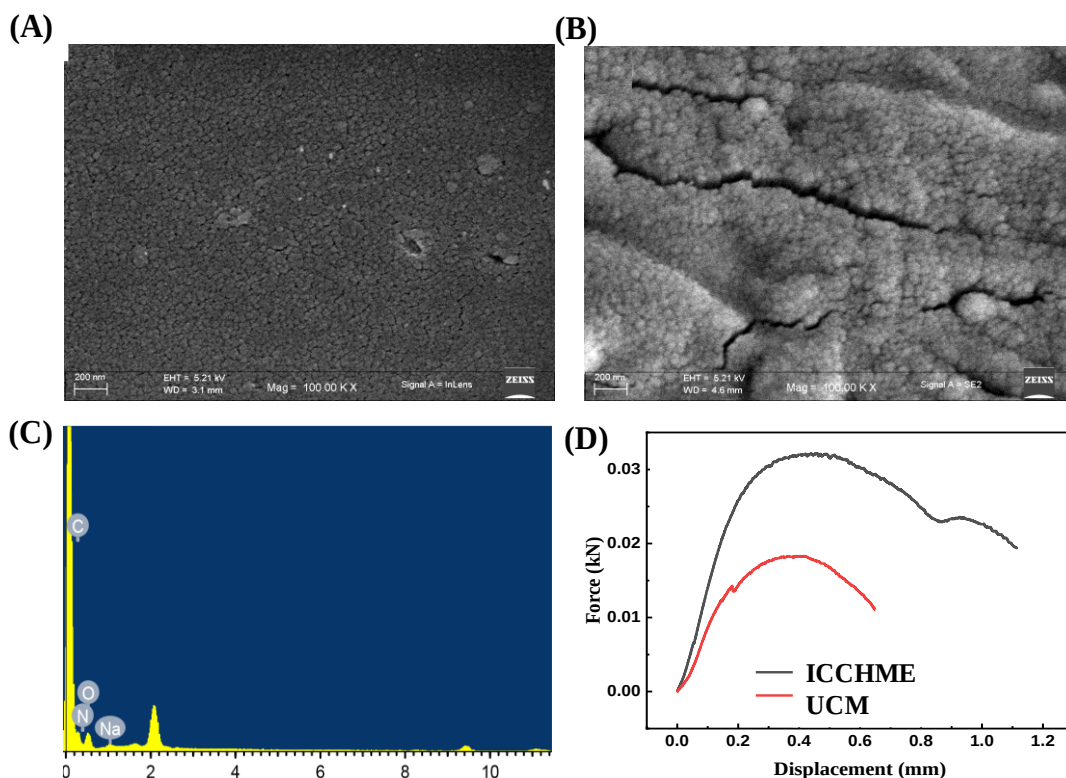


Fig.2.3 (A) FE-SEM picture of the surface of ICCHME; (B) FE-SEM picture of the cross-section of ICCHME; (C) EDX spectrum of ICCHME; (D) Force versus displacement plots of the UCM and ICCHME.

FE-SEM analysis of the ICCHME provided crucial insights into their structural characteristics. As shown in Fig.2.3 (A) and 2.3 (B), FE-SEM picture of ICCHME portrayed a uniform surface for both surface and cross-section, thus showing a homogenous structure of ICCHME. This observation suggests that chitosan chains within ICCHME are probably bound together by ionic crosslinking, resulting in a more integrated and uniformly porous structure. This is associated with an increase of surface area, permeability, and ion transport. This uniformity strongly indicates the effectiveness of ionic crosslinking method in synthesizing a homogeneous and structurally stable membrane. However, cracks observed in the cross-sectional image may be attributed to the breaking of the network of polymers during drying. The EDX

spectrum, shown in Fig.2.3 (C) for ICCHMEs, the data displays peaks that correlate to the presence of Na, as well as C, N, and O [90,91]. The presence of these elements is on expected lines as sodium originates from Na_2CO_3 crosslinker and the remaining elements originate from chitosan.

Table 2.3: Summary of the mechanical strength characterization data of UCM and ICCHME.

Material	Tensile strength (MPa)	Elongation (%)	Young's modulus (MPa)
UCM	30.51	6.48	470.84
ICCHME	53.29	11.13	478.80

The force-displacement curves obtained from the mechanical strength characterization of the UCM and ICCHME are presented in Fig.2.3 (D). The data related to the mechanical strength studies are summarized in Table 2.3. The results show that the ICCHME displays significantly superior mechanical properties as compared to the UCM. The tensile strengths of ICCHME and UCM are 53.29 and 30.51 MPa, respectively. This indicates that ionic crosslinking with Na_2CO_3 has effectively strengthened the membrane. The elongation at break for ICCHME is 11.13 %, which is higher than 6.48 % observed for UCM. This shows that the ionic crosslinking also improves the flexibility and ductility of the chitosan membrane, allowing it to withstand more strain before breaking. Similar observations were reported in studies of cross-linked chitosan-based membranes, where the mechanical strengths were improved by crosslinking of the polymers [92–95]. Furthermore, the Young's modulus values of ICCHME and UCM are found to be 478.80 and 470.84 MPa, respectively. This suggests that the ICCHME possesses better stiffness as compared to that of the UCM. These observations indicate that the ICCHME with superior tensile strength, flexibility, and stiffness is a better candidate for application as electrolyte membrane in durable electrochemical energy devices.

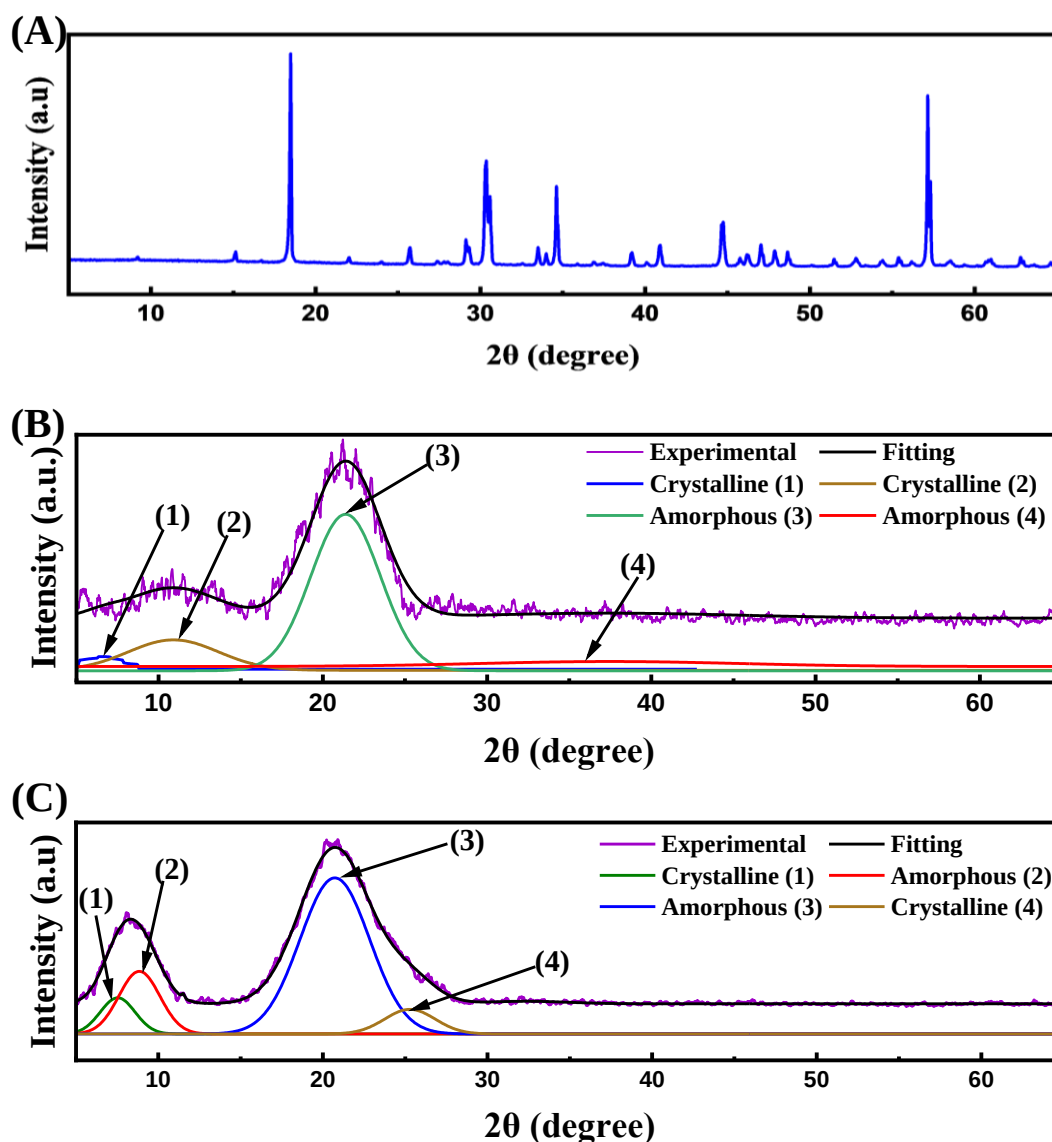


Fig.2.4 (A) XRD pattern of pure Na_2CO_3 ; (B) Deconvoluted XRD pattern of pure UCM; (C) Deconvoluted XRD pattern of ICCHME.

The XRD pattern of pure Na_2CO_3 , and the deconvoluted XRD patterns of UCM and ICCHME are shown in Fig.2.4 (A), 2.4 (B), and 2.4 (C), respectively. From Fig.2.4 (A), it is seen that the XRD pattern of pure Na_2CO_3 exhibited many sharp well-defined peaks, indicating its highly crystalline structure. As seen from Fig.2.4 (B), the deconvoluted XRD pattern of pure UCM exhibited two crystalline bands (1 and 2) at 2θ values of 6° and 11° , respectively, and two amorphous bands (3 and 4) at 2θ values of 21° and 38° , respectively. This pattern is consistent with findings of Anawi et al.

[69] for UCM. Interestingly, the deconvoluted XRD pattern of the ICCHME shown in Fig.2.4 (C) also exhibited two crystalline bands (1 and 4) at 2θ values of 7° and 25° , respectively, and two amorphous bands (2 and 3) at 2θ values of 8° and 20° , respectively. The degrees of crystallinity of both the membranes were quantitatively determined using Eq. (4). The crystallinity of UCM and ICCHME are found to be 19.50 and 15.02 %, respectively. This indicates semi-crystalline nature of the two membranes. The reduction in crystallinity of the chitosan membrane could be due to the disruption of the crystalline regions by the crosslinker, resulting in an increase in the amorphous phase. The sharp peaks seen in the XRD pattern of pure Na_2CO_3 salt do not appear in the XRD pattern of ICCHME, thereby confirming the complete dissolution of crystalline Na_2CO_3 in the chitosan hydrogel matrix. Moreover, the amorphous band around 2θ of 8° for ICCHME is significantly broader than that observed for the UCM. This broadening is due to the increase in the amorphous nature induced by the crosslinking. The crosslinking reaction between sodium carbonate and chitosan results in the formation of new bonds, which disrupt the existing intermolecular and intramolecular hydrogen bonds in chitosan [96]. This reduction in crystallinity is expected to improve the ionic conductivity of the chitosan membrane, making it a promising candidate for application in electrochemical energy systems.

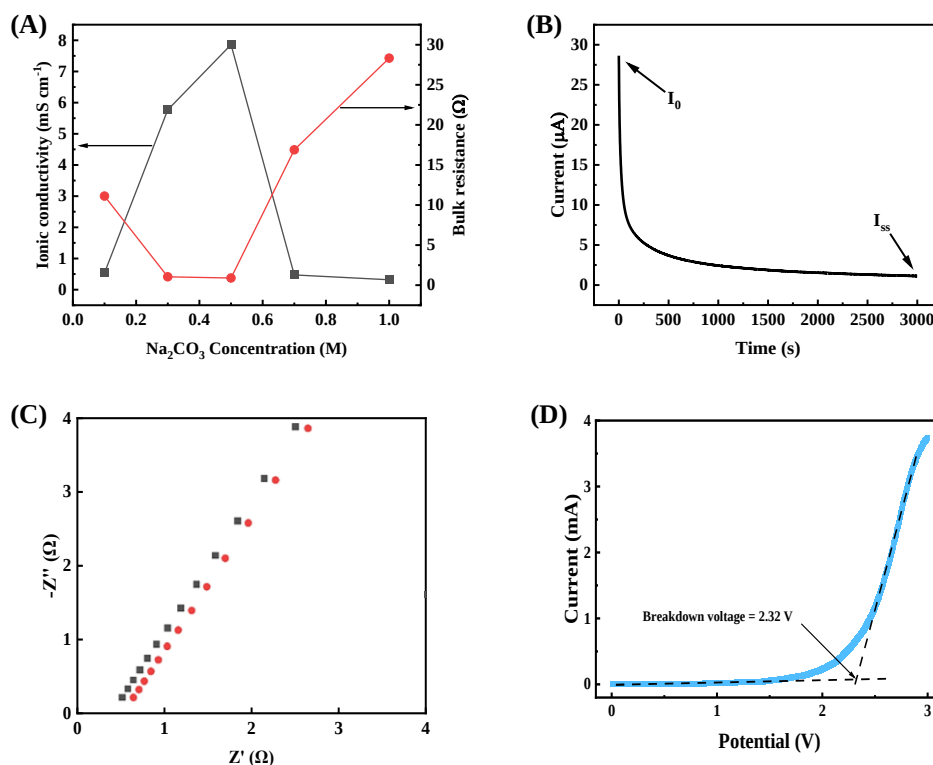


Fig.2.5 (A) Graph of ionic conductivity as a function of Na₂CO₃ concentration; (B) Polarization current versus time for ICCHME; (C) Impedance spectra recorded before and after polarization; (D) LSV plot of the ICCHME sandwiched between two SS blocking electrode.

The variations of ionic conductivities and R_b of ICCHMEs with varying concentrations of Na₂CO₃ are presented in Fig.2.5 (A). With increase of Na₂CO₃ concentrations, the ionic conductivity of ICCHMEs initially increased steeply and attained a peak value of 7.89 mS cm⁻¹ at a Na₂CO₃ concentration of 0.5 M. Beyond the peak value, the ionic conductivity decreased sharply, and attained a nearly saturation value. The variation of the R_b with increasing Na₂CO₃ concentrations followed a trend that is roughly opposite to the trend of the variation of ionic conductivity. The smallest value of R_b that corresponds to the largest value of ionic conductivity was found to be 0.76 Ω. Similar trends of ionic conductivity were observed in literature for several polymer-based electrolytes [97,98]. The observed trend of ionic conductivity variation may be explained on the basis of the balance between electrolytic dissociation and ionic mobility within the ICCHMEs. At lower concentrations, the number of ions available

for conduction is limited, leading to a low ionic conductivity [99]. As the salt concentration increased to 0.5 M, more ions are available for charge transport within the ICCHMEs. This led to an enhanced ionic conductivity [100]. Additionally, the membrane structure remained favourable for ion transport at this concentration with minimal obstruction to ionic movement, which explains the optimal ionic conductivity observed [101]. However, when the salt concentration increased beyond 0.5 M, the ionic conductivity decreased. This reduction may be attributed to several factors, including formation of ion aggregates or ion pairs, which reduced the number of free ions available for ionic conduction [102]. Moreover, as observed during membrane preparation, usage of higher concentrations of Na_2CO_3 led to the formation of air bubbles and localized gelation, which disrupted the uniformity of the ICCHME and hinder ion mobility. These structural changes in the ICCHME increased resistance to ion transport, outweighing the benefits of a higher salt concentration, and thus led to a decreased ionic conductivity at 0.7 and 1 M.

The DC polarization plot for the ICCHME is shown in Fig.2.5 (B). The value of t_{ion} determined using Eq. (9) is found to be 0.96. This indicates that ionic transport is the primary mode of charge conduction in the ICCHME with minimal contribution from electronic transport. Fig.2.5 (C) displays the Nyquist plots recorded before and after the DC polarization. The t_{cation} value evaluated by Eq. (10) employing outputs from Fig.2.5 (B) and Fig.2.5 (C) is found to be 0.04. This indicates that anions are the predominant charge carriers in the ICCHME, with cations playing a relatively minor role in the overall ionic conductivity [103].

The electrochemically stable potential window for a given electrolyte is an important parameter that determines the energy density electrochemical energy storage devices [104]. The LSV plot for the ICCHME recorded at ambient temperature is shown in Fig.2.5 (D), which reveals no apparent change in the current within the potential range of 0-2.32 V. This implies the absence of any undesired electrochemical reaction. When the potential was scanned beyond 2.32 V, the current increased due to electrolyte decomposition. The LSV study thus reveals a stable potential window of 0-2.32 V for the ICCHME [105]. In the work reported by Aziz et al. [106], the chitosan-based

polymer electrolyte exhibited a stable voltage window of 0-2.13 V, which is comparable to the observation being reported in the current paper. Since 0-1 V is considered to be suitable voltage window for water-based electrochemical cells, the ICCHME being reported here can safely utilized in aqueous energy storage devices [106].

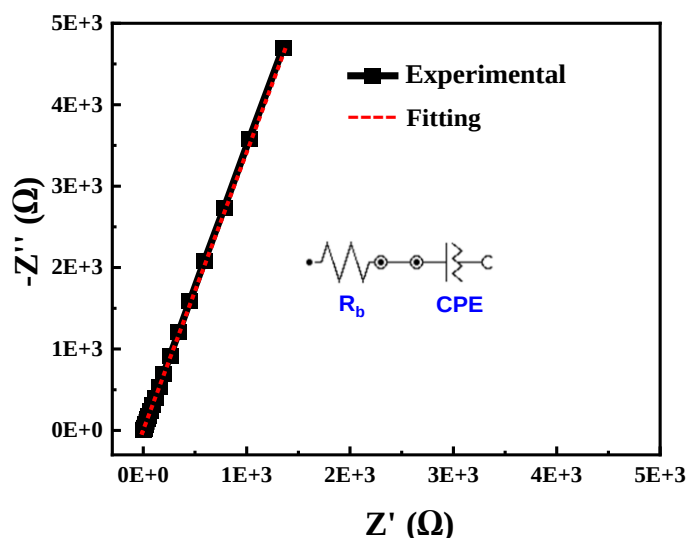


Fig.2.6 Nyquist plot, its fitting, and the related electrochemical equivalent circuit (shown in the inset) for the optimized ICCHME.

The ion transport parameters for the optimized ICCHME prepared with 0.5 M Na_2CO_3 , which demonstrated the highest ionic conductivity, were evaluated by EIS fitting employing Nova 2.1.5 software. During the ionic conductivity study, since only a spike was observed in the Nyquist plot of the ICCHME, the electrochemical equivalent circuit was modelled on the basis of the combined effects of its R_b and CPE as shown in Fig.2.6 [69]. The CPE value derived from the Nyquist plot was found to be 1.38×10^{-5} F, which demonstrates the capacitive nature of the ICCHME and its potential to store charge at electrode-electrolyte interface. The calculated diffusion coefficient (D) of $8.36 \times 10^{-7} \text{ m}^2\text{s}^{-1}$ suggests a moderate ion diffusion, characteristic of polymer electrolytes where crosslinking influences the diffusion pathways [107]. The ion mobility (μ) was found to be $3.24 \times 10^{-5} \text{ m}^2\text{V}^{-1}\text{s}^{-1}$, which indicates that ions migrate efficiently under the influence of an electric field. These results point towards the structural integrity provided by the sodium carbonate crosslinker [108]. Moreover, the

ion number density (n) was found to be $1.51 \times 10^{21} \text{ m}^{-3}$, signifying a high concentration of mobile ions, which is crucial for maintaining elevated ionic conductivity. These values are in line with other studies on polymer-based electrolyte membranes [69,109,110], underscoring the suitability of the ICCHME for application in electrochemical energy devices that require stable and efficient ion transport.

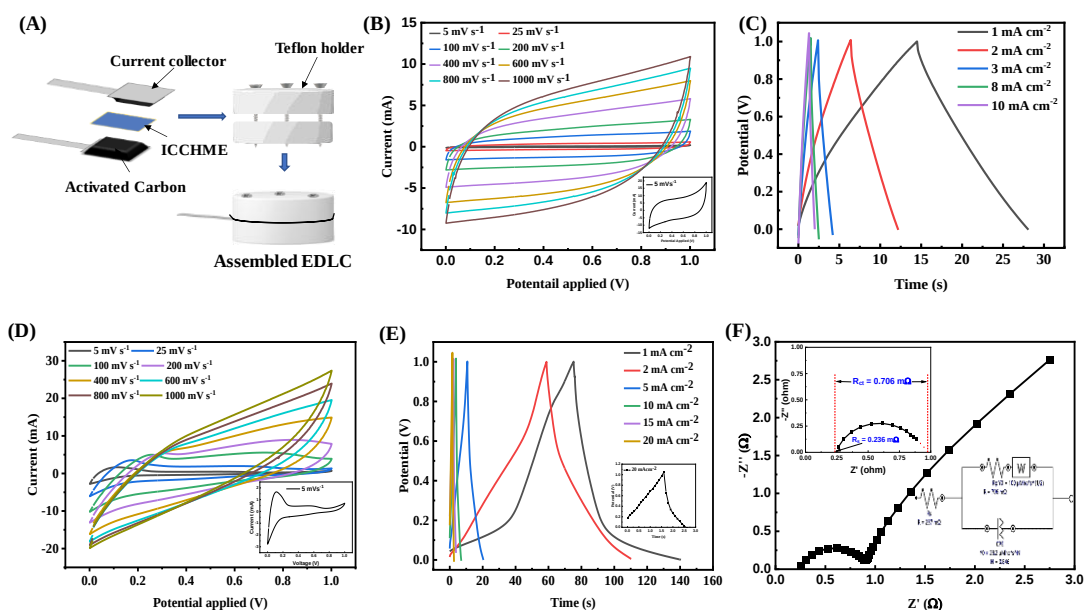


Fig.2.7 (A) A graphic demonstrating the assembling of EDLC used in this research; (B) CVs of the EDLC at varied scan rates recorded immediately after its assembling; (C) GCD plots of the EDLC at varied current densities recorded immediately after its assembling; (D) CVs of the EDLC at varied scan rates measured after it attained its peak performance stage; (E) GCD graphs of the EDLC at varied current densities recorded after attaining peak performance stage; (F) Nyquist plot of the EDLC recorded immediately after its assembling (the insert at the right bottom shows expanded view of high-frequency end of Nyquist plot and the insert at the left top shows the equivalent circuit diagram for EIS data).

Supercapacitor performance of ICCHME was investigated using a symmetrical EDLC assembled with ICCHME as the electrolyte-cum-separator and BPC as the electrode. Fabrication of the EDLC in two-electrode system is schematically illustrated by a flowchart in Fig.2.7 (A). During the cycle life study of the EDLC, it was observed that

the initial areal capacitance was low when recorded immediately after assembling it. The areal capacitance improved with successive charge-discharge cycles recorded during the cycle life study. At 2 mAcm^{-2} , the EDLC showed highest areal capacitance after attaining 4500 charge-discharge cycles. However, when the cycle life was studied at 5 mAcm^{-2} , the EDLC showed the highest areal capacitance after attaining 18500 charge-discharge cycles. The aging of the EDLC was observed after it attained its peak performance. In this manuscript, the areal capacitance at peak performance stage henceforth, referred to as peak capacitance is reported instead of the initial performance recorded immediately assembling the EDLC. The observed highest areal capacitance could be due to the adaptation of the pores of the ICCHME to the electrode structure, thereby improving the electrolyte accessibility and ion transport within the electrode [111,112].

The CVs of the EDLC at varied scan rates recorded after immediately assembling it are shown in Fig.2.7 (B). The inset in Fig.2.7 (B) shows the CV of the EDLC at the lowest scan rate of 5 mVs^{-1} . No redox peaks are visible in the CVs, suggesting a lack of redox reaction within the potential window of 0-1 V. The absence of redox peaks serves as a reliable indicator for the double-layer type of capacitance for the EDLC reported here. As evident from Fig.2.7 (B), the EDLC has been tested up to a very high scan rate of 1000 mVs^{-1} . Fig.2.7 (B) clearly demonstrates a transition in the shape of the CV from a nearly rectangular to a leaf shape as the scan rate increased. The ideal rectangular CV shapes arise from efficient charge transport properties [113]. At higher scan rates, the CV shape deviates from the rectangular form due to diffusion-controlled ionic transport [114]. Both carbon porosity and internal resistance have been reported to influence the current-voltage relationship [115].

Table 2.4: Summary of the electrochemical performance data recorded after the EDLC attained its peak performance stage by GCD at varied current densities.

Current density (mA cm ⁻²)	Areal capacitance (mF cm ⁻²)	Energy density (μWh cm ⁻²)	Power density (μW cm ⁻²)	IR drop (mV)	Coulombic efficiency (%)
1	269.01	37.36	2000.07	63	89
2	260.40	36.17	2000	64	91
5	98.49	13.68	5025	83	84
10	64.68	8.98	10106.25	165	81
15	48.51	6.74	15159.38	271	66
20	39.69	5.51	22050	379	57

The GCD plots at varied current densities recorded immediately after assembling the EDLCs are given in Fig.2.7 (C) and those recorded after the EDLC attained its peak performance stage are given in Fig.2.7 (E). The inset in Fig.2.7 (E) shows the GCD plot at the highest current density of 20 mA cm⁻². The maximum current density withstood by the EDLC immediately after its assembling was 10 mA cm⁻² and that withstood by the EDLC after it attained its peak performance was 20 mA cm⁻². The higher current density withstood at the peak performance stage could be due to the low R_s of the ICCHME. The GCD plots given in Fig.2.7 (C) have nearly triangular shapes with negligible IR drop values. In contrast, the GCD plots given in Fig.2.7 (E) have non-triangular shapes with low IR drop values. The electrochemical performance data evaluated from the GCD plots given in Fig.2.7 (E) are presented in Table 2.4. From Table 2.4, it is seen that when the current density was increased from 1 to 20 mA cm⁻², the peak areal capacitance decreased from 269.01 to 39.69 mF cm⁻²; the energy density decreased from 37.36 to 5.51 μWh cm⁻²; the power density increased from 2000.07 to 22050 μW cm⁻²; and the IR drop increased from 63 to 379 mV. At lower current densities, the electrolyte ions are able to diffuse more effectively into the interior structure of the electrode material due to the increased amount of time available. As a result, more of the carbon material gets utilized for forming electrical double layers and thus contributes to improved electrochemical performance [8].

Because of the limited temporal access of electrolytic ions at higher current densities, the electrolytic ions interact with only the exterior of the electrode [116]. During the peak performance stage, the maximum coulombic efficiency is found to be 91% at 2 mA cm⁻² and with increasing current density it decreased upto 57 % at 20 mA cm⁻². This could be due to the gradual increase of IR drops in higher current densities. The high value of power density at high current density could be due to the R_s and high value of ionic conductivity of the ICCHME.

The charge transport process occurring in the EDLC was investigated by EIS. The Nyquist plot in Fig.2.7 (F) shows a semi-circle in the high frequency region and a straight line in the low frequency region. The inset in Fig.2.7 (F) depicts an expanded view of the semi-circle in the high frequency region. The electric equivalent circuit diagram shown as an insert in Fig.2.7 (F) was achieved through systematic analysis of the EIS data using the "Fit and Simulation" function of the Nova 2.1 software of the Multi Autolab workstation. The fitting approach is based on a non-linear least square fitting algorithm. The methodology involved optimizing the fit between the experimental EIS data and the theoretical model by minimizing the difference between observed and calculated impedance values. This was indicated by the lowest chi-squared (χ^2) value [117]. The χ^2 value is a statistical indicator of how well the equivalent circuit model fits the EIS data. The lower the χ^2 value, the better is the fit. This represents the accuracy of the model in capturing electrochemical processes occurring within the hydrogel electrolyte [118]. The fitting parameters included solution resistance (R_s), charge transfer resistance (R_{ct}), CPE, and Warburg impedance (W). The distance from origin to the point of intersection of the Nyquist plot with real impedance axis is equal to R_s . The diameter of the semicircle at the high-frequency end is equal to R_{ct} of the active material [119–121]. R_s represents the bulk electrolyte resistance, which is associated with the ion transport in the electrolyte. The R_s increases with decrease in ion mobility and increase in electrolyte thickness. The R_s can be divided into two components, viz. the electronic and the ionic resistances. The electronic resistance arises from the inherent resistance of electrode material and the contact resistance between the active material and current collector. The ionic resistance arises from the resistance to the transport of ions within the electrolyte and

that inside the pores of electrode [122]. R_{ct} corresponds to the charge transfer resistance, which is indicative of the interfacial resistance at the electrode-electrolyte interface during the charge/discharge processes. The CPE is used to model the non-ideal capacitive behavior of the supercapacitor and W is the optimal capacitive behavior implied by the linear portion of the Nyquist plot in the lower frequency region [123]. The equivalent circuit model demonstrates a strong electrochemical performance, with each component providing insightful information about the system's bulk and interfacial regions. The R_s value of 237 m Ω reflects a high ionic conductivity within the polymer hydrogel electrolyte, thereby ensuring minimal resistive losses and efficient ion transport throughout the system. The R_{ct} value of 706 m Ω is indicative of effective charge transfer processes at the electrode-electrolyte interface, which is crucial for maintaining high power density and fast response times in the supercapacitor. The CPE, characterized by $Y_0=282.2 \mu\Omega^{-1}\times s^N$ and $N=0.846$, represents a non-ideal capacitive behavior due to the porous structure of the carbon electrodes. The value of N approaching unity indicates a capacitive response close to ideal behaviour, which is a desirable feature for EDLCs [124]. Additionally, the presence of a Warburg element further indicates that the ion diffusion processes within the porous electrode and electrolyte architectures are well-managed, thereby contributing to the overall impedance. This ensures a stable and reliable performance across the range of frequencies [123].

To investigate the real-life applicability of ICCHME, two identical EDLCs were subjected to repeated GCD cycling at 2 and 5 mA cm⁻². After every 500 cycles, values of areal capacitances, Coulombic efficiencies, resistances (R_s , R_{ct} , and ESR), and IR drop were evaluated. The related data presented in Fig.2.8 (A) to Fig.2.8 (F) reveal that the EDLCs exhibited 51,500 and 33,000 cycles at respective current densities of 2 and 5 mA cm⁻². The total charge-discharge time until death for the EDLCs operating at 2 and 5 mA cm⁻² were about 1564 and 1080 h, respectively.

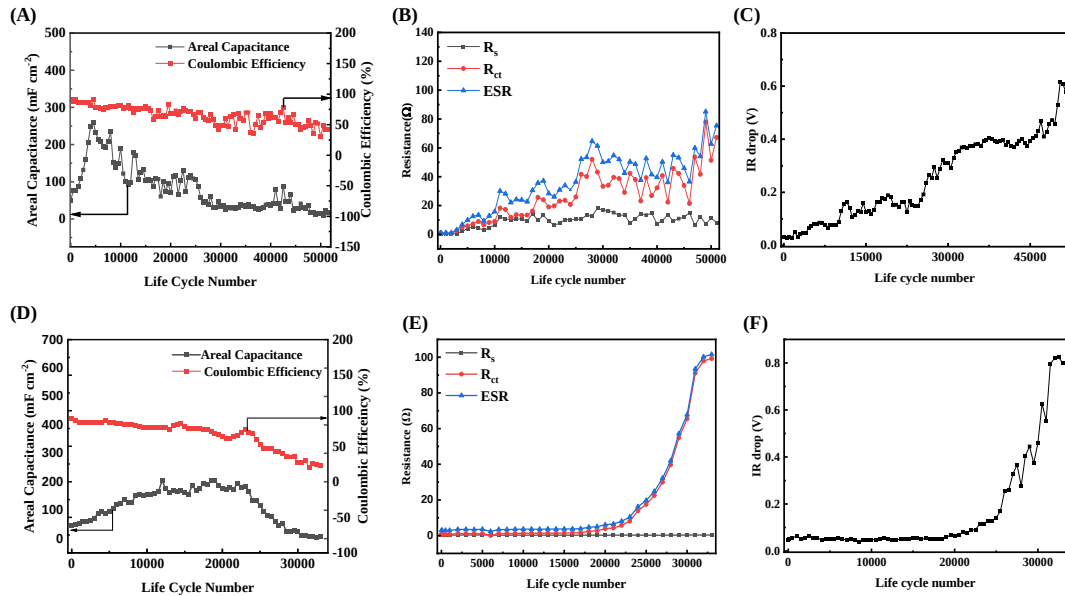


Fig.2.8 (A) Areal capacitance and Coulombic efficiency of the EDLC as a function of life cycle number at 2 mA cm⁻²; (B) Values of R_s , R_{ct} , and ESR of the EDLC as a function of life cycle number at 2 mA cm⁻²; (C) IR drop values of the EDLC as a function of life cycle number at 2 mA cm⁻²; (D) Areal capacitance and Coulombic efficiency of the EDLC as a function of life cycle number at 5 mA cm⁻²; (E) Values of R_s , R_{ct} , and ESR of EDLC as a function of life cycle number at 5 mA cm⁻²; (F) IR drop values of the EDLC as a function of life cycle number at 5 mA cm⁻².

Fig.2.8 (A) and 2.8 (D) present the variations of areal capacitance and Coulombic efficiency as a function of cycle number for the EDLCs subjected to GCD studies at 2 and 5 mA cm⁻², respectively. For the EDLC undergoing GCD cycling at 2 mA cm⁻², the areal capacitance increased by 529.26 % from an initial value of 49.2 mF cm⁻² to a peak value of 260.40 mF cm⁻² after 4,500 GCD cycles. Similarly, the EDLC undergoing GCD cycling at 5 mA cm⁻² exhibited an increase of areal capacitance by 425% from an initial value of 48 mF cm⁻² to a peak value of 204 mF cm⁻² after 18,500 GCD cycles. Similar results have been observed in many other studies on ESs using polymer hydrogel electrolytes, and the increased areal capacitances have been explained as caused by slow and gradual infiltration of electrolytes into the porous electrodes [125–127]. Table 2.5 summarizes the capacitive performance data of the EDLC at the intervals of 500 GCD cycles during the cycle life study carried out at 2

mA cm^{-2} . Table 2.6 summarizes the capacitive performance data of the EDLC at the intervals of 500 GCD cycles during the cycle life study carried out at 5 mA cm^{-2} .

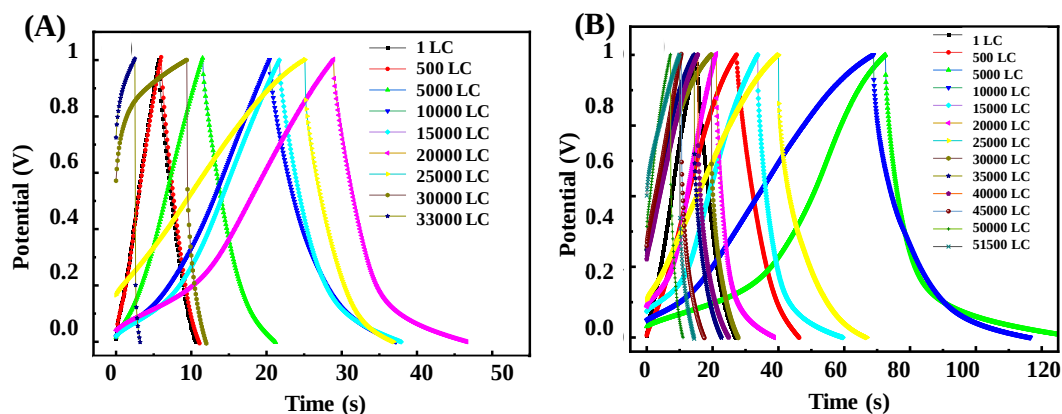


Fig.2.9 Plot of GCDs during life cycle studies of: (A) EDLC that exhibited 33,000 life cycles in a current density of 5 mA cm^{-2} ; (B) EDLC having 51,500 life cycles in a current density of 2 mA cm^{-2} .

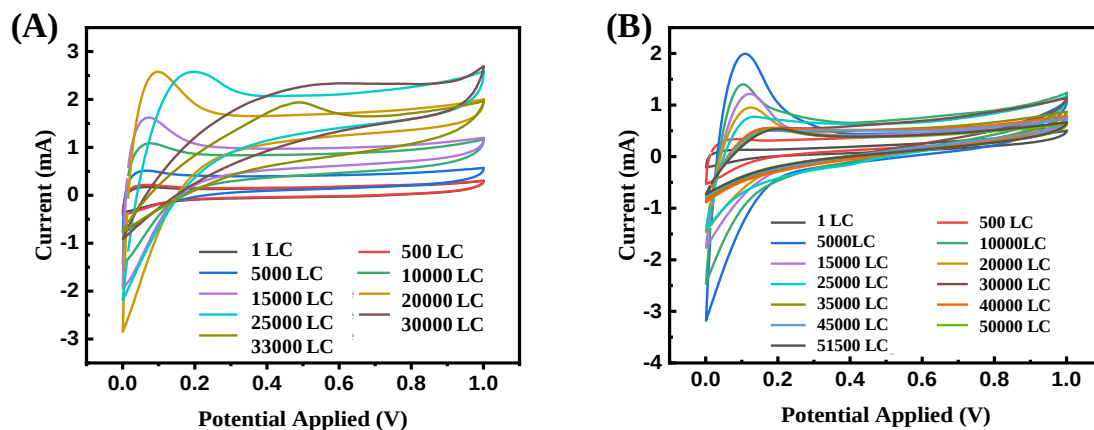


Fig.2.10 Plot of CVs during life cycle studies of: (A) EDLC that exhibited 33,000 life cycles in a current density of 5 mA cm^{-2} ; (B) EDLC having 51,500 life cycles in a current density of 2 mA cm^{-2} .

Fig.2.9 (A) presents GCD plots of some selected charge/discharge cycles during the life cycle studies carried out at 5 mA cm^{-2} and Fig.2.9 (B) presents GCD plots of some selected charge-discharge cycles during the life cycle studies carried out at 2 mA cm^{-2} . Fig.2.10 (A) presents CVs of some selected charge/discharge cycles during the life

cycle studies carried out at 5 mA cm^{-2} and Fig.2.10 (B) presents CVs plots of some selected charge/discharge cycles during the life cycle studies carried out at 2 mA cm^{-2} . With increasing cycle numbers, the shape of the CVs progressively changed resulting in the development of redox-like broad peak in the potential range of 0 to 0.3 V. This explains the gradual increase of areal capacitance while the EDLC reaches the peak performance stage. These redox peaks are primarily caused by functional groups containing nitrogen or oxygen atoms suggesting pseudo capacitance activation in the EDLCs [128,129]. This activation could have happened due to the penetration of electrolyte ions deep into the electrode structure over time, thereby exposing new active sites to Faradaic reactions. This process is facilitated by the excellent ionic conductivities of the ICCHMEs. While a little less significant, the changes in the structure and properties of the electrical double layer due to extended cycling could have influenced the peak-like features observed in the CVs [130,131]. The main factor contributing to the capacitance is the non-Faradaic behavior of EDLCs, which is primarily influenced by the surface area of electrode and electrostatic interaction between oxygen-containing functional groups of the ICCHME [132]. The Coulombic efficiency of the first GCD cycle for both EDLCs was 91 %. It remained nearly constant till 20,000 cycles for both the EDLCs and then subsequently decreases to about 45 % for the last GCD cycle. The wearing out of the EDLCs as revealed by lowering of Coulombic efficiency performances could be due to the same factors as discussed above. This emphasizes the remarkable overall stability of the ICCHMEs, as the EDLCs continued to perform exceptionally well over such an extended period of time.

Table 2.5: Summary of capacitive performance data for EDLC employing ICCHME in GCD current density of 2 mA cm^{-2} , that performed 51,500 charge-discharge cycles.

Cycle number	Areal capacitance (mF cm^{-2})	Energy density ($\mu\text{Wh cm}^{-2}$)	R_s (Ω)	R_{ct} (Ω)	ESR (Ω)	Coulombic efficiency (%)
1	49.2	6.83	0.25	0.74	0.99	89
500	75.6	10.5	0.26	0.75	1.01	88
1000	76.8	10.66	0.28	0.78	1.06	91
1500	87.6	12.16	0.38	0.71	1.09	86
2000	107.6	14.94	0.4	0.71	1.11	86
2500	132	18.33	0.42	1.55	1.97	86
3000	159.6	22.16	0.55	2.55	3.10	87
3500	206.8	28.72	0.84	3.3	4.14	87
4000	248.8	34.55	2.09	4.81	6.90	89
4500	260.40	36.16	4.2	6.57	10.77	91
5000	233.2	32.38	4.09	5.93	10.02	78
5500	214.4	29.77	5.43	6.4	11.83	78
6000	208.8	29	5.26	7.29	12.55	77
6500	195.6	27.16	5.33	8.11	13.44	75
7000	192	26.66	4.56	8.94	13.50	78
7500	208.8	29	4.08	7.69	11.77	77
8000	234.8	32.61	2.83	6.55	9.38	80
8500	150.8	20.94	5.89	5.05	10.94	80
9000	137.96	19.16	4.61	8.24	12.85	80
9500	148.48	20.62	4.1	9.37	13.47	81
10000	190.4	26.44	6.77	8.99	15.76	81
10500	122	16.94	10.2	13.77	23.97	76
11000	102	14.16	11.85	18.24	30.09	78
11500	94	13.05	11.73	20.76	32.49	81
12000	98.8	13.72	10.92	17.3	28.22	76
12500	178.8	24.83	8.28	11.72	20	70
13000	170.8	23.72	10.2	11.93	22.13	76
13500	106.4	14.77	11.07	13.15	24.22	75

14000	124.4	17.27	10.62	13.65	24.27	76
14500	132.8	18.44	12.1	16.51	28.61	77
15000	103.2	14.33	10.72	13.23	23.95	80
15500	105.6	14.66	10.33	15.41	25.74	77
16000	103.2	14.33	9.33	13.38	22.71	74
16500	87.2	12.11	9.92	16.72	26.64	58
17000	110	15.27	14.28	16.28	30.56	64
17500	107.2	14.88	12.36	19.85	32.21	73
18000	60.8	8.44	9.9	25.73	35.63	63
18500	101.6	14.11	8.52	27.29	35.81	65
19000	72.8	10.11	13.18	23.98	37.16	63
19500	96	13.33	10.85	23.9	34.75	83
20000	70	9.72	9.38	19	28.38	68
20500	113.6	15.77	8.19	21.86	30.05	68
21000	116.4	16.16	6.36	19.76	26.12	73
21500	66	9.16	10.12	21.89	32.01	67
22000	103.2	14.33	7.79	23.12	30.91	72
22500	131.6	18.27	8.62	15.66	24.28	76
23000	74.8	10.38	10.37	23.63	34	73
23500	112.4	15.61	9.86	21.14	31	71
24000	117.2	16.27	10.1	20.81	30.91	71
24500	108.8	15.11	9.93	20.7	30.63	67
25000	107.2	14.88	10.48	25.98	36.46	60
25500	86.4	12	11.7	25.43	37.13	70
26000	57.2	7.94	10.6	41.65	52.25	70
26500	44.8	6.22	15.14	36.34	51.48	62
27000	46	6.38	13.34	40.14	53.48	58
27500	37.6	5.22	16.48	21.49	37.97	57
28000	61.2	8.5	12.59	52.03	64.62	67
28500	31.6	4.38	16.8	19.05	35.85	58
29000	31.6	4.38	18.2	43.2	61.4	48
29500	46	6.38	15.72	24.86	40.58	42
30000	32.4	4.5	16.68	33.39	50.07	48
30500	35.2	4.88	13.48	40.02	53.5	49

31000	26	3.61	16.6	34.1	50.7	60
31500	30	4.16	14.46	40.31	54.77	47
32000	28.4	3.94	15.18	39.57	54.75	64
32500	32	4.44	13.37	35.27	48.64	66
33000	27.6	3.83	13.32	38.73	52.05	42
33500	30.8	4.27	14.01	38.6	52.61	68
34000	40	5.55	13.4	29.13	42.53	60
34500	36.8	5.11	13.37	27.86	41.23	57
35000	32.8	4.55	8.01	42.33	50.34	70
35500	37.6	5.22	14.29	29.01	43.3	70
36000	33.2	4.61	10.7	38.04	48.74	38
36500	33.2	4.61	14.96	23.87	38.83	35
37000	28	3.88	14.48	23.21	37.69	51
37500	26	3.61	12.97	43.38	56.35	65
38000	28	3.88	13.38	39.33	52.71	46
38500	31.6	4.38	13.84	26.36	40.2	54
39000	38.4	5.33	14.64	26.88	41.52	68
39500	39.6	5.5	12.85	28.8	41.65	60
40000	37.2	5.16	7.36	32.24	39.6	68
40500	40.4	5.61	6.8	27.98	34.78	62
41000	80.4	11.16	9.6	40.74	50.34	62
41500	40.4	5.61	7.75	59.05	66.8	56
42000	29.2	4.05	13.71	22.4	36.11	70
42500	88.4	12.27	11.14	37.9	49.04	78
43000	47.2	6.55	9.23	45.74	54.97	53
43500	48	6.66	11.62	63.4	75.02	62
44000	66.8	9.27	10.97	42.28	53.25	54
44500	24	3.33	14.75	32.04	46.79	66
45000	27.6	3.83	11.93	33.99	45.92	51
45500	27.2	3.77	12.81	35.83	48.64	50
46000	41.2	5.72	15.04	21.5	36.54	42
46500	30	4.16	13.76	30.75	44.51	46
47000	27.6	3.83	6.26	53.7	59.96	47
47500	35.6	4.94	13.03	33.5	46.53	57

48000	17.2	2.38	12.39	41.72	54.11	49
48500	16.8	2.33	10.61	52.57	63.18	35
49000	12.8	1.77	7.21	77.91	85.12	53
49500	14.4	2	10.27	54.91	65.18	52
50000	14.8	2.05	11.3	51.4	62.7	30
50500	9.2	1.27	8.37	84.51	92.88	48
51000	22	3.05	8.26	67.16	75.42	43
51500	17.2	2.38	4.56	77.8	82.36	43

Table 2.6: Summary of capacitive performance data for EDLC employing ICCHME in GCD current density of 5 mA cm⁻², that performed 33,000 charge-discharge cycles.

Cycle number	Areal capacitance (mF cm ⁻²)	Energy density (μWh cm ⁻²)	R _s (Ω)	R _{ct} (Ω)	ESR (Ω)	Coulombic efficiency (%)
1	48	0.66	0.27	0.6	0.87	86
500	50	0.69	0.27	0.59	0.87	84
1000	54	0.75	0.27	0.59	0.87	83
1500	59	0.81	0.26	0.56	0.83	83
2000	61	0.84	0.27	1.16	1.44	84
2500	64	0.88	0.27	1.15	1.42	84
3000	71	0.98	0.37	1.1	1.47	84
3500	90	1.25	0.4	1.05	1.45	84
4000	96	1.33	0.26	1.08	1.35	86
4500	89	1.23	0.29	1.12	1.41	84
5000	96	1.33	0.4	1.11	1.52	83
5500	107	1.48	0.28	1.06	1.35	82
6000	119	1.65	0.26	0.07	0.33	82
6500	123	1.70	0.28	1.11	1.39	81
7000	138	1.91	0.24	1.12	1.36	80
7500	126	1.75	0.25	1.17	1.43	80
8000	128	1.77	0.21	1.13	1.35	79
8500	152.4	2.11	0.33	1.18	1.51	78
9000	155.1	2.15	0.33	1.18	1.51	76

9500	151.5	2.10	0.21	1.28	1.5	76
10000	153.9	2.13	0.25	1.33	1.59	76
10500	154.8	2.15	0.22	1.32	1.54	76
11000	158.1	2.19	0.22	1.34	1.56	76
11500	165	2.29	0.23	1.31	1.54	76
12000	203.1	2.82	0.23	1.3	1.53	76
12500	175	2.43	0.23	1.3	1.54	74
13000	162	2.25	0.27	1.37	1.65	79
13500	168	2.33	0.25	1.37	1.62	80
14000	167	2.31	0.26	1.35	1.61	82
14500	170	2.36	0.26	1.38	1.65	78
15000	161	2.23	0.25	1.44	1.69	75
15500	156	2.16	0.23	1.45	1.68	75
16000	187	2.59	0.19	1.51	1.71	75
16500	170	2.36	0.24	1.54	1.78	75
17000	175	2.43	0.26	1.61	1.87	74
17500	195	2.70	0.24	2.06	2.31	74
18000	191	2.65	0.23	2.4	2.64	71
18500	204	2.83	0.22	2.47	2.69	68
19000	203	2.81	0.24	2.66	2.91	67
19500	188	2.61	0.23	3.17	3.4	64
20000	176	2.44	0.17	3.88	4.05	61
20500	173	2.40	0.2	4.2	4.41	61
21000	180	2.50	0.24	4.25	4.5	64
21500	174	2.41	0.21	4.29	4.5	65
22000	195	2.70	0.24	5.75	5.99	69
22500	179	2.48	0.27	7.86	8.13	73
23000	182	2.52	0.29	8.06	8.35	69
23500	167	2.31	0.29	8.21	8.51	68
24000	134	1.86	0.21	13.93	14.15	59
24500	133	1.84	0.21	15.11	15.33	53
25000	117	1.62	0.23	17.48	17.72	47
25500	96	1.33	0.26	21.35	21.62	47
26000	83	1.15	0.21	22.51	22.72	47

26500	79	1.09	0.19	23.45	23.64	43
27000	62	0.86	0.2	29.91	30.12	43
27500	47	0.65	0.23	34.86	35.1	40
28000	53	0.73	0.24	39.68	39.93	36
28500	27	0.37	0.28	51.13	51.42	35
29000	24	0.33	0.26	54.86	55.13	35
29500	29	0.40	0.27	57.46	57.73	27
30000	25	0.34	0.27	65.44	65.72	27
30500	11	0.15	0.29	87.1	87.39	30
31000	11	0.15	0.31	91.1	91.41	20
31500	6	0.08	0.3	87.35	87.65	26
32000	8	0.11	0.29	97.91	98.2	25
32500	5	0.06	0.3	97	97.31	23
33000	6	0.08	0.31	99.26	99.58	24

Fig.2.8 (B) and 2.8 (E) present the variations of R_s , R_{ct} , and ESR as a function of cycle number for the EDLCs subjected to GCD studies at 2 and 5 mA cm⁻², respectively. For the EDLC stationed at ambient atmosphere and undergoing GCD cycling at 2 mA cm⁻², the R_s increased slightly from 0.24 to 4.56 Ω and then remained constant during its entire cycle life of 51,500 cycles spanning over 66 days. The EDLC stationed at ambient atmosphere and undergoing GCD cycling at 5 mA cm⁻² exhibited a constant R_s value within a very narrow range of 0.268 to 0.318 Ω during its entire cycle life of 33,000 cycles spanning over 45 days. This very low and constant value of R_s during the cycle life indicates a stable performance of the EDLCs, which is a very important requirement for commercialization of solid-state EDLCs. This constant and very low value of R_s suggests a constant and high value of ionic conductivity throughout the cycling, which could be due to the efficient ion transport taking place through the pores of the ICCHME. The pores in the ICCHME are understood to have formed due to the evolution of CO₂ during the crosslinking process as discussed above and as revealed by the FE-SEM studies [133,134]. The constant ionic conductivity indicates that water trapped in the pores of the ICCHME did not evaporate during the cycle life test. The retention of water by the ICCHMEs could be because of the high hydrophilicity of chitosan polymer [135].

This minimal resistance ensures efficient charge transfer within the EDLCs, thus contributing to the exceptional cycle life. In contrast to R_s , the R_{ct} gradually increased from 0.71 to 77.8 Ω for the EDLC undergoing GCD cycling at 2 mA cm⁻² during its entire life of 51,500 cycles and from 0.59 to 99.26 Ω for the EDLC undergoing GCD cycling at 5 mA cm⁻² during its entire life of 33,000 cycles. The value R_{ct} increases to 77.8 and 99.264 Ω from its initial values of 0.71 and 0.59 Ω , respectively, over the cycle life for both the EDLCs. This gradual increase in R_{ct} with increasing cycles could be due to the progressive interfacial resistance buildup at the electrode-electrolyte interface [136]. From Fig.2.8 (B) and 2.8 (E), it is also observed that the ESR values increased from 0.95 to 82.36 Ω for the EDLC undergoing GCD cycling at 2 mAcm⁻² during its life time and from 0.87 to 99.58 Ω for the EDLC undergoing GCD cycling at 5 mAcm⁻² during its life time, respectively. This increase of ESR is mainly due to the increase of R_{ct} because as mentioned above, the ESR is the sum of R_s and R_{ct} , and R_s remains nearly constant during the cycle life study. This indicates that the electrolyte conductivity remains unchanged and there is little degradation of ICCHME during the entire lifespan of the EDLCs. This further indicates that the aging of the EDLC happened due to increase of R_{ct} . The R_s , R_{ct} , and ESR values of the EDLC observed during the cycle life studies carried out at 2 and 5 mA cm⁻² are given in Tables 2.5 and 2.6, respectively. The aging process during cycle life studies was followed by EIS spectroscopy.

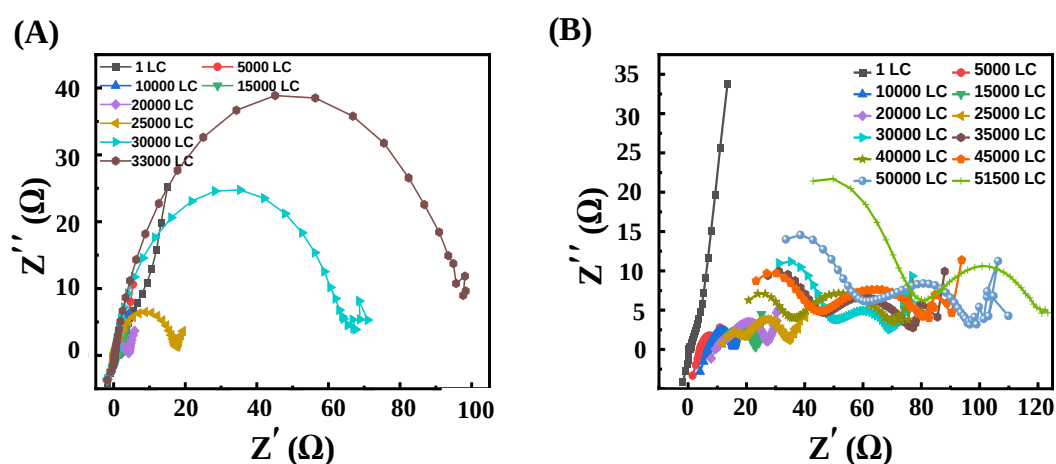


Fig. 2.11 Plot of FRAs during life cycle studies of: (A) EDLC having 33,000 life cycles in a current density of 5 mA cm⁻²; (B) EDLC that exhibited 51,500 life cycles in a current density of 2 mA cm⁻².

The Nyquist plots recorded at some given intervals during the cycle life studies are presented in Fig.2.11, which clearly shows that there is only one semicircle in the low frequency region at the initial stage. As the cycle life progressed, a second semicircle appeared in the lower frequency region by shortening of Warburg region. This could be due to the increase of electrode resistance [137]. As the cycle life progressed further, both the semicircles merged into a single one, thereby increasing the R_{ct} while maintaining a constant R_s . This could be due to the aging resulting from the gradual degradation of the pore structure of the electrode, thereby adversely affecting ion transport pathways and creating additional charge-transfer resistance [132,138].

Fig.2.8 (C) and 2.8 (F) show the variation of IR drop values as a function of cycle number for the EDLCs subjected to GCD studies at 2 and 5 mA cm⁻², respectively. The IR drop values remained constant at 0.064 V till 4,500 cycles for the EDLC undergoing GCD cycling at 2 mA cm⁻² and at 0.053 V till 18,500 cycles for the EDLC undergoing GCD cycling at 5 mA cm⁻². Subsequently, the IR drop increases a bit steeply reaching 0.58 V for the EDLC undergoing GCD cycling at 2 mA cm⁻² and 0.80 V for the EDLC undergoing GCD cycling at 5 mA cm⁻² at the end of life.

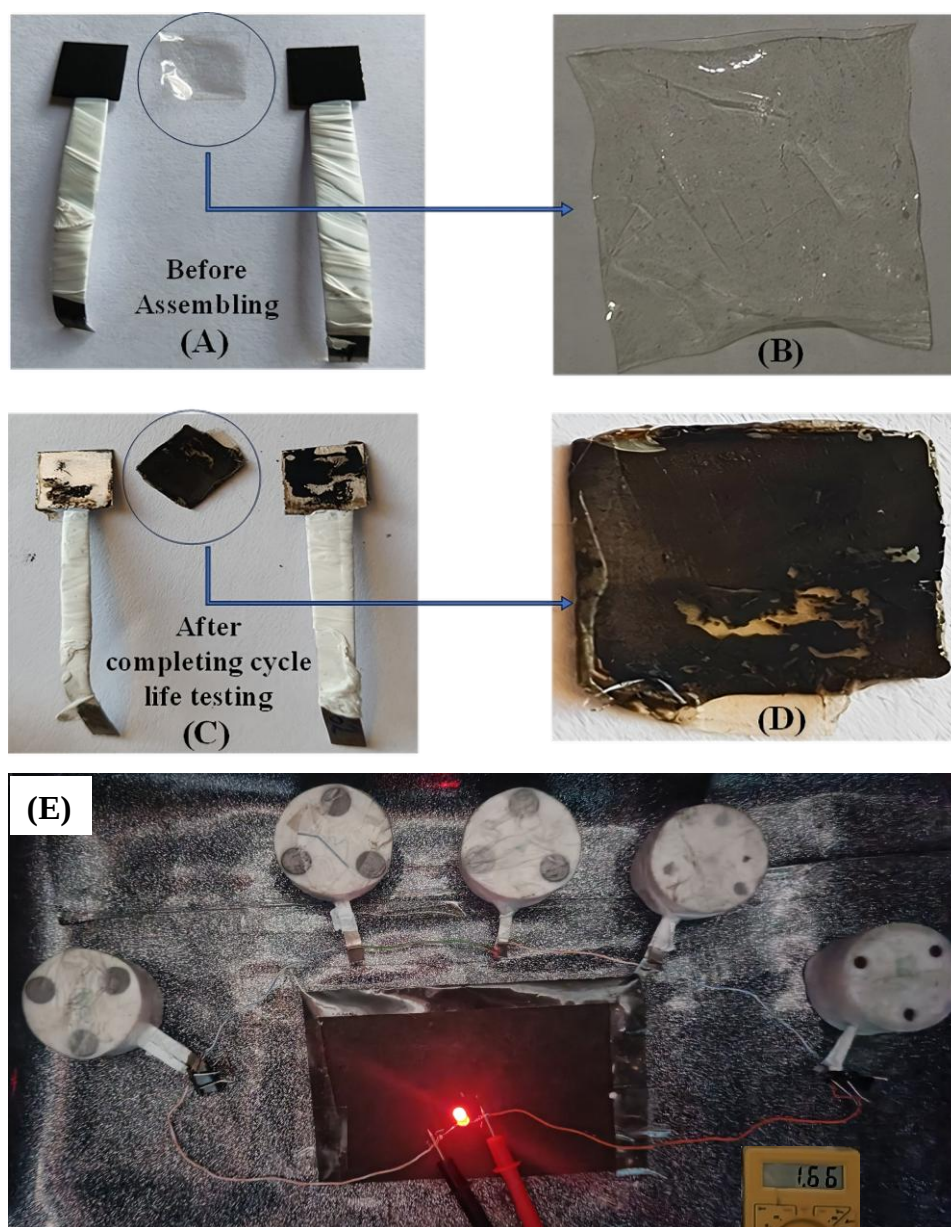


Fig.2.12 (A) An image of the ICCHME and a pair of BPC-coated SS electrode before assembling into an HMEA; (B) Closer image of the ICCHME before assembling into an HMEA; (C) Postmortem image of the HMEA after disassembling into the ICCHME and a pair of BPC-coated SS electrode after completing the cycle life test of the EDLC; (D) A closer postmortem image of the ICCHME after cycle life test; (E) Image of a red LED bulb being illuminated by a prototype device comprising of five EDLCs connected in series.

Fig.2.12 (A) shows an image of a pair of BPC-coated SS-electrodes and the ICCHME that were used to assemble an HMEA. Fig.2.12 (B) shows that the ICCHME is colorless, transparent, and mechanically strong film. Enthused by the excellent cycle life exhibited by the EDLC, we performed a postmortem on the EDLC. The postmortem image of the disassemble HMEA at the end of the cycle life is shown in Fig.2.12 (C). A closer postmortem image of the ICCHME is shown in Fig.2.12 (D). It is clearly visible that most of the BPC paste gets detached from the SS current collectors and gets stuck onto the ICCHME. The ICCHME was as stable as it was before assembling. This indicates to the outstanding performance of the ICCHME in the EDLC.

Table 2.7: Summary of the longest cycle life data exhibited by EDLCs employing different types of electrolytes reported in literature vis-à-vis the same exhibited by EDLCs employing ICCHME being reported in the current manuscript.

Electrolyte type	Electrolyte	Electrode used	Type of electrode system	Life cycle number	Ref.
Liquid	Hybrid of aq. Sulfuric acid and aq. Sodium sulphate	Tungsten oxide (WO_{3-x})	Integrated two-electrode	250,000	[139]
	Sodium perchlorate dissolved in a mixture of water & Trimethyl phosphate	Graphene	Three-electrode	100,000	[140]
	Azepanium-based ionic liquid N-methyl, N-butyl	Activated carbon	Three-electrode	55,000	[141]

	azepanium bis [(trifluoro methane) sulfonyl] imide and propylene carbonate				
	N-butyl- azepanium bis (trifluoro methane sulfonyl) imide and N-methyl, N-hexyl- azepanium bis (trifluoro methane sulfonyl) imide	Activated carbon	Three- electrode	35,000	[142]
Ionogel	Tetra methoxy silane, dimethyl dimethoxy silane, formic acid and the IL 1-ethyl-3 methyl imidazolium bis (trifluoro methyl sulfonyl) imide	Activated carbon	Two- electrode	25,000	[143]
	1-Ethyl-3- Methyl Imidazolium Bis (trifluoro	Activated carbon	Two- electrode	10,000	[144]

	methane sulfonyl imide)				
Organogel	Chemically cross-linked PAAm organo-hydrogel	Polyaniline	Two-electrode	100,000	[145]
	Poly (vinylidene fluoride-co-hexafluoropropylene)	Carbon Nanotube	Three-electrode	15,000	[146]
Hydrogel	Agar- Sodium sulfate	N-doped carbon	Three-electrode	20,000	[147]
	Montmorillonite /PVA	Graphene	Two-electrode	10000	[148]
	Glutaraldehyde-cross-linked gelatin chemical hydrogel membrane	BPC	Two-electrode	9500	[61]
	Sodium Acetate, Trihydrate, PVA and glycerol	Activated carbon	Two-electrode	5000	[149]
	PVA/phytic acid	Activated carbon	Two-electrode	5000	[150]
	PAA and polyallylamine hydrochloride	Carbon nanotube	Three-electrode	5000	[151]
	PAAm	Carbon nanotube	Three-electrode	5000	[152]

	Chitosan-sodium sulfate	BPC	Two-electrode	1400	[15]
	PVA - Perchloric acid	BPC	Two-electrode	1000	[22]
	Gelatin-sodium chloride	BPC	Two-electrode	900	[71]
	Chitosan-Sodium carbonate	BPC	Two-electrode	51,500	This work

Table 2.7 presents a summary of the longest cycle life data for EDLCs employing different types electrolytes (viz. liquid, ionogel, organogel, and hydrogel electrolytes) reported in literature. It is seen from the table that the longest cycle life of 2,50,000 cycles was exhibited by tungsten oxide-based supercapacitor using an aqueous liquid electrolyte [139]. The next longest cycle life of 1,00,000 cycles was reported in two papers, one for a liquid electrolyte [140] and the other for an organohydrogel [145]. The next highest cycle life of 55,000 cycles was reported for an EDLC employing an ionic liquid electrolyte [141]. A cycle life of 51,500 cycles being reported in the current work is very high. Moreover, commonly available cheap and environmentally benign materials, viz. chitosan, Na_2CO_3 , and water have been used. The technique for the synthesis of the electrolyte material is also very simple and cost-effective. The cycle life reported in the current work is much longer than those reported so far from our research group [15,22,61,71].

The superior cycle life performance of the EDLC motivated us to assemble of a workable prototype cell. For this, five EDLCs were connected in series, which powered a red LED bulb. All five EDLCs were charged at 5 mA cm^{-2} . The image of the prototype is shown in Fig.2.12 (E). The device intensely illuminated the LED bulb for 1.83 minutes by exhibiting a net cell voltage of 1.66 V. This study proves that a novel and low-cost Na_2CO_3 cross-linked chitosan biopolymer hydrogel membrane can be used as an excellent electrolyte for developing commercially viable supercapacitors.

2.4 Conclusions

A novel, cost-effective, and high-performance chitosan hydrogel membrane electrolyte was synthesized by ionically crosslinking chitosan with Na_2CO_3 . The ionic crosslinking reaction chitosan and Na_2CO_3 leading to the formation of ICCHME was verified using FTIR spectroscopy. The pores in the ICCHME are believed to be produced due to the evolution of CO_2 during hydrogel formation. The pore formation is similar to the pores formed in bakery items by evolution of gaseous CO_2 molecules during baking process using baking powder. The ICCHMEs are transparent, mechanically strong, and flexible films having a high-WU and DR of 226 and 18.24 %, respectively. The tensile strength and Young's modulus of the ICCHME was found to be 53.29 and 478.80 MPa, respectively. The ICCHME exhibited ionic conductivity of 7.89 mS cm^{-1} . EDLCs have been assembled using ICCHMEs as SSE and BPC as electrode. The EDLC showed areal capacitances of $260.40 \text{ mF cm}^{-2}$ at 2 mA cm^{-2} , respectively; energy and power densities of $36.16 \text{ } \mu\text{Wh cm}^{-2}$ and $2000 \text{ } \mu\text{W cm}^{-2}$, respectively; and a very low R_s of $0.24 \text{ } \Omega$. The EDLC exhibited remarkably high cycle life of 51,500 and 33,000 charge-discharge cycles at 2 and 5 mA cm^{-2} , respectively. The R_s remained almost constant till the end of the cycle life during the cycle life test. A prototype power device comprising five EDLCs wired in series has powered a red LED bulb with intense illumination for 1.83 minutes. A significant drop in Coulombic efficiency and areal capacitance has been observed upon prolonged cycling. The observed degradation in performances could be due to the accumulation of electrode material, and decrease in adhesion between the electrode material and current collectors. We plan to address these issues in our future works by further optimizing the electrolyte composition, and exploring alternative electrode materials as well as electrode binders. In fine, the robustness of the examined biopolymer-based hydrogel membrane electrolyte under extremely high current densities holds significant potential to be explored in other energy devices, viz. batteries, fuel cells, etc.

2.5 References

- [1] R.E. Hester, R.M. Harrison, eds., Front matter, in: Sustainability and Environmental Impact of Renewable Energy Sources, Royal Society of Chemistry, Cambridge, n.d.: pp. P001–P004. <https://doi.org/10.1039/9781847551986-FP001>.
- [2] C. Zhong, Y. Deng, W. Hu, J. Qiao, L. Zhang, J. Zhang, A review of electrolyte materials and compositions for electrochemical supercapacitors, *Chem Soc Rev* 44 (2015) 7484–7539. <https://doi.org/10.1039/C5CS00303B>.
- [3] X. Chen, R. Paul, L. Dai, Carbon-based supercapacitors for efficient energy storage, *Natl Sci Rev* 4 (2017) 453–489. <https://doi.org/10.1093/nsr/nwx009>.
- [4] T.M. Gür, Review of electrical energy storage technologies, materials and systems: challenges and prospects for large-scale grid storage, *Energy Environ Sci* 11 (2018) 2696–2767. <https://doi.org/10.1039/C8EE01419A>.
- [5] H. Gao, K. Lian, Proton-conducting polymer electrolytes and their applications in solid supercapacitors: a review, *RSC Adv.* 4 (2014) 33091–33113. <https://doi.org/10.1039/C4RA05151C>.
- [6] A.K. Samantara, S. Ratha, Materials Development for Active/Passive Components of a Supercapacitor, Springer Singapore, Singapore, 2018. <https://doi.org/10.1007/978-981-10-7263-5>.
- [7] B.E. Conway, Electrochemical Supercapacitors, Springer US, Boston, MA, 1999. <https://doi.org/10.1007/978-1-4757-3058-6>.
- [8] B. Pal, S. Yang, S. Ramesh, V. Thangadurai, R. Jose, Electrolyte selection for supercapacitive devices: a critical review, *Nanoscale Adv* 1 (2019) 3807–3835. <https://doi.org/10.1039/C9NA00374F>.
- [9] N.A. Choudhury, S. Sampath, A.K. Shukla, Hydrogel-polymer electrolytes for electrochemical capacitors: an overview, *Energy Environ. Sci.* 2 (2009) 55–67. <https://doi.org/10.1039/B811217G>.
- [10] A.A. Bazmi, G. Zahedi, Sustainable energy systems: Role of optimization modeling techniques in power generation and supply—A review, *Renewable and Sustainable Energy Reviews* 15 (2011) 3480–3500. <https://doi.org/10.1016/j.rser.2011.05.003>.

-
- [11] S.T. Senthilkumar, R.K. Selvan, J.S. Melo, Redox additive/active electrolytes: a novel approach to enhance the performance of supercapacitors, *J Mater Chem A Mater* 1 (2013) 12386. <https://doi.org/10.1039/c3ta11959a>.
- [12] S. Alipoori, S. Mazinani, S.H. Aboutalebi, F. Sharif, Review of PVA-based gel polymer electrolytes in flexible solid-state supercapacitors: Opportunities and challenges, *J Energy Storage* 27 (2020) 101072. <https://doi.org/10.1016/j.est.2019.101072>.
- [13] Y. Wang, W. Zhong, Development of Electrolytes towards Achieving Safe and High-Performance Energy-Storage Devices: A Review, *ChemElectroChem* 2 (2015) 22–36. <https://doi.org/10.1002/celec.201402277>.
- [14] A.B. Samui, P. Sivaraman, Solid polymer electrolytes for supercapacitors, in: *Polymer Electrolytes*, Elsevier, 2010: pp. 431–470. <https://doi.org/10.1533/9781845699772.2.431>.
- [15] N.A. Choudhury, P.W.C. Northrop, A.C. Crothers, S. Jain, V.R. Subramanian, Chitosan hydrogel-based electrode binder and electrolyte membrane for EDLCs: experimental studies and model validation, *J Appl Electrochem* 42 (2012) 935–943. <https://doi.org/10.1007/s10800-012-0469-2>.
- [16] N.A. Choudhury, A.K. Shukla, S. Sampath, S. Pitchumani, Cross-Linked Polymer Hydrogel Electrolytes for Electrochemical Capacitors, *J Electrochem Soc* 153 (2006) A614. <https://doi.org/10.1149/1.2164810>.
- [17] S.B. Aziz, M.A. Brza, M.M. Nofal, R.T. Abdulwahid, S.A. Hussien, A.M. Hussein, W.O. Karim, A Comprehensive Review on Optical Properties of Polymer Electrolytes and Composites, *Materials* 13 (2020) 3675. <https://doi.org/10.3390/ma13173675>.
- [18] K.S. Ngai, S. Ramesh, K. Ramesh, J.C. Juan, A review of polymer electrolytes: fundamental, approaches and applications, *Ionics (Kiel)* 22 (2016) 1259–1279. <https://doi.org/10.1007/s11581-016-1756-4>.
- [19] N. Chen, H. Zhang, L. Li, R. Chen, S. Guo, Ionogel Electrolytes for High-Performance Lithium Batteries: A Review, *Adv Energy Mater* 8 (2018). <https://doi.org/10.1002/aenm.201702675>.

-
- [20] N. Peppas, Hydrogels in pharmaceutical formulations, *European Journal of Pharmaceutics and Biopharmaceutics* 50 (2000) 27–46. [https://doi.org/10.1016/S0939-6411\(00\)00090-4](https://doi.org/10.1016/S0939-6411(00)00090-4).
- [21] F. Ullah, M.B.H. Othman, F. Javed, Z. Ahmad, H.Md. Akil, Classification, processing and application of hydrogels: A review, *Materials Science and Engineering: C* 57 (2015) 414–433. <https://doi.org/10.1016/j.msec.2015.07.053>.
- [22] S. Sampath, N.A. Choudhury, A.K. Shukla, Hydrogel membrane electrolyte for electrochemical capacitors, *Journal of Chemical Sciences* 121 (2009) 727–734. <https://doi.org/10.1007/s12039-009-0087-7>.
- [23] S. Bashir, M. Hina, J. Iqbal, A.H. Rajpar, M.A. Mujtaba, N.A. Alghamdi, S. Wageh, K. Ramesh, S. Ramesh, Fundamental Concepts of Hydrogels: Synthesis, Properties, and Their Applications, *Polymers (Basel)* 12 (2020) 2702. <https://doi.org/10.3390/polym12112702>.
- [24] K. Sun, F. Ran, G. Zhao, Y. Zhu, Y. Zheng, M. Ma, X. Zheng, G. Ma, Z. Lei, High energy density of quasi-solid-state supercapacitor based on redox-mediated gel polymer electrolyte, *RSC Adv* 6 (2016) 55225–55232. <https://doi.org/10.1039/C6RA06797B>.
- [25] S. Zallouz, J.-M. Le Meins, C. Matei Ghimbeu, Alkaline hydrogel electrolyte from biosourced chitosan to enhance the rate capability and energy density of carbon-based supercapacitors, *Energy Advances* 1 (2022) 1051–1064. <https://doi.org/10.1039/D2YA00250G>.
- [26] N. Patra, P. Ramesh, V. Donthu, A. Ahmad, Biopolymer-based composites for sustainable energy storage: recent developments and future outlook, *Journal of Materials Science: Materials in Engineering* 19 (2024) 34. <https://doi.org/10.1186/s40712-024-00181-9>.
- [27] G. Gopinath, S. Ayyasamy, P. Shanmugaraj, R. Swaminathan, K. Subbiah, S. Kandasamy, Effects of biopolymers in energy storage applications: A state-of-the-art review, *J Energy Storage* 70 (2023) 108065. <https://doi.org/10.1016/j.est.2023.108065>.
- [28] Md.S. Islam, Md.M. Islam, K.N. Islam, Md.H.R. Sobuz, Biodegradable and Bio-Based Environmentally Friendly Polymers, in: *Encyclopedia of Materials:*

- Plastics and Polymers, Elsevier, 2022: pp. 820–836. <https://doi.org/10.1016/B978-0-12-820352-1.00271-6>.
- [29] H. Lu, A. Cornell, F. Alvarado, M. Behm, S. Leijonmarck, J. Li, P. Tomani, G. Lindbergh, Lignin as a Binder Material for Eco-Friendly Li-Ion Batteries, *Materials* 9 (2016) 127. <https://doi.org/10.3390/ma9030127>.
- [30] J. Jin, B. Yu, Z. Shi, C. Wang, C. Chong, Lignin-based electrospun carbon nanofibrous webs as free-standing and binder-free electrodes for sodium ion batteries, *J Power Sources* 272 (2014) 800–807. <https://doi.org/10.1016/j.jpowsour.2014.08.119>.
- [31] U.K. Sanivada, G. Mármol, F.P. Brito, R. Figueiro, PLA Composites Reinforced with Flax and Jute Fibers—A Review of Recent Trends, Processing Parameters and Mechanical Properties, *Polymers (Basel)* 12 (2020) 2373. <https://doi.org/10.3390/polym12102373>.
- [32] Z. Zhou, F. Chen, T. Kuang, L. Chang, J. Yang, P. Fan, Z. Zhao, M. Zhong, Lignin-derived hierarchical mesoporous carbon and NiO hybrid nanospheres with exceptional Li-ion battery and pseudocapacitive properties, *Electrochim Acta* 274 (2018) 288–297. <https://doi.org/10.1016/j.electacta.2018.04.111>.
- [33] R.T. Abdulwahid, S.B. Aziz, M.F.Z. Kadir, Environmentally friendly plasticized electrolyte based on chitosan (CS): Potato starch (PS) polymers for EDLC application: Steps toward the greener energy storage devices derived from biopolymers, *J Energy Storage* 67 (2023) 107636. <https://doi.org/10.1016/j.est.2023.107636>.
- [34] N.A. Rahman, S.A. Hanifah, N.N. Mobarak, A. Ahmad, N.A. Ludin, F. Bella, M.S. Su'ait, Chitosan as a paradigm for biopolymer electrolytes in solid-state dye-sensitised solar cells, *Polymer (Guildf)* 230 (2021) 124092. <https://doi.org/10.1016/j.polymer.2021.124092>.
- [35] D. Xu, Y. Heng, X. Qin, D. Hu, Membrane-based symmetric supercapacitors composed of cellulose solution-derived polydopamine-modified separators and polypyrrole/graphene-doped polydopamine-modified electrodes, *J Energy Storage* 50 (2022) 104640. <https://doi.org/10.1016/j.est.2022.104640>.

-
- [36] J. Sun, Y. Deng, J. Jiang, Y. Hu, Q. Cui, Z. Lou, Y. Hou, F. Teng, Cationic effects on solid polymer electrolyte-gated organic transistors, *Org Electron* 106 (2022) 106529. <https://doi.org/10.1016/j.orgel.2022.106529>.
- [37] D. Getya, I. Gitsov, Synthesis and Applications of Hybrid Polymer Networks Based on Renewable Natural Macromolecules, *Molecules* 28 (2023) 6030. <https://doi.org/10.3390/molecules28166030>.
- [38] H. El Knidri, R. Belaabed, A. Addaou, A. Laajeb, A. Lahsini, Extraction, chemical modification and characterization of chitin and chitosan, *Int J Biol Macromol* 120 (2018) 1181–1189. <https://doi.org/10.1016/j.ijbiomac.2018.08.139>.
- [39] M.M. Abo Elsoud, E.M. El Kady, Current trends in fungal biosynthesis of chitin and chitosan, *Bull Natl Res Cent* 43 (2019) 59. <https://doi.org/10.1186/s42269-019-0105-y>.
- [40] J. Berger, M. Reist, J.M. Mayer, O. Felt, R. Gurny, Structure and interactions in chitosan hydrogels formed by complexation or aggregation for biomedical applications, *European Journal of Pharmaceutics and Biopharmaceutics* 57 (2004) 35–52. [https://doi.org/10.1016/S0939-6411\(03\)00160-7](https://doi.org/10.1016/S0939-6411(03)00160-7).
- [41] F. Sami El-banna, M.E. Mahfouz, S. Leporatti, M. El-Kemary, N. A. N. Hanafy, Chitosan as a Natural Copolymer with Unique Properties for the Development of Hydrogels, *Applied Sciences* 9 (2019) 2193. <https://doi.org/10.3390/app9112193>.
- [42] J. Fu, F. Yang, Z. Guo, The chitosan hydrogels: from structure to function, *New Journal of Chemistry* 42 (2018) 17162–17180. <https://doi.org/10.1039/C8NJ03482F>.
- [43] H. Liu, C. Wang, C. Li, Y. Qin, Z. Wang, F. Yang, Z. Li, J. Wang, A functional chitosan-based hydrogel as a wound dressing and drug delivery system in the treatment of wound healing, *RSC Adv* 8 (2018) 7533–7549. <https://doi.org/10.1039/C7RA13510F>.
- [44] T.T. Demirtaş, G. Irmak, M. Gümüşderelioğlu, A bioprintable form of chitosan hydrogel for bone tissue engineering, *Biofabrication* 9 (2017) 035003. <https://doi.org/10.1088/1758-5090/aa7b1d>.

-
- [45] M. Qu, D. Lei, H. Zhang, X. Zhang, Z. Shang, R. Wang, L. Wan, Z. Li, C. Si, One-pot method for in situ synthesis of triple cross-linked hydrogel electrolytes for flexible supercapacitors with high mechanical and electrochemical properties, *J Energy Storage* 72 (2023) 108644. <https://doi.org/10.1016/j.est.2023.108644>.
- [46] L. Dai, Y. Wang, Z. Li, X. Wang, C. Duan, W. Zhao, C. Xiong, S. Nie, Y. Xu, Y. Ni, A multifunctional self-crosslinked chitosan/cationic guar gum composite hydrogel and its versatile uses in phosphate-containing water treatment and energy storage, *Carbohydr Polym* 244 (2020) 116472. <https://doi.org/10.1016/j.carbpol.2020.116472>.
- [47] M. Yu, X. Ji, F. Ran, Chemically building interpenetrating polymeric networks of Bi-crosslinked hydrogel macromolecules for membrane supercapacitors, *Carbohydr Polym* 255 (2021) 117346. <https://doi.org/10.1016/j.carbpol.2020.117346>.
- [48] J. Xu, R. Jin, X. Ren, G. Gao, A wide temperature-tolerant hydrogel electrolyte mediated by phosphoric acid towards flexible supercapacitors, *Chemical Engineering Journal* 413 (2021) 127446. <https://doi.org/10.1016/j.cej.2020.127446>.
- [49] X. Wang, Q. Zhang, L. Zhao, M.K. Hadi, S. Sambasivam, Q. Zhou, F. Ran, A renewable hydrogel electrolyte membrane prepared by carboxylated chitosan and polyacrylamide for solid-state supercapacitors with wide working temperature range, *J Power Sources* 560 (2023) 232704. <https://doi.org/10.1016/j.jpowsour.2023.232704>.
- [50] R. Liu, Q. Zhang, F. Ran, All-natural hydrogel electrolytes prepared by a universal strategy for supercapacitors, *New Journal of Chemistry* 46 (2022) 19523–19533. <https://doi.org/10.1039/D2NJ03698C>.
- [51] C.-H. Lin, W.-C. Li, T.-T. Cheng, P.-H. Wang, W.-N. Lee, T.-C. Wen, An investigation of carboxylated chitosan hydrogel electrolytes for symmetric carbon-based supercapacitors at low temperatures, *J Taiwan Inst Chem Eng* 126 (2021) 324–331. <https://doi.org/10.1016/j.jtice.2021.07.006>.
- [52] C.-H. Lin, P.-H. Wang, W.-N. Lee, W.-C. Li, T.-C. Wen, Chitosan with various degrees of carboxylation as hydrogel electrolyte for pseudo solid-state

- supercapacitors, *J Power Sources* 494 (2021) 229736. <https://doi.org/10.1016/j.jpowsour.2021.229736>.
- [53] V.K. Vorobiov, M.A. Smirnov, N. V. Bobrova, M.P. Sokolova, Chitosan-supported deep eutectic solvent as bio-based electrolyte for flexible supercapacitor, *Mater Lett* 283 (2021) 128889. <https://doi.org/10.1016/j.matlet.2020.128889>.
- [54] H. Wang, Y. Deng, J. Qiu, J. Wu, K. Zhang, J. Shao, L. Yan, In Situ Formation of “Dimethyl Sulfoxide/Water-in-Salt”-Based Chitosan Hydrogel Electrolyte for Advanced All-Solid-State Supercapacitors, *ChemSusChem* 14 (2021) 632–641. <https://doi.org/10.1002/cssc.202002236>.
- [55] Q. Zhang, L. Zhao, H. Yang, L. Kong, F. Ran, Alkali-tolerant polymeric gel electrolyte membrane based on cross-linked carboxylated chitosan for supercapacitors, *J Memb Sci* 629 (2021) 119083. <https://doi.org/10.1016/j.memsci.2021.119083>.
- [56] N.A. Choudhury, J. Ma, Y. Sahai, High performance and eco-friendly chitosan hydrogel membrane electrolytes for direct borohydride fuel cells, *J Power Sources* 210 (2012) 358–365. <https://doi.org/10.1016/j.jpowsour.2012.03.013>.
- [57] I.A. Fadzallah, S.R. Majid, M.A. Careem, A.K. Arof, A study on ionic interactions in chitosan–oxalic acid polymer electrolyte membranes, *J Memb Sci* 463 (2014) 65–72. <https://doi.org/10.1016/j.memsci.2014.03.044>.
- [58] S.F.A. Zaidi, A. Saeed, V.-C. Ho, J.H. Heo, H.H. Cho, N. Sarwar, N.-E. Lee, J. Mun, J.H. Lee, Chitosan-reinforced gelatin composite hydrogel as a tough, anti-freezing, and flame-retardant gel polymer electrolyte for flexible supercapacitors, *Int J Biol Macromol* 234 (2023) 123725. <https://doi.org/10.1016/j.ijbiomac.2023.123725>.
- [59] C.-H. Lin, W.-C. Li, T.-T. Cheng, P.-H. Wang, W.-N. Lee, T.-C. Wen, An investigation of carboxylated chitosan hydrogel electrolytes for symmetric carbon-based supercapacitors at low temperatures, *J Taiwan Inst Chem Eng* 126 (2021) 324–331. <https://doi.org/10.1016/j.jtice.2021.07.006>.
- [60] J. Qian, X. Wang, J. Shu, C. Su, J. Gong, Z. Xu, J. Jin, J. Shi, A Novel Complex of Chitosan–Sodium Carbonate and Its Properties, *Mar Drugs* 16 (2018) 416. <https://doi.org/10.3390/md16110416>.

-
- [61] D. Kamei, N.A. Choudhury, KI-doped redox-active gelatin chemical hydrogel membrane electrolytes for solid-state electrical double layer capacitors, *Mater Today Chem* 37 (2024) 101891. <https://doi.org/10.1016/j.mtchem.2023.101891>.
- [62] N.A. Choudhury, Y. Sahai, R.G. Buchheit, Polyvinyl Alcohol Chemical Hydrogel Electrode Binder for Direct Borohydride Fuel Cells, *J Electrochem Soc* 158 (2011) B712. <https://doi.org/10.1149/1.3581021>.
- [63] H. Nagahama, H. Maeda, T. Kashiki, R. Jayakumar, T. Furuike, H. Tamura, Preparation and characterization of novel chitosan/gelatin membranes using chitosan hydrogel, *Carbohydr Polym* 76 (2009) 255–260. <https://doi.org/10.1016/j.carbpol.2008.10.015>.
- [64] J. Biscarat, B. Galea, J. Sanchez, C. Pochat-Bohatier, Effect of chemical cross-linking on gelatin membrane solubility with a non-toxic and non-volatile agent: Terephthalaldehyde, *Int J Biol Macromol* 74 (2015) 5–11. <https://doi.org/10.1016/j.ijbiomac.2014.11.022>.
- [65] A.P. Hurt, G. Getti, N.J. Coleman, Bioactivity and biocompatibility of a chitosan-tobermorite composite membrane for guided tissue regeneration, *Int J Biol Macromol* 64 (2014) 11–16. <https://doi.org/10.1016/j.ijbiomac.2013.11.020>.
- [66] Y. Hu, V. Topolkaraev, A. Hiltner, E. Baer, Measurement of water vapor transmission rate in highly permeable films, *J Appl Polym Sci* 81 (2001) 1624–1633. <https://doi.org/10.1002/app.1593>.
- [67] M.A. Jahid, J. Hu, Water vapor transmission and water resistant: opposite but may coexist, *Mater Today Proc* 16 (2019) 1485–1490. <https://doi.org/10.1016/j.matpr.2019.05.328>.
- [68] S. Iizuka, K. Murata, M. Sekine, C. Sato, A novel cup with a pressure-adjusting mechanism for high-temperature water vapor transmission rate measurements, *Polym Test* 50 (2016) 73–78. <https://doi.org/10.1016/j.polymertesting.2015.11.018>.
- [69] A.S.F.M. Asnawi, S.B. Aziz, I. Brevik, M.A. Brza, Y.M. Yusof, S.M. Alshehri, T. Ahamad, M.F.Z. Kadir, The Study of Plasticized Sodium Ion Conducting Polymer Blend Electrolyte Membranes Based on Chitosan/Dextran

- Biopolymers: Ion Transport, Structural, Morphological and Potential Stability, *Polymers (Basel)* 13 (2021) 383. <https://doi.org/10.3390/polym13030383>.
- [70] Y. Wan, K.A.M. Creber, B. Peppley, V.T. Bui, Synthesis, Characterization and Ionic Conductive Properties of Phosphorylated Chitosan Membranes, *Macromol Chem Phys* 204 (2003) 850–858. <https://doi.org/10.1002/macp.200390056>.
- [71] N.A. Choudhury, S. Sampath, A.K. Shukla, Gelatin Hydrogel Electrolytes and Their Application to Electrochemical Supercapacitors, *J Electrochem Soc* 155 (2008) A74. <https://doi.org/10.1149/1.2803501>.
- [72] A.K. Arof, S. Amirudin, S.Z. Yusof, I.M. Noor, A method based on impedance spectroscopy to determine transport properties of polymer electrolytes, *Phys. Chem. Chem. Phys.* 16 (2014) 1856–1867. <https://doi.org/10.1039/C3CP53830C>.
- [73] R.T. Abdulwahid, S.B. Aziz, M.F.Z. Kadir, N.M. Sadiq, N.A. Halim, M.H. Hamsan, S.R. Saeed, H.J. Woo, Biodegradable polymer membrane K⁺ ion conductor for electrochemical device application, *J Mater Sci* 57 (2022) 19902–19923. <https://doi.org/10.1007/s10853-022-07825-1>.
- [74] Y. Khan, S. Bashir, M. Hina, S. Ramesh, K. Ramesh, M.A. Mujtaba, I. Lahiri, S. Ramesh, Effect of Charge Density on the Mechanical and Electrochemical Properties of Poly (acrylic acid) Hydrogel Electrolytes Based Flexible Supercapacitors, *Mater Today Commun* 25 (2020) 101558. <https://doi.org/10.1016/j.mtcomm.2020.101558>.
- [75] R. Deivanayagam, R. Shahbazian-Yassar, Electrochemical Methods and Protocols for Characterization of Ceramic and Polymer Electrolytes for Rechargeable Batteries, *Batter Supercaps* 4 (2021) 596–606. <https://doi.org/10.1002/batt.202000221>.
- [76] S. Bublil, G. Peta, M. Fayena-Greenstein, H. Alon-Yehezkel, O. Raskin, Y. Elias, D. Aurbach, Electrochemical Methods of Transference Number Determination for Polymer Electrolyte Systems: A Comparative Study, *J Electrochem Soc* 169 (2022) 110523. <https://doi.org/10.1149/1945-7111/ac9f75>.
- [77] A.K. Arof, N.E.A. Shuhaimi, S. Amirudin, M.Z. Kufian, H.J. Woo, M.A. Careem, Polyacrylonitrile-lithium bis(oxalato) borate polymer electrolyte for

- electrical double layer capacitors, *Polym Adv Technol* 25 (2014) 265–272. <https://doi.org/10.1002/pat.3231>.
- [78] R. Na, Y. Liu, N. Lu, S. Zhang, F. Liu, G. Wang, Mechanically robust hydrophobic association hydrogel electrolyte with efficient ionic transport for flexible supercapacitors, *Chemical Engineering Journal* 374 (2019) 738–747. <https://doi.org/10.1016/j.cej.2019.06.004>.
- [79] S. Yeasmin, M. Bora, B.K. Saikia, D. Mahanta, Binder mediated enhanced electrochemical capacitance in sodium silicate-graphite paint coated filter paper electrodes for all-solid-state symmetric electrochemical capacitors, *J Energy Storage* 73 (2023) 108945. <https://doi.org/10.1016/j.est.2023.108945>.
- [80] X. He, T. Zhuang, S. Ruan, X. Xia, Y. Xia, J. Zhang, H. Huang, Y. Gan, W. Zhang, An innovative poly(ionic liquid) hydrogel-based anti-freezing electrolyte with high conductivity for supercapacitor, *Chemical Engineering Journal* 466 (2023) 143209. <https://doi.org/10.1016/j.cej.2023.143209>.
- [81] Z. Liu, G. Liang, Y. Zhan, H. Li, Z. Wang, L. Ma, Y. Wang, X. Niu, C. Zhi, A soft yet device-level dynamically super-tough supercapacitor enabled by an energy-dissipative dual-crosslinked hydrogel electrolyte, *Nano Energy* 58 (2019) 732–742. <https://doi.org/10.1016/j.nanoen.2019.01.087>.
- [82] D. Sikorski, K. Gzyra-Jagięła, Z. Draczyński, The Kinetics of Chitosan Degradation in Organic Acid Solutions, *Mar Drugs* 19 (2021) 236. <https://doi.org/10.3390/md19050236>.
- [83] T. Loerting, J. Bernard, Aqueous Carbonic Acid (H_2CO_3), *ChemPhysChem* 11 (2010) 2305–2309. <https://doi.org/10.1002/cphc.201000220>.
- [84] M. Al-Remawi, N. Jaber, A. Elsayed, D. Alsafadi, K.A. Salah, Stabilization of insulin using low molecular weight chitosan carbonate nanocarrier, *Carbohydr Polym* 291 (2022) 119579. <https://doi.org/10.1016/j.carbpol.2022.119579>.
- [85] G. Mahmodi, P. Zarrintaj, A. Taghizadeh, M. Taghizadeh, S. Manouchehri, S. Dangwal, A. Ronte, M.R. Ganjali, J.D. Ramsey, S.-J. Kim, M.R. Saeb, From microporous to mesoporous mineral frameworks: An alliance between zeolite and chitosan, *Carbohydr Res* 489 (2020) 107930. <https://doi.org/10.1016/j.carres.2020.107930>.

-
- [86] N.A. Choudhury, J. Ma, Y. Sahai, R.G. Buchheit, High performance polymer chemical hydrogel-based electrode binder materials for direct borohydride fuel cells, *J Power Sources* 196 (2011) 5817–5822. <https://doi.org/10.1016/j.jpowsour.2011.03.004>.
- [87] V.D. Patake, T.T. Ghogare, A.D. Gulbake, C.D. Lokhande, The electrochemical performance of electrodeposited chitosan bio-nanopolymer in non-aqueous electrolyte: a new anodic material for supercapacitor, *SN Appl Sci* 1 (2019) 1063. <https://doi.org/10.1007/s42452-019-1054-7>.
- [88] J.R. Rodríguez-Núñez, T.J. Madera-Santana, D.I. Sánchez-Machado, J. López-Cervantes, H. Soto Valdez, Chitosan/Hydrophilic Plasticizer-Based Films: Preparation, Physicochemical and Antimicrobial Properties, *J Polym Environ* 22 (2014) 41–51. <https://doi.org/10.1007/s10924-013-0621-z>.
- [89] A.S. Htay, S.H. Teoh, D.W. Hutmacher, Development of perforated microthin poly(ϵ -caprolactone) films as matrices for membrane tissue engineering, *J Biomater Sci Polym Ed* 15 (2004) 683–700. <https://doi.org/10.1163/156856204323046933>.
- [90] N. Sankararamakrishnan, R. Sanghi, Preparation and characterization of a novel xanthated chitosan, *Carbohydr Polym* 66 (2006) 160–167. <https://doi.org/10.1016/j.carbpol.2006.02.035>.
- [91] B. Doshi, A. Ayati, B. Tanhaei, E. Repo, M. Sillanpää, Partially carboxymethylated and partially cross-linked surface of chitosan versus the adsorptive removal of dyes and divalent metal ions, *Carbohydr Polym* 197 (2018) 586–597. <https://doi.org/10.1016/j.carbpol.2018.06.032>.
- [92] S. Valizadeh, M. Naseri, S. Babaei, S.M.H. Hosseini, A. Imani, Development of bioactive composite films from chitosan and carboxymethyl cellulose using glutaraldehyde, cinnamon essential oil and oleic acid, *Int J Biol Macromol* 134 (2019) 604–612. <https://doi.org/10.1016/j.ijbiomac.2019.05.071>.
- [93] F. Jahan, R.D. Mathad, S. Farheen, Effect of mechanical strength on chitosan-pva blend through ionic crosslinking for food packaging application, *Mater Today Proc* 3 (2016) 3689–3696. <https://doi.org/10.1016/j.matpr.2016.11.014>.

-
- [94] T. Mitra, G. Sailakshmi, A. Gnanamani, A.B. Mandal, Studies on Cross-linking of succinic acid with chitosan/collagen, *Materials Research* 16 (2013) 755–765. <https://doi.org/10.1590/S1516-14392013005000059>.
- [95] J. Ma, Y. Sahai, R.G. Buchheit, Evaluation of multivalent phosphate cross-linked chitosan biopolymer membrane for direct borohydride fuel cells, *J Power Sources* 202 (2012) 18–27. <https://doi.org/10.1016/j.jpowsour.2011.11.003>.
- [96] V. Cyriac, Ismayil, K. Mishra, Y.N. Sudhakar, Z.E. Rojudi, S.P. Masti, I.M. Noor, Suitability of NaI complexed sodium alginate-polyvinyl alcohol biodegradable polymer blend electrolytes for electrochemical device applications: Insights into dielectric relaxations and scaling studies, *Solid State Ion* 411 (2024) 116578. <https://doi.org/10.1016/j.ssi.2024.116578>.
- [97] L.T. Khoon, M.-L.W. Fui, N.H. Hassan, M.S. Su'ait, R. Vedarajan, N. Matsumi, M. Bin Kassim, L.K. Shyuan, A. Ahmad, In situ sol–gel preparation of ZrO₂ in nano-composite polymer electrolyte of PVDF-HFP/MG49 for lithium-ion polymer battery, *J Solgel Sci Technol* 90 (2019) 665–675. <https://doi.org/10.1007/s10971-019-04936-1>.
- [98] A. Poosapati, K. Negrete, N. Jang, L. Hu, Y. Lan, D. Madan, Wood cellulose-based thin gel electrolyte with enhanced ionic conductivity, *MRS Commun* 9 (2019) 1015–1021. <https://doi.org/10.1557/mrc.2019.79>.
- [99] H. Yang, N. Wu, Ionic conductivity and ion transport mechanisms of solid-state lithium-ion battery electrolytes: A review, *Energy Sci Eng* 10 (2022) 1643–1671. <https://doi.org/10.1002/ese3.1163>.
- [100] J. Owen, Ionic Conductivity, *Comprehensive Polymer Science and Supplements* (1989) 669–686. <https://doi.org/10.1016/B978-0-08-096701-1.00058-6>.
- [101] M.A. Hickner, Water-mediated transport in ion-containing polymers, *J Polym Sci B Polym Phys* 50 (2012) 9–20. <https://doi.org/10.1002/polb.22381>.
- [102] H.T. Ahmed, O.Gh. Abdullah, Impedance and ionic transport properties of proton-conducting electrolytes based on polyethylene oxide/methylcellulose blend polymers, *Journal of Science: Advanced Materials and Devices* 5 (2020) 125–133. <https://doi.org/10.1016/j.jsamd.2020.02.001>.

-
- [103] A. Rosdi, N.H. Zainol, Z. Osman, Ionic transport and electrochemical stability of PVDF-HFP based gel polymer electrolytes, in: 2016: p. 050003. <https://doi.org/10.1063/1.4941629>.
- [104] K.A. Francis, C.-W. Liew, S. Ramesh, K. Ramesh, S. Ramesh, Ionic liquid enhanced magnesium-based polymer electrolytes for electrical double-layer capacitors, *Ionics (Kiel)* 22 (2016) 919–925. <https://doi.org/10.1007/s11581-015-1619-4>.
- [105] L. Sampathkumar, P. Christopher Selvin, S. Selvasekarapandian, P. Perumal, R. Chitra, M. Muthukrishnan, Synthesis and characterization of biopolymer electrolyte based on tamarind seed polysaccharide, lithium perchlorate and ethylene carbonate for electrochemical applications, *Ionics (Kiel)* 25 (2019) 1067–1082. <https://doi.org/10.1007/s11581-019-02857-1>.
- [106] S.B. Aziz, A.S.F.M. Asnawi, P.A. Mohammed, R.T. Abdulwahid, Y.M. Yusof, R.M. Abdullah, M.F.Z. Kadir, Impedance, circuit simulation, transport properties and energy storage behavior of plasticized lithium ion conducting chitosan based polymer electrolytes, *Polym Test* 101 (2021) 107286. <https://doi.org/10.1016/j.polymertesting.2021.107286>.
- [107] H.L. Yeager, B. Kipling, Ionic diffusion and ion clustering in a perfluorosulfonate ion-exchange membrane, *J Phys Chem* 83 (1979) 1836–1839. <https://doi.org/10.1021/j100477a008>.
- [108] R.J. Klein, S. Zhang, S. Dou, B.H. Jones, R.H. Colby, J. Runt, Modeling electrode polarization in dielectric spectroscopy: Ion mobility and mobile ion concentration of single-ion polymer electrolytes, *J Chem Phys* 124 (2006). <https://doi.org/10.1063/1.2186638>.
- [109] E.M.A. Dannoun, S.B. Aziz, S.N. Abdullah, M.M. Nofal, K.H. Mahmoud, A.R. Murad, R.M. Abdullah, Mohd.F.Z. Kadir, Characteristics of Plasticized Lithium Ion Conducting Green Polymer Blend Electrolytes Based on CS: Dextran with High Energy Density and Specific Capacitance, *Polymers (Basel)* 13 (2021) 3613. <https://doi.org/10.3390/polym13213613>.
- [110] A. Arya, A.L. Sharma, Structural, electrical properties and dielectric relaxations in Na^+ -ion-conducting solid polymer electrolyte, *Journal of Physics: Condensed Matter* 30 (2018) 165402. <https://doi.org/10.1088/1361-648X/aab466>.

- [111] H. Xuan, Y. Guan, X. Han, X. Liang, Z. Xie, P. Han, Y. Wu, Hierarchical MnCo-LDH/rGO@NiCo₂S₄ heterostructures on Ni foam with enhanced electrochemical properties for battery-supercapacitors, *Electrochim Acta* 335 (2020) 135691. <https://doi.org/10.1016/j.electacta.2020.135691>.
- [112] P. Simon, Y. Gogotsi, Materials for electrochemical capacitors, *Nat Mater* 7 (2008) 845–854. <https://doi.org/10.1038/nmat2297>.
- [113] R. Kant, M.B. Singh, Theory of the Electrochemical Impedance of Mesoporous Electrodes Embedded with Heterogeneous Micropores, *The Journal of Physical Chemistry C* 121 (2017) 7164–7174. <https://doi.org/10.1021/acs.jpcc.7b01287>.
- [114] X. Zhang, M. Kar, T.C. Mendes, Y. Wu, D.R. MacFarlane, Supported Ionic Liquid Gel Membrane Electrolytes for Flexible Supercapacitors, *Adv Energy Mater* 8 (2018). <https://doi.org/10.1002/aenm.201702702>.
- [115] C.-W. Liew, S. Ramesh, Electrical, structural, thermal and electrochemical properties of corn starch-based biopolymer electrolytes, *Carbohydr Polym* 124 (2015) 222–228. <https://doi.org/10.1016/j.carbpol.2015.02.024>.
- [116] C.-C. Hu, E. Chen, J.-Y. Lin, Capacitive and textural characteristics of polyaniline-platinum composite films, *Electrochim Acta* 47 (2002) 2741–2749. [https://doi.org/10.1016/S0013-4686\(02\)00139-1](https://doi.org/10.1016/S0013-4686(02)00139-1).
- [117] Metrohm, Electrochemical Impedance Spectroscopy (EIS) on battery electrodes using NOVA, Application Note AN-EIS-005 (2014).
- [118] A.Ch. Lazanas, M.I. Prodromidis, Electrochemical Impedance Spectroscopy—A Tutorial, *ACS Measurement Science Au* 3 (2023) 162–193. <https://doi.org/10.1021/acsmesuresciau.2c00070>.
- [119] C. Portet, P.L. Taberna, P. Simon, C. Laberty-Robert, Modification of Al current collector surface by sol–gel deposit for carbon–carbon supercapacitor applications, *Electrochim Acta* 49 (2004) 905–912. <https://doi.org/10.1016/j.electacta.2003.09.043>.
- [120] C. Lei, F. Markoulidis, Z. Ashitaka, C. Lekakou, Reduction of porous carbon/Al contact resistance for an electric double-layer capacitor (EDLC), *Electrochim Acta* 92 (2013) 183–187. <https://doi.org/10.1016/j.electacta.2012.12.092>.

-
- [121] I. Yang, S.-G. Kim, S.H. Kwon, M.-S. Kim, J.C. Jung, Relationships between pore size and charge transfer resistance of carbon aerogels for organic electric double-layer capacitor electrodes, *Electrochim Acta* 223 (2017) 21–30. <https://doi.org/10.1016/j.electacta.2016.11.177>.
- [122] S.H. Kwon, E. Lee, B.-S. Kim, S.-G. Kim, B.-J. Lee, M.-S. Kim, J.C. Jung, Preparation of activated carbon aerogel and its application to electrode material for electric double layer capacitor in organic electrolyte: Effect of activation temperature, *Korean Journal of Chemical Engineering* 32 (2015) 248–254. <https://doi.org/10.1007/s11814-014-0215-z>.
- [123] M.E. Orazem, B. Tribollet, *Electrochemical Impedance Spectroscopy*, Wiley, 2008. <https://doi.org/10.1002/9780470381588>.
- [124] N. Mahato, T.V.M. Sreekanth, K. Yoo, J. Kim, Semi-Polycrystalline Polyaniline-Activated Carbon Composite for Supercapacitor Application, *Molecules* 28 (2023) 1520. <https://doi.org/10.3390/molecules28041520>.
- [125] N. Anjum, N. Joyal, J. Iroegbu, D. Li, C. Shen, Humidity-modulated properties of hydrogel polymer electrolytes for flexible supercapacitors, *J Power Sources* 499 (2021) 229962. <https://doi.org/10.1016/j.jpowsour.2021.229962>.
- [126] J.A. Lee, M.K. Shin, S.H. Kim, H.U. Cho, G.M. Spinks, G.G. Wallace, M.D. Lima, X. Lepró, M.E. Kozlov, R.H. Baughman, S.J. Kim, Ultrafast charge and discharge bicroiled yarn supercapacitors for textiles and microdevices, *Nat Commun* 4 (2013) 1970. <https://doi.org/10.1038/ncomms2970>.
- [127] C. Shen, Y. Xie, M. Sanghadasa, Y. Tang, L. Lu, L. Lin, Ultrathin Coaxial Fiber Supercapacitors Achieving High Energy and Power Densities, *ACS Appl Mater Interfaces* 9 (2017) 39391–39398. <https://doi.org/10.1021/acsami.7b12047>.
- [128] C. Jiang, M. Gao, S. Zhang, L. Huang, S. Yu, Z. Song, Q. Wu, Chitosan/graphene oxide hybrid hydrogel electrode with porous network boosting ultrahigh energy density flexible supercapacitor, *Int J Biol Macromol* 225 (2023) 1437–1448. <https://doi.org/10.1016/j.ijbiomac.2022.11.201>.
- [129] S. Balasubramaniam, A. Mohanty, S.K. Balasingam, S.J. Kim, A. Ramadoss, Comprehensive Insight into the Mechanism, Material Selection and Performance Evaluation of Supercapatteries, *Nanomicro Lett* 12 (2020) 85. <https://doi.org/10.1007/s40820-020-0413-7>.

-
- [130] Z. Liu, L. Jiang, L. Sheng, Q. Zhou, T. Wei, B. Zhang, Z. Fan, Oxygen Clusters Distributed in Graphene with “Paddy Land” Structure: Ultrahigh Capacitance and Rate Performance for Supercapacitors, *Adv Funct Mater* 28 (2018). <https://doi.org/10.1002/adfm.201705258>.
- [131] M. Udayakumar, P. Tóth, H. Wiinikka, J.S. Malhotra, B. Likozar, S. Gyergyek, A.K. Leskó, R. Thangaraj, Z. Németh, Hierarchical porous carbon foam electrodes fabricated from waste polyurethane elastomer template for electric double-layer capacitors, *Sci Rep* 12 (2022) 11786. <https://doi.org/10.1038/s41598-022-16006-8>.
- [132] P. Forouzandeh, V. Kumaravel, S.C. Pillai, Electrode Materials for Supercapacitors: A Review of Recent Advances, *Catalysts* 10 (2020) 969. <https://doi.org/10.3390/catal10090969>.
- [133] M.A. Brza, S. B. Aziz, H. Anuar, E.M.A. Dannoun, F. Ali, R.T. Abdulwahid, S. Al-Zangana, M.F.Z. Kadir, The Study of EDLC Device with High Electrochemical Performance Fabricated from Proton Ion Conducting PVA-Based Polymer Composite Electrolytes Plasticized with Glycerol, *Polymers (Basel)* 12 (2020) 1896. <https://doi.org/10.3390/polym12091896>.
- [134] S.B. Aziz, M.H. Hamsan, M.A. Brza, M.F.Z. Kadir, S.K. Muzakir, R.T. Abdulwahid, Effect of glycerol on EDLC characteristics of chitosan:methylcellulose polymer blend electrolytes, *Journal of Materials Research and Technology* 9 (2020) 8355–8366. <https://doi.org/10.1016/j.jmrt.2020.05.114>.
- [135] N.A. Choudhury, J. Ma, Y. Sahai, R.G. Buchheit, High performance polymer chemical hydrogel-based electrode binder materials for direct borohydride fuel cells, *J Power Sources* 196 (2011) 5817–5822. <https://doi.org/10.1016/j.jpowsour.2011.03.004>.
- [136] R. Kötz, P.W. Ruch, D. Cericola, Aging and failure mode of electrochemical double layer capacitors during accelerated constant load tests, *J Power Sources* 195 (2010) 923–928. <https://doi.org/10.1016/j.jpowsour.2009.08.045>.
- [137] B.-A. Mei, J. Lau, T. Lin, S.H. Tolbert, B.S. Dunn, L. Pilon, Physical Interpretations of Electrochemical Impedance Spectroscopy of Redox Active

- Electrodes for Electrical Energy Storage, *The Journal of Physical Chemistry C* 122 (2018) 24499–24511. <https://doi.org/10.1021/acs.jpcc.8b05241>.
- [138] R. Weber, A.J. Louli, K.P. Plucknett, J.R. Dahn, Resistance Growth in Lithium-Ion Pouch Cells with $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ Positive Electrodes and Proposed Mechanism for Voltage Dependent Charge-Transfer Resistance, *J Electrochem Soc* 166 (2019) A1779–A1784. <https://doi.org/10.1149/2.0361910jes>.
- [139] J. Liu, C. Wu, I.D. Gates, B. Jia, Z. Huang, T. Ma, Integrated Electrode-Electrolyte Optimization to Manufacture a Real-Life Applicable Aqueous Supercapacitor with Record-Breaking Lifespan, *ENERGY & ENVIRONMENTAL MATERIALS* 6 (2023). <https://doi.org/10.1002/eem2.12520>.
- [140] S. Wu, B. Su, M. Sun, S. Gu, Z. Lu, K. Zhang, D.Y.W. Yu, B. Huang, P. Wang, C. Lee, W. Zhang, Dilute Aqueous-Aprotic Hybrid Electrolyte Enabling a Wide Electrochemical Window through Solvation Structure Engineering, *Advanced Materials* 33 (2021). <https://doi.org/10.1002/adma.202102390>.
- [141] S. Pohlmann, T. Olyschläger, P. Goodrich, J.A. Vicente, J. Jacquemin, A. Balducci, Mixtures of Azepanium Based Ionic Liquids and Propylene Carbonate as High Voltage Electrolytes for Supercapacitors, *Electrochim Acta* 153 (2015) 426–432. <https://doi.org/10.1016/j.electacta.2014.11.189>.
- [142] S. Pohlmann, T. Olyschläger, P. Goodrich, J. Alvarez Vicente, J. Jacquemin, A. Balducci, Azepanium-based ionic liquids as green electrolytes for high voltage supercapacitors, *J Power Sources* 273 (2015) 931–936. <https://doi.org/10.1016/j.jpowsour.2014.09.167>.
- [143] B. Asbani, C. Douard, T. Brousse, J. Le Bideau, High temperature solid-state supercapacitor designed with ionogel electrolyte, *Energy Storage Mater* 21 (2019) 439–445. <https://doi.org/10.1016/j.ensm.2019.06.004>.
- [144] M. Brachet, T. Brousse, J. Le Bideau, All Solid-State Symmetrical Activated Carbon Electrochemical Double Layer Capacitors Designed with Ionogel Electrolyte, *ECS Electrochemistry Letters* 3 (2014) A112–A115. <https://doi.org/10.1149/2.0051411eel>.
- [145] X. Jin, L. Song, H. Yang, C. Dai, Y. Xiao, X. Zhang, Y. Han, C. Bai, B. Lu, Q. Liu, Y. Zhao, J. Zhang, Z. Zhang, L. Qu, Stretchable supercapacitor at $-30\text{ }^{\circ}\text{C}$,

- Energy Environ Sci 14 (2021) 3075–3085.
<https://doi.org/10.1039/D0EE04066E>.
- [146] C. Yang, M. Sun, X. Wang, G. Wang, A Novel Flexible Supercapacitor Based on Cross-Linked PVDF-HFP Porous Organogel Electrolyte and Carbon Nanotube Paper@ π -Conjugated Polymer Film Electrodes, ACS Sustain Chem Eng 3 (2015) 2067–2076. <https://doi.org/10.1021/acssuschemeng.5b00334>.
- [147] Q. Liu, D. Wu, T. Wang, Y. Guo, Polysaccharide of agar based ultra-high specific surface area porous carbon for superior supercapacitor, Int J Biol Macromol 228 (2023) 40–47. <https://doi.org/10.1016/j.ijbiomac.2022.12.126>.
- [148] C. Lu, X. Chen, All-Temperature Flexible Supercapacitors Enabled by Antifreezing and Thermally Stable Hydrogel Electrolyte, Nano Lett 20 (2020) 1907–1914. <https://doi.org/10.1021/acs.nanolett.9b05148>.
- [149] G. Li, X. Zhang, M. Sang, X. Wang, D. Zuo, J. Xu, H. Zhang, A supramolecular hydrogel electrolyte for high-performance supercapacitors, J Energy Storage 33 (2021) 101931. <https://doi.org/10.1016/j.est.2020.101931>.
- [150] X. Gao, Q. Hu, K. Sun, H. Peng, X. Xie, H.A. Hamouda, G. Ma, A novel all-in-one integrated flexible supercapacitor based on self-healing hydrogel electrolyte, J Alloys Compd 888 (2021) 161554. <https://doi.org/10.1016/j.jallcom.2021.161554>.
- [151] G. Zhou, L. Yang, W. Li, C. Chen, Q. Liu, A Regenerable Hydrogel Electrolyte for Flexible Supercapacitors, IScience 23 (2020) 101502. <https://doi.org/10.1016/j.isci.2020.101502>.
- [152] H. Li, T. Lv, N. Li, Y. Yao, K. Liu, T. Chen, Ultraflexible and tailorable all-solid-state supercapacitors using polyacrylamide-based hydrogel electrolyte with high ionic conductivity, Nanoscale 9 (2017) 18474–18481. <https://doi.org/10.1039/C7NR07424G>.

CHAPTER 3

Structure–property Insights into CO₃²⁻ cross-linked Chitosan Hydrogel Membranes: Facile Synthesis via Gradient Crosslinking of Quasi-solid Electrolytes for Electrical Double Layer Capacitors with Remarkable Cycle Lives

This chapter focuses on the synthesis, physiochemical and electrochemical characterizations of GCCHMEs using a time efficient and facile gradient ionic crosslinking using sodium carbonate crosslinker. The influence of crosslinker concentration on membrane properties was studied with detailed characterizations. Electrochemical techniques, including EIS, CV, and GCD analysis, were employed to evaluate energy storage performance of the GCCHMEs in EDLC applications. Cycle life studies and prototype testing were also performed to know real world viabilities.

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3.1 Introduction

The global energy requirement has long been satisfied by fossil fuels. However, the finite availability of these resources, coupled with their detrimental environmental impact, has accelerated a transition toward cleaner and renewable alternatives such as wind energy, solar power, and green hydrogen [1]. While these renewable sources are essential for sustainable development, their intermittent and location-dependent nature presents significant challenges for maintaining a consistent and reliable energy supply [2]. To mitigate these issues, it has become critical to develop sustainable energy storage technologies. One such energy storage device is the ESs [3]. ESs are generally categorized into three types: EDLCs, PCs, and hybrid supercapacitors [4]. Among these, EDLCs have emerged as especially promising owing to their high power density and long lifespan [5]. These features make EDLCs applicable in EVs, military systems, and medical devices.

The performance of EDLCs is highly dependent on the electrolyte properties such as the operating voltage, ion transport efficiency, and energy density [6]. Both liquid and SSEs have been used in EDLCs, each with distinct advantages and drawbacks. Liquid electrolytes offer superior ion mobility but suffer from leakage and limited mechanical stability. In contrast, SSEs, especially polymer-based systems, provide leak-proof operation, compact design, and enhanced durability [7]. Polymer-based electrolytes are generally prepared by dispersing ionic salts or liquid electrolytes within a polymer matrix to achieve enhanced mechanical stability and ionic conductivity. GPEs are a type of polymer-based electrolyte in which a liquid plasticizer or solvent is entrapped within it, resulting in enhanced flexibility and ionic conductivity [8]. Due to their excellent electrochemical stability, thermal robustness, and non-volatility, GPEs are increasingly being employed in EDLCs. A specialized class of GPEs, known as hydrogels, comprises a three-dimensional polymer matrix encapsulating significant quantities of water. These quasi-solid materials combine the positive traits of solid electrolytes and liquid electrolytes [9]. The functionality of hydrogels can be further tailored through chemical or ionic crosslinking strategies that improve structural integrity and mechanical strength [10]. Hydrogels can be fabricated using either synthetic [11] or natural polymers [12]. Synthetic polymers such as PVA, and PAA

have been widely employed in energy storage applications [13]. However, these materials raise environmental concerns due to their non-biodegradability and the energy-intensive nature of their synthesis processes, which involve hazardous chemicals and complex manufacturing steps. These drawbacks have hindered the widespread adoption of synthetic polymer-based systems. In contrast, biopolymers derived from animal or plant sources offer a more sustainable alternative. Their biodegradability, low toxicity, and reduced environmental impact have made them increasingly attractive for applications in energy storage devices [14]. With annual growth rates projected at 10-20%, biopolymers are witnessing a rapid expansion in energy-related sectors [15]. They have shown promise in batteries and supercapacitors, where their favourable mechanical, thermal, and dielectric properties provide a compelling case for replacing fossil fuel-based polymers in next-generation technologies, such as flexible electronics and EVs [16]. Among various biopolymers, chitosan which is a polysaccharide derived from crustacean shells and fungal cell walls, has attracted substantial interest. Its unique ability to form positively charged gels under acidic conditions enables the creation of versatile hydrogel matrices [17]. Chitosan-based hydrogels have demonstrated exceptional mechanical integrity and have been widely utilised in biomedical fields for purposes such as drug delivery, wound dressings, and tissue engineering. For energy storage applications, chitosan-based hydrogels have demonstrated favourable electrochemical properties. For instance, Qu et al. [18] developed a chitosan-based hydrogel electrolyte using a triple chemical crosslinking strategy for supercapacitor applications. Dai et al. [19] reported chitosan-guar gum hydrogels for dual applications in water purification and energy storage.

Despite considerable research into chemically cross-linked chitosan hydrogels, studies focusing on ionically cross-linked chitosan membranes for supercapacitor applications remain limited [20]. Only a few efforts have explored the use of ionic crosslinkers such as Na_2SO_4 [21] and oxalic acid [22] to develop hydrogel electrolytes for energy and fuel cell technologies. The properties of hydrogel electrolytes and their performance in EDLCs are significantly influenced by the spatial architecture of the cross-linked network. This architecture can be tuned using either ionic or covalent crosslinking

[23], and is typically implemented via one of two methods i.e., homogeneous mixing [20,24] or submersion [25]. In the homogeneous mixing approach, the polymer precursor is mixed with an ionic (e.g., multivalent salts) or covalent (e.g., glutaraldehyde, genipin) crosslinker in solution. This results in isotropic crosslinking, where the network is uniformly formed throughout the hydrogel. Such structures typically offer high mechanical strength, interconnected voids, and efficient ion transport which are qualities essential for supercapacitor and bioelectronic applications. In our previous study [20] of Chapter 2, isotropic bulk crosslinking of chitosan with Na_2CO_3 resulted in a porous structure due to CO_2 evolution, enhancing its electrochemical properties in EDLCs. In contrast, the submersion method involves immersing a preformed chitosan membrane into a crosslinker solution. The diffusion-limited process gives rise to a gradient crosslinking profile, where crosslinking is more pronounced at the surface and gradually diminishes toward the core. This structure, achievable via both ionic and covalent means, offers specific advantages like controlled surface stiffness and more viable fabrication process.

Building on our prior success with isotropically cross-linked chitosan- Na_2CO_3 hydrogels [20] as studied in Chapter 2, this study explores the gradient ionic crosslinking of chitosan membranes using the same crosslinker. The goal is to assess how the gradient architecture influences hydrogel morphology, ion transport behaviour, and overall electrochemical performance in EDLC configurations. By comparing gradient and isotropic systems, we aim to offer deeper insights into crosslinking strategies that can guide the logical design of next-generation smart hydrogel electrolytes.

3.2 Materials and methods

3.2.1 Materials

Chitosan (CAS No.: 9012-76-4, Loba Chemie Pvt. Ltd., 75 % deacetylation, sodium carbonate anhydrous (Molychem India, AR), glacial CH_3COOH (Merck, 90-100 %), Cabot BPC, PVA (Loba Chemie Pvt. Ltd), ethanol (99.9 %), and glutaraldehyde (25 %).

3.2.2 Preparation of aqueous chitosan stock solution

To prepare 100 mL of 2 % aq. chitosan stock solution (w/v), 2 g of chitosan flakes were solubilized in 100 mL of 2 % (v/v) aq. acetic acid. The mixture was continuously stirred at room temperature for around 24 hours to ensure complete solubilization. Subsequently, the prepared solution was further mixed at 93 °C in a water bath for an additional 2 hours to maximize homogeneity with enhance solubility.

3.2.3 Uncross-linked Chitosan Membrane preparation

A 10 mL of the prepared aq. chitosan stock solution was cast onto a Petri dish and left to dry at room temperature for approximately 48 hours. This was further dried in an air-convection oven at 34 °C for 6 hours. This results in the formation of the UCM.

3.2.4 Synthesis of Gradient cross-linked chitosan hydrogel membrane electrolytes

UCM was used to prepare the GCCHMEs. The solid UCM was peeled off from Petri dish, cut, and immersed various molar Na_2CO_3 solutions. This setup was covered to prevent evaporation, and left at ambient temperature for 24 hours to allow sufficient absorption of the salt solution. During this period, carbonate ions (CO_3^{2-}) in the solution interact with the ammonium moieties ($-\text{NH}_3^+$) of the chitosan, forming ionic cross-links that transform the films into GCCHMEs. The GCCHMEs were then removed from the crosslinker solution, thoroughly rinsed with DI water, and stored in a DI water bath for subsequent use in supercapacitors.

3.2.5 FT-IR spectroscopic studies

A Perkin Elmer Spectrum Two FT-IR spectrometer was employed to record the FTIR spectra of Na_2CO_3 powder, chitosan flakes and GCCHME. All samples were scanned

from 4000 to 500 cm^{-1} wavenumber. For chitosan flakes and Na_2CO_3 powder, FTIR pellets were prepared by thoroughly mixing the samples with KBr powder followed by compression under a hydraulic press applying a force of 255 kg cm^{-2} .

3.2.6 WU studies

WU measurements of GCCHMEs were conducted on samples cut into $4 \times 4 \text{ cm}^2$ portions. The GCCHMEs were immersed in DI water within a beaker to ensure complete absorption of water in their polymeric matrices. Following the removal of excess water using filter paper, the hydrated membranes were weighed (W_h). The GCCHMEs were subjected to drying in an oven for 48 hours at 45 °C to eliminate absorbed moisture. GCCHMEs were weighted every 12 hours until a consistent dry weight (W_d) was achieved to ensure full evaporation. The percentage of WU was calculated from the dry and wet weights employing the formula shown below [25]

$$\text{WU (\%)} = \left(\frac{W_h - W_d}{W_d} \right) \times 100 \quad (1)$$

3.2.7 Ionic conductivity studies

Ionic conductivity of the GCCHMEs were studied as a function of varying Na_2CO_3 concentration. This was done by placing a GCCHME having an area of 1 cm^2 between two SS electrodes of the same area. This assembly is referred to as the HMEA. EIS was conducted to determine the ionic conductivity employing potential amplitude of 5 mV_{rms} across a frequency range of 0.1 MHz to 0.1 Hz. From the Nyquist plot of EIS, the R_b value was evaluated. Finally, the value of R_s was employed to calculate the ionic conductivity using the equation given below [26].

$$\sigma = \frac{L}{A \times R_b} \quad (2)$$

where, L and A are the thickness and area of the GCCHME.

3.2.8 AC conductivity studies

AC conductivities (σ_{AC}) of GCCHMEs with varying concentration of Na_2CO_3 were evaluated by using the following equation [26].

$$\sigma_{AC} = \left[\frac{z'}{z'^2 + z''^2} \right] \times \left(\frac{L}{A} \right) \quad (3)$$

Where, z' and z'' are the real and imaginary parts of the Nyquist plot.

3.2.9 Dielectric studies

A range of analytical techniques are utilized to assess dielectric properties of materials. Key parameters, including the dielectric constant (ϵ'), dielectric loss (ϵ''), dielectric loss tangent ($\tan(\delta)$), and dielectric modulus of real (M') as well as imaginary (M'') are important to know the ion transport within polymer-based electrolytes. Here, ϵ' , ϵ'' , and $\tan(\delta)$ for GCCHMEs were analysed using the following equations [27,28].

$$\epsilon' = \frac{z''}{\omega C_0 (z'^2 + z''^2)} \quad (4)$$

$$\epsilon'' = \frac{z'}{\omega C_0 (z'^2 + z''^2)} \quad (5)$$

$$\tan(\delta) = \frac{\epsilon''}{\epsilon'} \quad (6)$$

$$M' = \frac{\epsilon'}{\epsilon'^2 + \epsilon''^2} \quad (7)$$

$$M'' = \frac{\epsilon''}{\epsilon'^2 + \epsilon''^2} \quad (8)$$

Here, $\omega = 2\pi f$, where f is frequency; $C_0 = \frac{\epsilon_0 A}{L}$ is vacuum capacitance, where ϵ_0 (equal to $8.85 \times 10^{-14} \text{ F cm}^{-1}$) is the permittivity of free space, L is the membrane thickness, A is blocking electrode area.

3.2.10 Determination of ion transport parameters

EIS method was employed to calculate the ion transport parameters. The diffusion coefficient (D), ionic mobility (μ), and ion number density (n) were calculated based on the following established equations that provide the theoretical framework for interpreting impedance data [29]. The following equation can be used to determine D value [30].

$$D = \left(\frac{(k\varepsilon_0\varepsilon'A)^2}{\tau} \right) \quad (9)$$

In Eq. (9), k denotes the reciprocal of CPE, while τ represents the reciprocal of the angular frequency (ω), which can be obtained using the frequency (f) from equation $\omega = 2\pi f$. A refers to the geometrical area of OCCMEs, and ε_0 is the vacuum permittivity, valued at $8.85 \times 10^{-12} \text{ Fm}^{-1}$. The dielectric constant (ε') is determined using the equation $\varepsilon_r = \frac{z''}{\omega C_0(z'^2 + z''^2)}$; where the vacuum capacitance (C_0) is calculated using $C_0 = \frac{\varepsilon_0 A}{L}$ with L denoting the thickness of GCCHMEs. Furthermore, ionic mobility, μ can be determined employing equation (10) [30].

$$\mu = \left(\frac{eD}{k_B T} \right) \quad (10)$$

Where, T, k_B , and e represents the absolute temperature, Boltzmann constant (valued as $1.38 \times 10^{-23} \text{ JK}^{-1}$), and electric charge (valued as $1.602 \times 10^{-19} \text{ C}$), respectively.

Ion number density, n for the GCCHMEs was obtained employing the Eq. (11) [30].

$$n = \left(\frac{\sigma k_B T \tau}{(ek\varepsilon_0\varepsilon'A)^2} \right) \quad (11)$$

3.2.11 DR studies

To determine DR (%), the GCCHMEs were initially cut into 4 cm^2 square. The initial wet weights (W_1) of the GCCHMEs were noted prior to testing. To evaluate their dissolution behaviour under accelerated conditions, the GCCHMEs were immersed in

boiling hot DI water for 6 hours. This was followed by oven-drying the samples at 35 °C for 48 hours to get the dry weight (W_2) of the GCCHMEs. The DR (%) was then calculated using the following equation [31].

$$\text{DR (\%)} = \left(\frac{W_1 - W_2}{W_1} \right) \times 100 \quad (12)$$

3.2.12 FE-SEM and EDX studies

The FE-SEM analysis of UCM and GCCHME were examined using a ZEISS Sigma Field Emission-Scanning Electron Microscope. While the elemental composition of the samples was analysed using an EDX equipment.

3.2.13 XRD studies

The XRD analysis was used to examine the structural characteristics of Na_2CO_3 powder, UCM and GCCHMEs. The analyses were conducted using a Bruker D8 Advance X-ray diffractometer (Germany), equipped with Cu radiated Ni-filter at 30 mA and 30 kV. Diffraction patterns were recorded over a 2θ range of 5° to 65°. XRD deconvolution for UCM and GCCHMEs were carried out using OriginPro software (2022). Gaussian fitting functions were applied to distinguish and quantify the crystalline (A_c) and amorphous (A_a) regions of the diffraction profiles. The degree of crystallinity (X_c), was then evaluated using the formula [32]

$$X_c = \left[\frac{A_c}{A_c + A_a} \right] \times 100 \% \quad (13)$$

3.2.14 Mechanical strength studies

The mechanical integrity of UCM and GCCHMEs were tested using Universal Testing Machine (Instron, E-3000) set at a stretching rate of 1 mm min⁻¹.

3.2.15 Transference number measurement

The DC polarization technique was employed to determine the ion transference number (t_{ion}). The HMEA was polarized by a constant voltage of 1 V and a current versus time plot was recorded. Initial current (I_0) reflects the contribution from both

electronic and ionic charge carriers. Over time, as the current stabilizes, a steady-state current (I_{ss}) was obtained, which corresponds exclusively to electronic conduction. The t_{ion} was calculated employing the following equation [32].

$$t_{ion} = \frac{I_0 - I_{ss}}{I_0} \quad (14)$$

Anionic and cationic transference numbers are critical parameters for evaluating the efficiency and performance of electrolytes. Accurate determination of the ionic conductivity requires the quantification of individual ion contributions. A widely adopted method for this purpose is the Bruce-Vincent technique, which integrate DC polarization employing AC impedance. AC impedance measurements are performed both before and after the polarization to determine any changes in the interfacial resistances. The cationic transference number (t_{cation}) is quantified by the following equation [33,34].

$$t_{cation} = \frac{I_{ss} (\Delta V - I_0 R_0)}{I_0 (\Delta V - I_{ss} R_{ss})} \quad (15)$$

Where, R_0 is the initial resistance and R_{ss} is the resistance at steady-state.

3.2.16 TGA studies

TGA of UCM and GCCHME was investigated using a TGA4000 PerkinElmer thermogravimetric analyser using controlled N_2 atmosphere and from room temperature to 800 °C, with heating rate of 10 °C min⁻¹.

3.2.17 LSV studies

LSV was employed to assess the decomposition voltage of the GCCHME. This was done by sweeping the HMEA with a voltage of 1 to 3 V. A sudden increase in the current during the sweep marks its decomposition.

3.2.18 Electrochemical characterizations of GCCHMEs

All electrochemical characterizations, excluding cycle life analysis, were performed using the same Metrohm M204 Multi Autolab and cycle life analysis was conducted using a Battery Analyzer (MTI Corporation, USA). The electrode material used for this experiment was prepared using established procedures [24]. Accordingly, 0.1 g of BPC was dispersed in 1 mL of ethanol and stirred magnetically for 1 hour to form a uniform suspension. Subsequently, 0.83 mL of 3% (w/v) aqueous PVA solution was added dropwise, followed by the gradual addition of 0.83 mL glutaraldehyde solution. Concentrated sulfuric acid was then introduced dropwise as a catalyst. The resulting mixture was sonicated in a water bath for 3 hours and further stirred for 48 hours to obtain a well-dispersed ink. This electrode ink was coated onto the SS current collectors using a paintbrush maintaining a consistent active material loading of approximately 1 mg cm^{-2} . The solid-state EDLCs were assembled using these electrodes and the GCCHMEs as electrolytes-cum-separators. The EDLCs were sealed with Teflon tape and secured with Teflon holders as depicted in Fig. 5(G). Parafilm was wrapped around the holder to prevent water evaporation or leakage. Electrochemical performance was evaluated via CV, GCD, and EIS. CV scans were performed within a potential window of 0–1 V at scan rates ranging from 5 to 100 mVs^{-1} . GCD testing was carried out over the same voltage range at current densities between 0.5 to 5 mAcm^{-2} . EIS measurements were conducted across a frequency range of 1 MHz to 0.1 Hz with a 5 mV rms amplitude [35].

From the Bode plot of phase angle versus frequency, obtained during EIS, the relaxation time constant (τ) was calculated by employing the following equation [36].

$$\tau = \frac{1}{2\pi f^*} \quad (16)$$

Where, f^* is the frequency in Hz corresponds to the phase angle of 45° .

The real and imaginary components (C' and C'') of capacitance obtained from the Bode plot were calculated from the following equations [37].

$$C'(\omega) = \frac{-z''(\omega)}{\omega|z(\omega)|^2} \quad (17)$$

$$C''(\omega) = \frac{z'(\omega)}{\omega|z(\omega)|^2} \quad (18)$$

The cycle life stability of the EDLCs was tested by analysing GCD at the constant current density of 1 mA cm^{-2} , examining their performance till the end of their charge-discharge behaviour.

Areal capacitance C_A (mF cm^{-2}), energy density E ($\mu\text{Wh cm}^{-2}$), as well as power density P (mW cm^{-2}) of EDLCs were mathematically calculated analysing GCD plots employing equations (19), (20), and (21), respectively [38,39].

$$C_A = 2 \times \frac{I \times t_d}{A \times \Delta V} \quad (19)$$

$$E = \frac{1}{2} \times \frac{1000}{3600} C_A \times (\Delta V)^2 \quad (20)$$

$$P = \frac{E}{t_d} \times 3600 \quad (21)$$

Where, I (mA) represents the current density, t_d represents discharge time, A denotes area (cm^2) of electrodes, and ΔV denotes potential window (V).

3.3 Results and discussion

The molecular structure of chitosan [40] is depicted in Fig.3.1 (A), which indicates the presence of primary amine groups ($-\text{NH}_2$). In neutral water, chitosan is poorly soluble because of the lack of electrolytic functional groups [25]. Its solubility can be enhanced in aqueous solutions of weak acids like acetic acid. This occurs through the protonation of the $-\text{NH}_2$ into positively charged ammonium ($-\text{NH}_3^+$) group resulting in the weakening of intermolecular interactions [41]. Concurrently, the dissociation of acetic acid generates free acetate ions (CH_3COO^-), while residual excess acetic acid contributes additional CH_3COO^- and hydrogen ions (H^+) to the mixture. Following the casting and drying of the UCM, the membrane is immersed into the Na_2CO_3 crosslinker solution to initiate gradient ionic crosslinking. In this step, the GCCHME is formed by the electrostatic attraction between the $-\text{NH}_3^+$ group on the chitosan chains and the CO_3^{2-} anions of the crosslinker as illustrated schematically in Fig.3.1 (A). Simultaneously, sodium ions (Na^+) dissociate and remain as free cations in the surrounding medium. In the presence of excess Na_2CO_3 , additional unbound CO_3^{2-} and Na^+ also persist in the system. Altogether, the synthesis reactions give rise to several mobile charge carriers within the GCCHME matrix, viz., H^+ , CH_3COO^- , Na^+ and CO_3^{2-} .

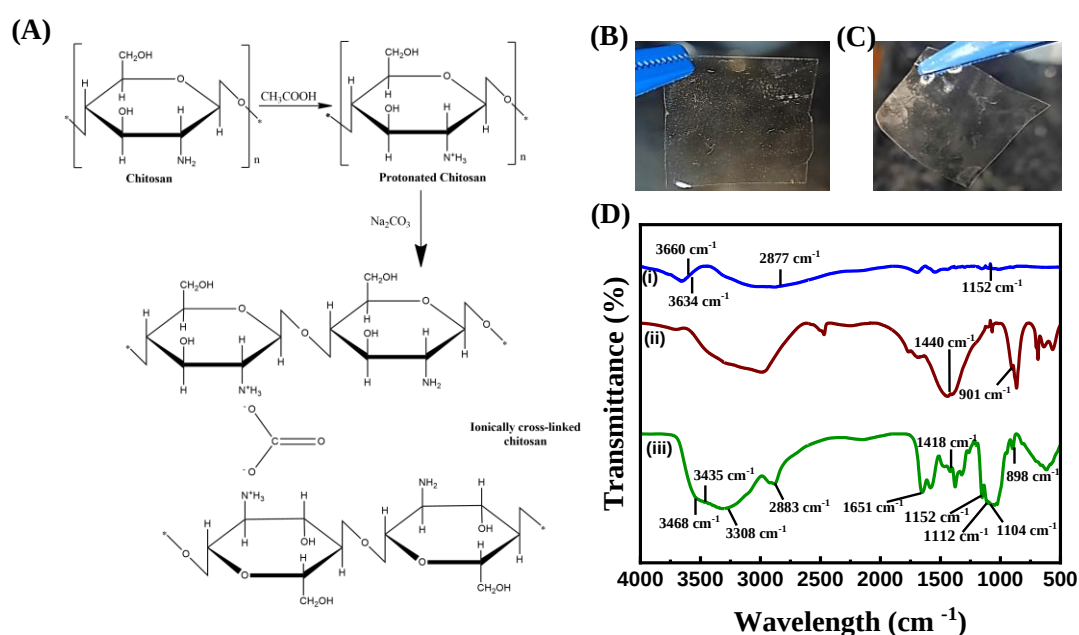


Fig.3.1 (A) Protonation of chitosan in acetic acid and interaction between NH_3^+ and CO_3^{2-} ; (B) Picture of dry GCCHMEs; (C) Picture of wet GCCHME took after 6 months

of dipping in DI water; (D) FTIR plots of Na_2CO_3 powder (i), chitosan flakes (ii), and GCCHME (iii).

Fig.3.1 (B) shows the fully dried GCCHME, while Fig.3.1 (C) shows the membrane immediately after removal from DI water following six months of immersion. The GCCHME appears as a see-through, colourless, and robust flexible thin film with an approximate thickness of 60 μm . As observed in Fig.3.1 (C), the membrane retains its structural integrity and dimensional stability even after prolonged water exposure, indicating effective ionic crosslinking. In contrast, an UCM typically undergoes dimensional changes and dissolves upon immersion in DI water. This physical observation confirms the evidence of crosslinking and the stability of GCCHME.

In order to verify the ionic crosslinking between the chitosan and Na_2CO_3 , FTIR spectra for Na_2CO_3 powder, chitosan powder, and GCCHME was recorded and displayed in Fig.3.1 (D). The FTIR spectra are identical with the isotropically cross-linked chitosan hydrogel membrane electrolyte reported by our group previously [20]. Table 3.1 summarizes the assignment of the characteristic FTIR bands to functional groups corresponds to each material.

Table 3.1: FTIR spectroscopic bands observed for UCM, Na_2CO_3 powder, and GCCHME.

Band position (cm^{-1}) for			Functional groups with their modes of vibration	Compound class/Functional groups
UCM	Na_2CO_3 powder	GCCHME		
3660		3468	O-H Stretching	Hydrogen bonded
3634	-	3435, 3308	N-H Stretching	Primary amine
2877		2883	C-H Stretching	Alkanes
-	1440 901	1418 898 1112, 1104	CO_3^{2-} stretching CO_3^{2-} bending antisymmetric stretching	Carbonate ion

		1651	antisymmetric deformation	Primary amine
1152,	-	1152	C-O-C stretching	Glycosidic bond

In chitosan powder, prominent NH and OH stretching vibrations appear at 3634 and 3600 cm^{-1} , respectively, due to the formation of hydrogen bonding among hydroxyl and amino groups. For GCCHME, a peak shift to 3468 cm^{-1} , along with strong peaks at 3435 and 3308 cm^{-1} , reveals the disruption of these hydrogen bonds, enhancing NH and OH stretching vibrations. Both chitosan powder and GCCHME exhibit CH stretching bands at 2877 and 2883 cm^{-1} , respectively. However, GCCHME shows additional distinct carbonate bands at 1418 and 898 cm^{-1} , confirming the integration of CO_3^{2-} ions through ionic crosslinking [42]. These bands serve as clear indicators of successful carbonate incorporation, which is further substantiated by the strong N-H antisymmetric deformation peak at 1651 cm^{-1} and CO_3^{2-} stretching peaks at 1112 and 1104 cm^{-1} . The interactions between CO_3^{2-} anions and NH_3^+ groups in GCCHME confirm ionic crosslinking, establishing a stable hydrogel structure with enhanced properties [43].

Table 3.2: WU, R_b , and ionic conductivity of GCCHME with variation of crosslinker concentration.

Concentration of Na_2CO_3 (M)	WU (%)	R_b (Ω)	Ionic conductivity (S cm^{-1})
0.5	112	11.09	5.41×10^{-4}
1	106	13.20	4.54×10^{-4}
1.5	94	17.99	3.33×10^{-4}
2	89	18.78	3.19×10^{-4}
2.5	86	20.53	2.92×10^{-4}
3	79	38.82	1.54×10^{-4}

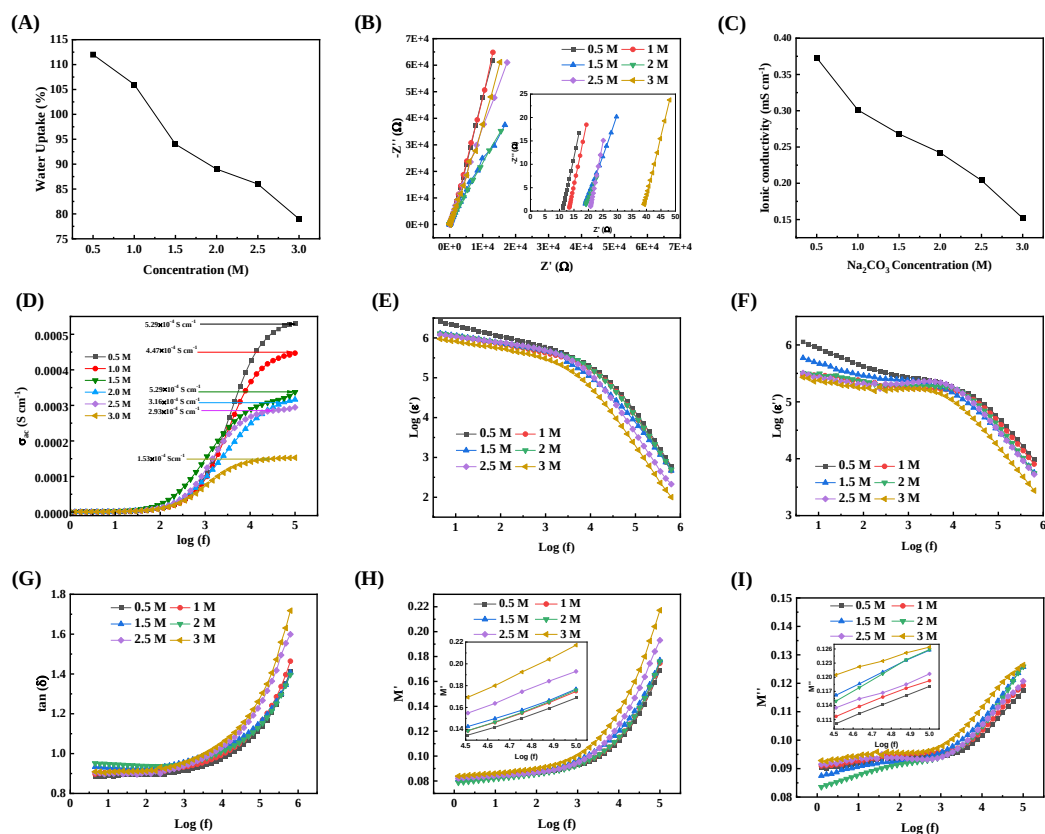


Fig.3.2 (A) WU of GCCHMEs with varying salt concentrations; (B) Nyquist plots obtained during ionic conductivity determination for GCCHMEs with varying crosslinker concentrations (the inserts provide enlarged views of the regions with higher frequencies); (C) Plot of ionic conductivities of GCCHMEs with varying crosslinker concentrations; (D) Plots of frequency dependent AC conductivities obtained for GCCHMEs with different crosslinker concentrations; (E) Variation of frequency dependent dielectric constant; (F) Variation of frequency dependent dielectric loss; (G) Variation of frequency dependent dielectric loss tangent; (H) Variation of frequency dependent real modulus; (I) Variation of frequency dependent imaginary modulus.

The WU of GCCHMEs at varying Na_2CO_3 concentrations, as presented in Fig.3.2 (A) and Table 3.2, exhibits a notable decline with increasing Na_2CO_3 concentration. This decline is attributed to the creation of a denser and more rigid polymer network at higher Na_2CO_3 concentrations, as presented in the Fig.3.3 (A), 3.3 (B), and 3.3 (C). At low Na_2CO_3 concentration viz., 0.5 M, shown in Fig.3.3 (A), relatively a smaller number of $-\text{NH}_3^+$ groups of chitosan chains participate during crosslinking with CO_3^{2-}

ions. The resulting matrix remains loosely connected, with large free volume and more accessible hydrophilic sites, thereby enabling higher water absorption [44]. At the intermediate concentration, viz., 1.5 M, shown in Fig.3.3 (B), a greater number of crosslinking interactions occur, leading to a more compact network that begins to restrict water mobility. As the concentration increased to higher, viz., 3 M, as shown in Fig.3.3 (C), extensive crosslinking produces a highly dense and rigid polymer architecture, significantly limiting the swelling capacity and WU. This structural changes across the concentrations clearly signifies the observed trend in WU behaviour in the GCCHMEs.

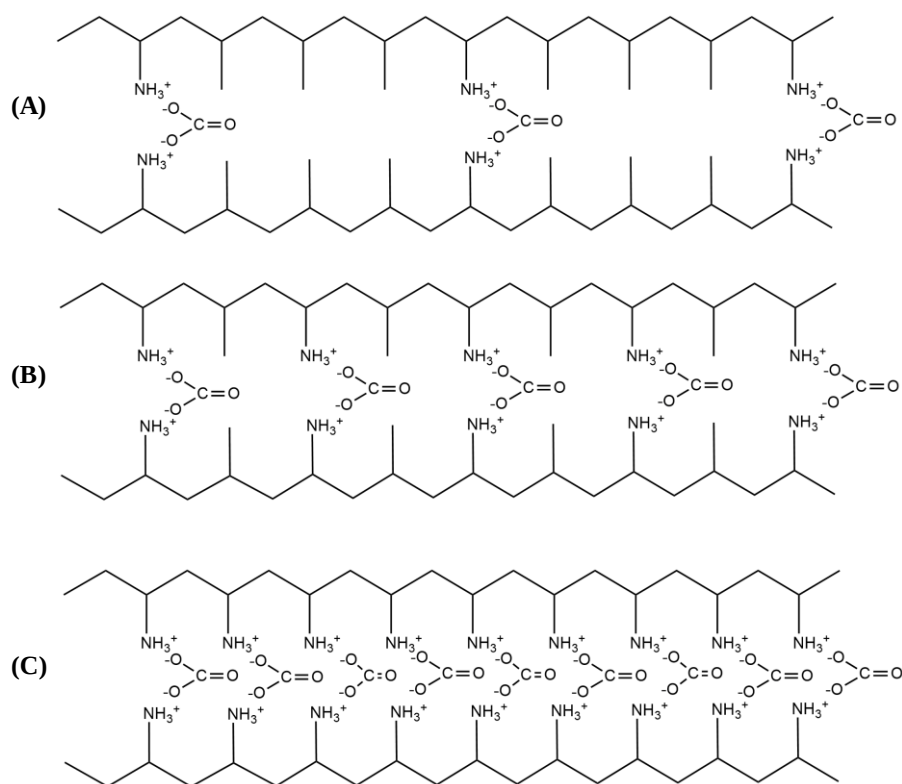


Fig.3.3 Schematic representation of the cross-linked network structures in GCCHMEs prepared with three different Na_2CO_3 concentrations: (A) 0.5 M; (B) 1.5 M; and (C) 3.0 M.

The Nyquist plots of all GCCHMEs, shown in Fig.3.2 (B), display a characteristic spike, with its intersection on the X-axis representing the R_b , as summarized in Table 3.2. Using R_b values in equation (2), the ionic conductivities of the GCCHMEs with varying crosslinker concentrations were evaluated and given in Table 3.2. As given in

Fig.3.2 (C), the results reveal an inverse relationship between Na_2CO_3 concentration and ionic conductivity. At 0.5 M Na_2CO_3 , the highest ionic conductivity of $5.41 \times 10^{-4} \text{ S cm}^{-1}$ was observed, while the lowest conductivity of $1.54 \times 10^{-4} \text{ S cm}^{-1}$ occurred at 3 M. A similar trend was reported by Tran et al. [45] for PVA-KOH membranes cross-linked with N,N-methylenebis(acrylamide). As GCCHME contains multiple mobile ions viz., H^+ , CH_3COO^- , Na^+ , and CO_3^{2-} , it is theoretically expected that increasing the Na_2CO_3 concentration would lead to a maximum number of charge carriers, thereby enhancing the ionic conductivity. However, in this case, the experimental results reveal the opposite trend. The decline in ionic conductivity with increasing Na_2CO_3 concentration can be explained by the observations from the WU study. As the concentration of the crosslinker increased, a higher degree of ionic crosslinking occurred between the $-\text{NH}_3^+$ groups of chitosan and the CO_3^{2-} anions, leading to the formation of a denser and more compact polymer hydrogel network. This structural densification reduces the free volume and limits WU, both of which are essential for facilitating ion mobility. Consequently, despite the increase in mobile ion concentration, the reduction in WU and restricted polymer chain dynamics at higher crosslinker concentrations collectively result in decreased ionic conductivity.

Fig.3.2 (D) depicts the AC conductivity plots of GCCHMEs with varying Na_2CO_3 concentrations. The conductivity plots exhibit two distinct regions: a frequency-dispersive region at lower frequencies and a plateau region at higher frequencies. The dispersive region is attributed to the accumulation of ions at the electrode/electrolyte interface, where the electric field is insufficient for effective ion mobilization [46]. As the frequency was increased, ion mobility improved, resulting in higher conductivity. At higher frequencies, the plateau region reflects frequency-independent conductivity due to reduced ion polarization and successful migration of ions from one available site to another, which contributes overall conductivity [46]. The GCCHME-0.5M exhibited the highest value of conductivity, indicating optimal ion mobility. In contrast, higher crosslinker concentrations created a denser polymer matrix, restricting ion transport and reducing conductivity. These AC conductivity values also align well with (DC conductivity) the ionic conductivity values determined from the R_b of GCCHMEs.

Fig.3.2 (E) and 3.2 (F) display the frequency-dependent characteristics of ϵ' and ϵ'' for GCCHMEs with varying Na_2CO_3 concentrations at room temperature. The parameter ϵ' signifies the storage ability of GCCHMEs and ϵ'' indicates the energy lost due to the movement of ions in response to high-frequency polarity changes in the electric field [47]. At low frequencies, both ϵ' and ϵ'' exhibit high values due to interfacial polarization and ion accumulation at the electrode-electrolyte interfaces. As frequency increases, these values decline because the dipoles and mobile ions can no longer follow the rapidly oscillating electric field, leading to diminished polarization effects [47–49]. Among the tested membranes, the GCCHME containing 0.5M Na_2CO_3 exhibits the highest ϵ' value. The reasoning behind this observation is grounded in equations (22) and (23) [47] as elaborated below.

$$n_i = n_0 \exp\left(-\frac{U}{\epsilon' k_B T}\right) \quad (22)$$

$$\sigma = \sum q n_i \mu_i \quad (23)$$

Equation (22) shows that an increase in ϵ' reduces the ion-pair dissociation energy (U), leading to a greater number of free charge carriers (n_i), while Equation (23) relates n_i and ionic mobility (μ_i) to ionic conductivity (σ). Thus, a higher dielectric constant promotes enhanced ionic conductivity by increasing the charge carrier density. Coulomb's law supports this interpretation. According to this law the force F between two ions with charges q_1 and q_2 is inversely proportional to the dielectric constant, i.e., $F = \frac{q_1 q_2}{4\pi\epsilon' r^2}$ [50]. Thus, a higher ϵ' reduces the electrostatic attraction between oppositely charged ions, facilitating their dissociation and mobility, which in turn enhances ionic conductivity [51]. The dielectric loss tangent ($\tan \delta = \epsilon''/\epsilon'$), plotted in Fig.3.2 (G), increases with frequency and crosslinker concentration. This behaviour is attributed to the presence of free ions contributing to dipolar relaxation processes [49]. Fig.3.2 (H) and 3.2 (I) present the frequency dependence of the real (M') and imaginary (M'') parts of the dielectric modulus. In the low-frequency region, all membranes show a pronounced tail in M' , indicative of electrode polarization and dominant ionic motion. As frequency increases, M' rises sharply, marking the suppression of

interfacial polarization and the onset of bulk relaxation [52]. Among the membranes, GCCHME prepared using 3M Na₂CO₃ shows the highest M' values, suggesting a denser, more rigid matrix that restricts ion mobility. In contrast, GCCHME prepared using 0.5M Na₂CO₃ exhibits the lowest M', consistent with its enhanced ionic conductivity and more open network structure. Similarly, M'' shifts toward higher frequencies with increased crosslinker concentration, indicating shorter relaxation times due to restricted ionic mobility [53]. The low modulus values observed for GCCHME prepared using 0.5M Na₂CO₃ affirm its superior ion transport behaviour. These results collectively highlight the critical influence of crosslinker concentration on dielectric relaxation and conductivity, underscoring the need for optimal crosslinker content to achieve high-performance electrochemical behaviour.

The GCCHME prepared with 0.5M Na₂CO₃ exhibited superior properties, including the lowest R_b, highest ionic conductivity, highest dielectric constant, and lowest dielectric modulus. In contrast, the GCCHME prepared with 3M Na₂CO₃ demonstrated the highest R_b, lowest ionic conductivity, lowest dielectric constant, and highest dielectric modulus. These distinct differences in electrical and dielectric properties led to the selection of these two membranes for further detailed comparative analysis. For clarity, the membrane with 0.5M Na₂CO₃ is designated as GCCHME-0.5M, while the membrane with 3M Na₂CO₃ is designated as GCCHME-3M.

The DR refers to the proportion of polymer in a membrane sample that dissolves in a specific solvent within a fixed time frame, relative to the total polymer content in the sample [24]. In this study, DR was used as an indirect method to evaluate the extent of crosslinking in the membranes. The rationale is that the solubility of chitosan decreased upon crosslinking with Na₂CO₃, reducing its dissolution in water. The DR values for GCCHMEs with 0.5 M and 3 M crosslinker concentrations were measured to assess the extent of crosslinking and its impact on membrane stability. The variation of DR with time of boiling is showed in Fig.3.4 (A). The DR values of GCCHME-0.5M and GCCHME-3M were 16.74% and 11.17%, respectively. With increasing Na₂CO₃ concentration, more and more segments of chitosan chains become involved in chitosan, which leads to the formation of a highly interconnected and rigid polymer

network. As a result, the membrane becomes more resistant to solubility, and the extent of dissolution is significantly reduced at higher Na_2CO_3 concentration.

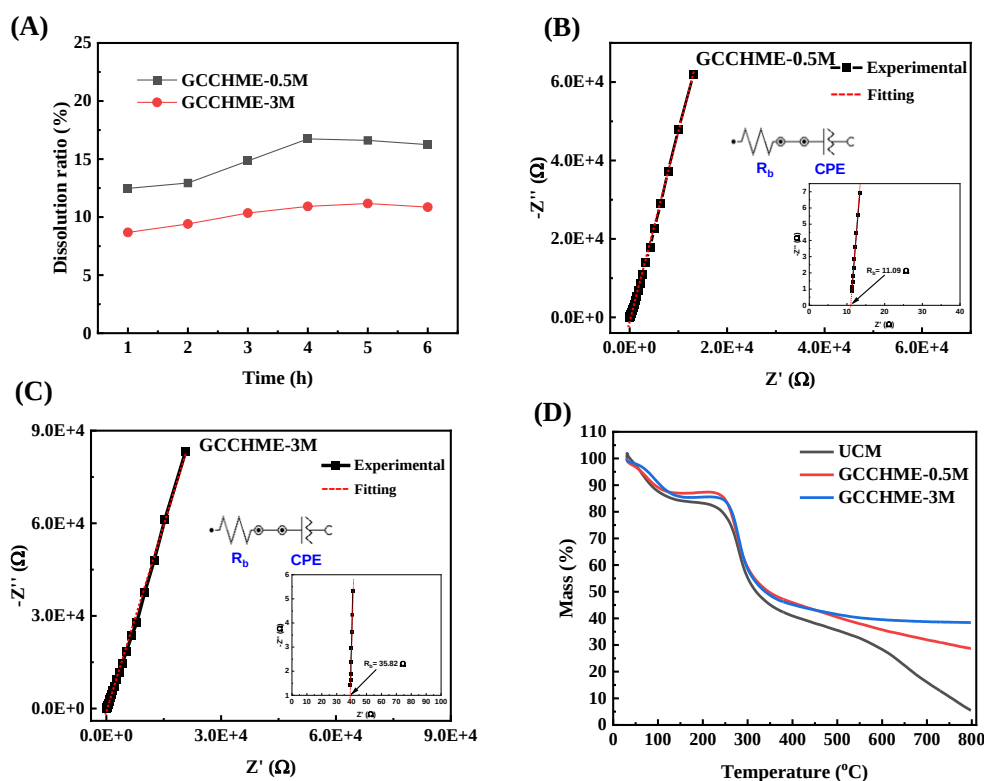


Fig.3.4 (A) Plots of DR vs boiling time for GCCHME-0.5M and GCCHME-3M; (B) Nyquist plot, its fitting, and the related electric equivalent circuit (shown in the inset) for the GCCHME-0.5M; (C) Nyquist plot, its fitting, and the related electric equivalent circuit (shown in the inset) for the GCCHME-3M; (D) TGA curves of UCM, GCCHME-0.5M and GCCHME-3M.

During ionic conductivity investigations, since only one spike appeared in the Nyquist plots of both the GCCHME-0.5M and GCCHME-3M, the Electric Equivalent Circuits (EECs) were modelled on the combined influence of their R_s and the CPE as presented in Fig.3.4 (B) and 3.4 (C), respectively [32]. The CPE values of GCCHME-0.5 and GCCHME-3M derived from the Nyquist plots were found to be 1.28×10^{-5} and 5.79×10^{-6} F, respectively. These parameters highlight the capacitive behaviour of GCCHMEs and their ability to store charge at the electrode-electrolyte interface. Table

3.3 presents the calculated diffusion coefficient (D), mobility (μ), and number density (n) for both the GCCHMEs.

Table 3.3: Summarization of ion transport parameters of GCCHME-0.5M and GCCHME-3M.

Electrolyte	Diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)	Ion mobility ($\text{m}^2 \text{V}^{-1} \text{s}^{-1}$)	Ion number density (m^{-3})
GCCHME-0.5M	1.11×10^{-9}	4.30×10^{-8}	1.65×10^{22}
GCCHME-3M	1.50×10^{-10}	5.82×10^{-9}	7.85×10^{22}

The value of D indicates a moderate rate of ion diffusion, which is typical for polymer-based electrolytes where the crosslinking impacts the diffusion pathways [54]. For GCCHME-0.5M, the calculated D value is significantly greater than GCCHME-3M. This difference suggests that the lower crosslinker concentration in GCCHME-0.5M results in a less dense network structure, enabling ions to diffuse more freely. The μ reflects the ion mobility, signifying that ions move effectively when subjected to an electric field. It is directly related to the ease with which ions migrate within the material. GCCHME-0.5M exhibits higher ion mobility than the GCCHME-3M. These findings highlight the structural reinforcement imparted by Na_2CO_3 crosslinker [55]. The evaluated n values for GCCHME-0.5M and GCCHME-3M is comparable to those reported for other polymer-based electrolyte membranes [32,56]. The values signify a substantial presence of mobile ions, which plays a key role in sustaining high ionic conductivity. However, GCCHME-3M, despite having a higher n value, exhibits lower ionic conductivity. This suggests that not all ions present within the matrix contribute to ionic conductivity, likely due to increased compactness and decreased ion transport pathways within the hydrogel matrix when prepared with a higher concentration of Na_2CO_3 .

TGA was performed to evaluate the thermal stability of the UCM, GCCHME-0.5M and GCCHME-3M and plotted in Fig.3.4 (D). All the membrane samples exhibited an early weight loss around 20 °C, due to the evaporation of physically adsorbed and

bound water [57]. A major weight loss occurring around 230 °C corresponded to the thermal degradation of the chitosan polymer backbone, primarily due to the cleavage of glycosidic linkages and depolymerization of the polysaccharide chains [58]. At this temperature, GCCHME-0.5M retained about 87 % of its initial weight, GCCHME-3M retained about 84 %, and UCM retained only 79 %. The higher weight retention in the cross-linked membranes can be because of the formation of ionic interactions between the chitosan chains and carbonate ions, which restricts molecular motion and delays the onset of thermal decomposition. Interestingly, GCCHME-0.5M showed slightly higher retention than GCCHME-3M at this point, possibly due to greater water retention or less densification of the polymer matrix at lower crosslinking levels, which can temporarily buffer heat-induced decomposition. At 350 °C, the cross-linked membranes, both GCCHME-0.5M and GCCHME-3M, retained approximately ~50% of their original mass, whereas UCM retained only ~45%, further demonstrating the stabilizing effect of ionic crosslinking. Beyond this, GCCHME-3M exhibited superior thermal resilience, retaining ~40% of its mass at 800 °C, compared to ~30% for GCCHME-0.5M and only ~5% for UCM. These results confirm that ionic crosslinking with significantly enhances the thermal stability of chitosan membranes [57,59,60]. The increased resistance to thermal decomposition with higher crosslinker concentration is likely due to the denser ionic network and stronger intermolecular interactions, which hinder thermal degradation pathways. Such improved thermal robustness is a desirable attribute for membrane electrolytes in electrochemical devices, where long-term operational durability under varying thermal conditions is critical.

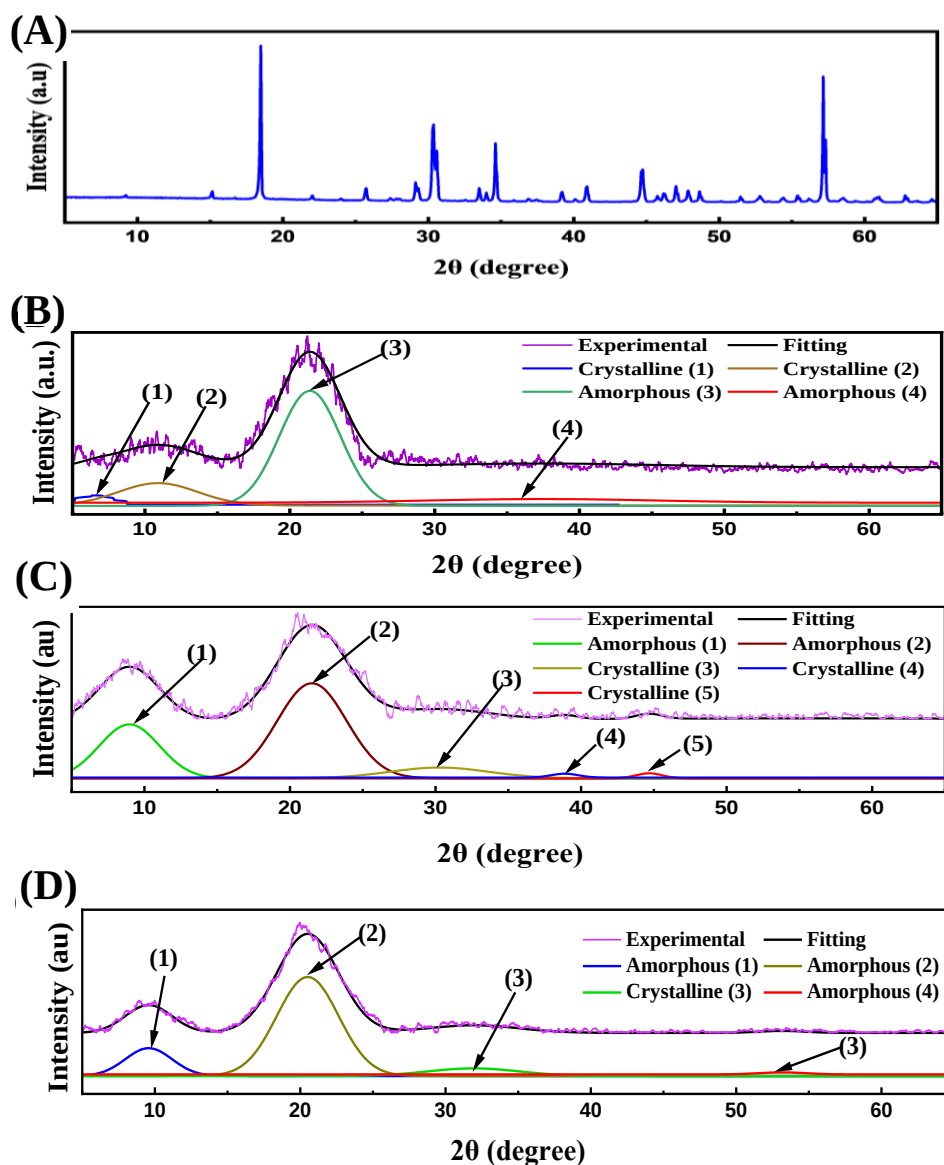


Fig.3.5 (A) XRD patterns of the powder Na_2CO_3 ; (B) Deconvoluted XRD plots of UCM; (C) Deconvoluted XRD plots of GCCHME-0.5M; (D) Deconvoluted XRD plots of GCCHME-3M.

The XRD pattern of pure Na_2CO_3 , and the deconvoluted XRD patterns of UCM, GCCHME-0.5M, and GCCHME-3M are shown in Fig.3.5 (E), 3.5 (F), 3.5 (G) and 3.5 (H), respectively. From Fig.3.5 (E), it is seen that the XRD pattern of pure Na_2CO_3 showed numerous distinct and sharp peaks, reflecting a highly ordered crystalline arrangement. Deconvoluted XRD profile of UCM, revealing two distinct crystalline

bands at 2θ values 6° and 11° (1 and 2), along with two broad amorphous bands at 2θ values 21° and 38° (3 and 4). Deconvoluted XRD profiles of GCCHME-0.5M and GCCHME-3M also showed two broad amorphous bands (1 and 2) at 2θ values of 9° and 20° , respectively. The crystallinity of UCM is found to be 19.50 %. To the contrary, the crystallinity of GCCHME-0.5M and GCCHME-3M are found to be 11.67 and 9.57 %, respectively. These quantities of crystallinity denote the semi-crystalline nature of all the three membranes. The observed decrease in crystallinity of the GCCHMEs is likely attributed to the interference of the crosslinker with the ordered crystalline regions, leading to the formation of a more amorphous structures. Notably, the distinct diffraction peaks of Na_2CO_3 powder are absent in the spectra of GCCHMEs, indicating that Na_2CO_3 has fully dissolved within the chitosan hydrogel network. The crosslinking interaction between Na_2CO_3 and chitosan introduce new bonds, which in terms disrupt the native intramolecular and intermolecular hydrogen bonding within the chitosan [61].

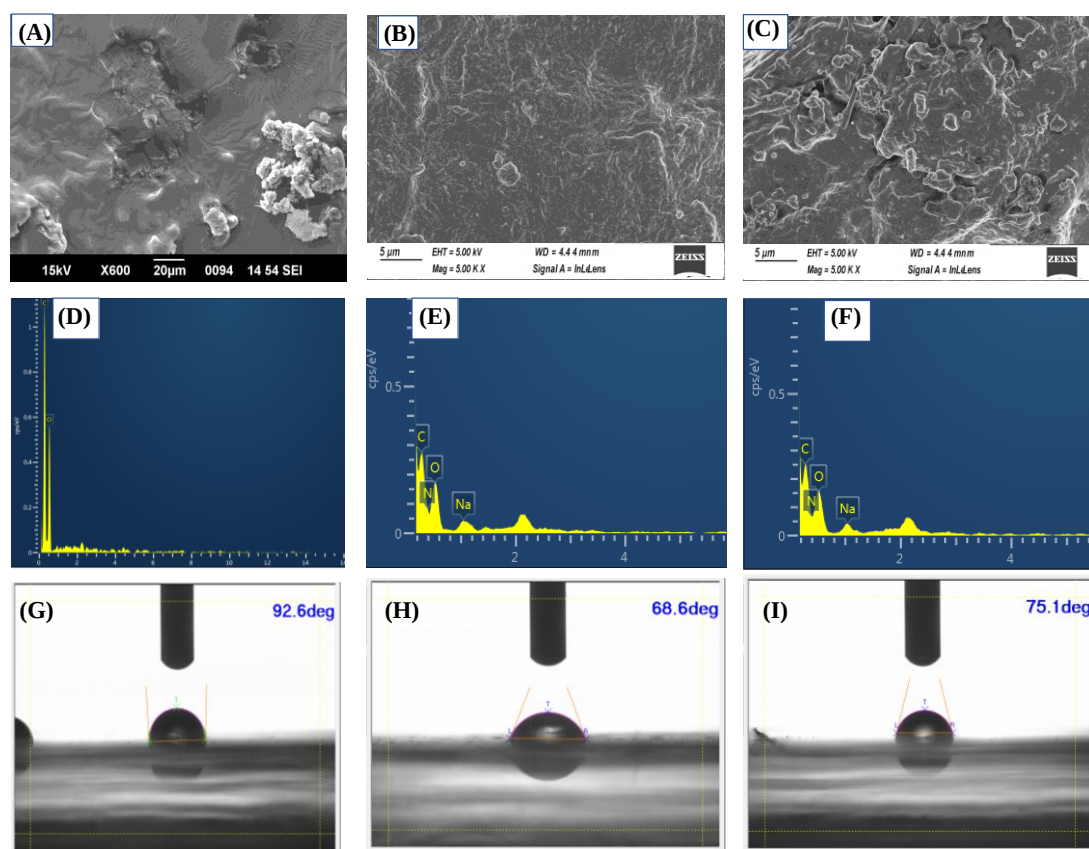


Fig.3.6 (A) FE-SEM image of the surface of UCM; (B) FE-SEM image of the surface of GCCHME-0.5M; (C) FE-SEM image of the surface of GCCHME-3M; (D) EDX spectrum of UC; (E) EDX spectrum of GCCHME-0.5M; (F) EDX spectrum of GCCHME-3M; (G) Contact angle of UCM; (H) Contact angle of GCCHME-0.5M; (I) Contact angle of GCCHME-3M.

As shown in Fig.3.6 (A), the surface of the UCM exhibited a rough and heterogeneous morphology with noticeable granularity, likely due to the irregular distribution of chitosan chains and the presence of undissolved chitosan [62]. In contrast, GCCHME-0.5M displayed a comparatively smoother and more uniform surface as seen in Fig.3.6 (B), indicating enhanced structural ordering due to ionic crosslinking between chitosan and carbonate ions [25]. The GCCHME-3M showed moderate smoothness with visible undulations and irregular textures as seen in Fig.3.6 (C), suggesting denser crosslinking that may have induced slight phase separation or localized stress regions during drying. EDX spectra given in Fig.3.6 (D-F) showed the presence of carbon (C), oxygen (O), and nitrogen (N) in all samples, confirming the chitosan backbone. Additionally, sodium (Na) was detected in the cross-linked membranes validating the incorporation of Na_2CO_3 . These results confirm that gradient ionic crosslinking significantly influences both surface morphology and elemental distribution, with implications for membrane homogeneity and electrochemical performance [63].

Contact angle is a crucial parameter for evaluating the surface wettability of membrane materials, directly influencing electrolyte uptake and ion transport efficiency. Fig.3.6 (G), (H), and (I) illustrate the contact angle values observed for the UCM, GCCHME-0.5M, and GCCHME-3M, respectively. The UCM exhibited a relatively high contact angle of 92.6° , signifying a moderately hydrophobic surface. However, this relatively high angle does not reflect true hydrophobicity, as the UCM rapidly dissolved or swelled upon contact with DI water. This behaviour is because of the absence of any crosslinking, which results in lower intermolecular attractions and poor mechanical stability in water. In contrast, the GCCHME-0.5M exhibited a significantly lower contact angle of 68.6° , indicating enhanced hydrophilicity and a structurally stable surface. The crosslinking likely improved network cohesion while exposing polar

functional groups, facilitating water affinity without compromising integrity [64]. The GCCHME-3M had a contact angle of 75.1° , slightly higher than GCCHME-0.5M, possibly due to excessive crosslinking leading to partial surface densification, which marginally hindered its wettability.

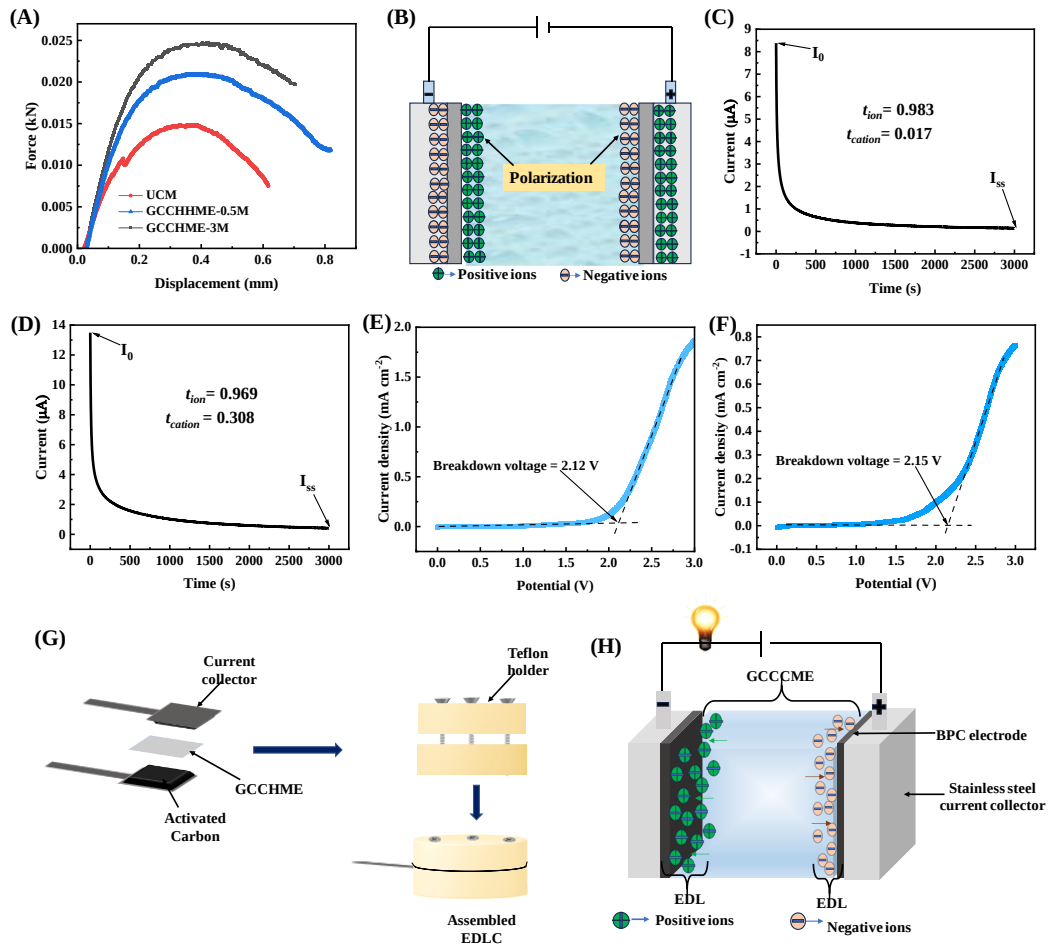


Fig.3.7 (A) Force versus displacement plots of UCM, GCCHME-0.5M and GCCHME-3M; (B) Schematic of DC polarization phenomena; (C) DC polarization curve of GCCHME-0.5M; (D) DC polarization curve of GCCHME-3M; (E) LSV curve of GCCHME-0.5M; (F) LSV curve of GCCHME-3M; (G) Schematic representation of fabrication of EDLC; (H) Schematic representation of working principle of EDLC.

Table 3.4: Summary of mechanical strength data.

Material	Tensile strength (MPa)	Elongation (%)	Young's modulus (MPa)
UCM	30.51	6.48	470.84
GCCHME-0.5M	41.22	8.53	483.23
GCCHME-3M	44.34	7.71	575.09

Fig.3.7 (A) presents the force-displacement curves derived from mechanical test of the UCM, GCCHME-0.5M and GCCHME-3M, while Table 3.4 provides a summary of their mechanical property data. The results clearly demonstrate that the GCCHMEs possess significantly enhanced mechanical strength in comparison to the UCM. This enhancement suggests that the gradient crosslinking successfully reinforced the hydrogel membrane structure. The UCM exhibited the lowest elongation percentage, which suggests that it is more brittle compared to the cross-linked membranes. GCCHME-0.5M shows the highest elongation at 8.53%, indicating enhanced flexibility, while GCCHME-3M has a slightly reduced elongation of 7.71%. Comparable findings were reported in research on chitosan-based membranes, where crosslinking led to enhanced mechanical strength [65–67]. Moreover, Young's modulus of GCCHMEs are found to be higher than that of UCM. This implies that both GCCHMEs have greater stiffness compared to the UCM. These findings suggest that due to their enhanced flexibility, tensile strength and stiffness, the GCCHMEs are more suitable candidates as electrolyte membranes in robust energy storage devices.

Fig.3.7 (B) shows the DC polarization technique employed to determine the ion transference number in GCCHMEs. Upon applying a constant DC voltage across the cell, an electric field is established, driving the migration of ions within the GCCHMEs. In response, cations move toward the negatively charged electrode, while anions migrate toward the positively charged electrode, generating an ionic flux. Since the SS electrodes are blocking in nature, they prevent charge transfer to the external circuit, meaning that the ions cannot cross the electrode-electrolyte interface. Instead, as migration progresses, a finite number of ions accumulate at the interfaces, becoming localized near the electrodes. This accumulation leads to the formation of a hetero-charge layer, resulting in what is known as electrode or interfacial polarization. The

build-up of these trapped ions establishes a concentration gradient within the electrolyte, effectively increasing its internal resistance. Initially, the applied voltage results in a high current due to the rapid ion migration. However, as the polarization layer develops and restricts further movement, the current gradually decreases. Over time, the system reaches a steady state which corresponds to the current predominantly arising from the electronic species in the system. By analysing the ratio of the steady-state current to the initial current, the ion transference number can be determined. This provides crucial insights into the ion transport characteristics of GCCHMEs, particularly regarding the relative contributions of different ionic species to overall charge conduction. Thus, the DC polarization technique serves as a valuable tool for assessing the efficiency of ionic transport in electrolytes.

The transference number measurement results for GCCHME-0.5M and GCCHME-3M, shown in Fig.3.7 (C) and 3.7 (D), clearly highlight differences in how ions move through each membrane. GCCHME-0.5M exhibited a high t_{ion} of 0.983. This indicates that GCCHME-0.5M allows more efficient ionic transport, with a greater proportion of current carried by mobile ions. The very low t_{cation} of 0.017 for GCCHME-0.5M suggests that the membrane predominantly supports anionic conduction, likely due to its relatively looser ionic network, which facilitates greater mobility of negatively charged species. In contrast, GCCHME-3M, with its denser cross-linked structure resulting from the higher Na_2CO_3 concentration, shows a slight reduction in t_{ion} of 0.969. However, it demonstrates a much higher t_{cation} of 0.308, indicating a significantly increased role of cations in charge transport. This shift suggests that the denser membrane matrix of GCCHME-3M imposes greater restrictions on anion mobility while favouring cation movement, possibly due to enhanced electrostatic interactions and tighter network formation [68]. These results highlight how crosslinker concentration modulates the ionic selectivity and transport dynamics within the membrane, thereby influencing its electrochemical performance.

The LSV profiles of GCCHME-0.5M and GCCHME-3M, presented in Fig.3.7 (E) and 3.7 (F), respectively, reveal that both membranes exhibit excellent electrochemical stability. Specifically, no significant rise in current is observed up to 2.12 V for

GCCHME-0.5M and 2.15 V for GCCHME-3M, indicating the absence of electrolyte decomposition within this range. The gradual increase in current beyond these voltages marks the onset of electrochemical breakdown. These values are well above the commonly required minimum stability window of ~ 1.0 V for electrochemical devices, confirming the suitability of both membranes for high-voltage energy storage applications [69].

EDLCs employing GCCHME-0.5M and GCCHME-3M are designated as EDLC-0.5M and EDLC-3M, respectively. The schematic representation for the fabrication of the EDLCs as a two-electrode system with GCCHMEs is shown in Fig.3.7 (G). This configuration utilizes the GCCHMEs as both the electrolyte and separator, effectively preventing electrical contact between the electrodes while allowing for efficient ionic conduction. Upon applying a potential across the electrodes, ions within the GCCHMEs migrate toward the electrodes, forming electric double layers (EDLs) at the electrode-electrolyte interfaces, as indicated in Fig.3.7 (H). These EDLs consist of a layer of oppositely charged ions from the GCCHMEs, balancing the charge on the electrode surfaces. The ionic crosslinking within the GCCHMEs enhances their ability to maintain a stable charge separation at the electrode interface, resulting in high capacitance. This configuration allows for the electrostatic storage of energy within the capacitor, which can be discharged as an electric current when needed.

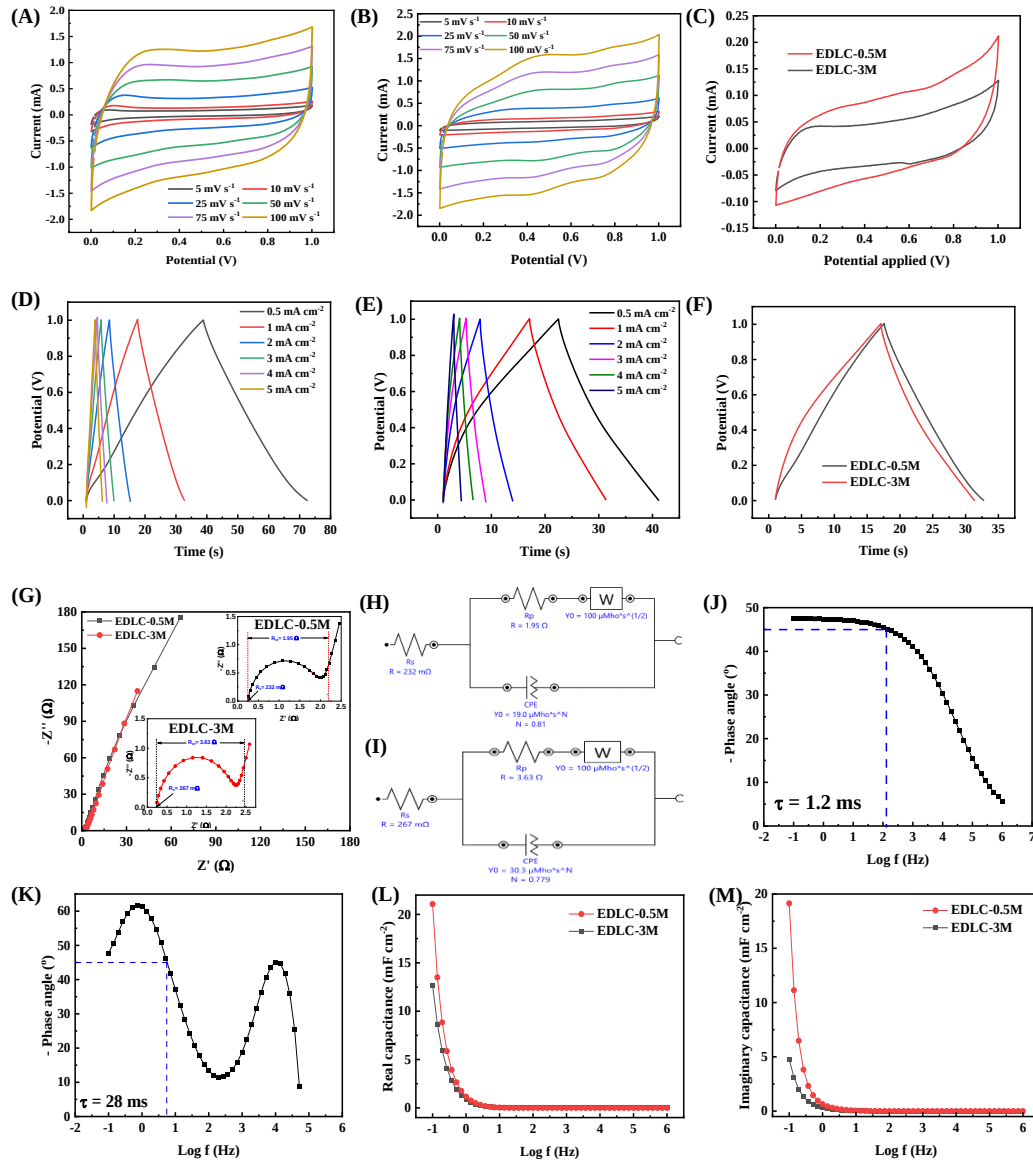


Fig.3.8 (A) CV plots of EDLC-0.5M with different scan rate; (B) CV plots of EDLC-3M with different scan rate; (C) Comparison of CV plots of EDLC-0.5M and EDLC-3M at 5 mVs⁻¹; (D) GCD plots of EDLC-0.5M with different current densities; (E) GCD plots of EDLC-3M with different current densities; (F) Comparison of GCD plots of EDLC-0.5M and EDLC-3M at 1 mA cm⁻²; (G) Nyquist plots of EDLC-0.5M and EDLC-3M (the inserts at the top and bottom shows expanded view of high-frequency end of Nyquist plot of EDLC-0.5M and EDLC-3M, respectively); (H) Equivalent circuit diagram of EDLC-0.5M; (I) Equivalent circuit diagram of EDLC-3M; (J) Bode plot of phase angle curve of EDLC-0.5M; (K) Bode plot of phase angle curve of EDLC-3M; (L) Plots of real part of capacitance versus frequency for EDLC-

0.5M and EDLC-3M; (M) Plots of imaginary part of capacitance versus frequency for EDLC-0.5M and EDLC-3M.

The CVs of EDLC-0.5M and EDLC-3M are shown in Fig.3.8 (A) and 3.8 (B). The CV curves at different scan rates exhibited a quasi-rectangular shape, indicating EDL capacitive behaviour. At lower scan rates, the CV curves exhibit symmetrical shapes, signifying effective ion transport and high charge storage capacity [70]. As the scan rate increases, slight deviations from the quasi-rectangular shape emerges, which can be attributed to diffusion-controlled ion transport [71]. It has been reported that both the carbon porosity of the carbon material and its internal resistance play significant roles to influence current-voltage relationship [72]. However, the overall capacitive nature of the device remains intact, indicating that both the EDLCs maintain robust performance even under rapid charging conditions.

The comparison of the CVs at 0.5 mV s^{-1} for both the devices are shown in Fig.3.8 (C). The CVs clearly demonstrate the superior performance of EDLC-0.5M compared to EDLC-3M. EDLC-0.5M exhibited significantly better charge–discharge behaviour across all scan rates, indicating higher capacitance and more efficient charge storage capability. This is primarily due to the superior ionic conductivity of the GCCHME-0.5M, which facilitates better ion mobility and promotes rapid ion mobility at the electrode-electrolyte interface. In contrast, EDLC-3M exhibits much lower current response due to the limited ion transport caused by the denser cross-linked structure of the GCCHME-3M.

The GCD plots recorded at different current densities are given in Fig.3.8 (D) and 3.8 (E) for EDLC-0.5M and EDLC-3M, respectively. The GCD plots have nearly triangular shapes with negligible IR drops. At lower current densities, both the devices exhibited longer discharge times and hence higher capacitances, indicating better energy storage efficiency. However, as the current density increased, the discharge time decreased due to the limited interaction time between ions and the electrode surface, which reduced the overall capacitance. EDLC-0.5M exhibited nearly triangular charge-discharge profiles, indicative of highly reversible processes. The

minimal voltage drops, even at higher current densities, confirms the low internal resistance of the device, which is essential for maintaining superior performance in practical applications. The behaviour of EDLC-3M follows a similar trend, but it has shorter discharge times compared to EDLC-0.5M. This indicates that the EDLC-3M device stores less energy, which may be attributed to the structural and ionic differences in the membrane resulting from the higher crosslinker concentration. Fig.3.8 (F) provides a direct comparison of the GCD profiles of both EDLCs at 1 mA cm⁻². EDLC-0.5M exhibited a longer discharge duration than that of EDLC-3M, highlighting its superior energy storage capacity at this current density. This can be due to the enhanced performance linked to its optimized crosslinking structure in GCCHME-0.5M, providing better ion mobility and interaction with the electrodes.

Table 3.5: GCD performance data at varying current densities for EDLC-0.5M and EDLC-3M.

Current density (mA cm ⁻²)	EDLC-0.5M			EDLC-3M		
	Areal capacitance (mF cm ⁻²)	Coulombic efficiency (%)	IR drop (mV)	Areal capacitance (mF cm ⁻²)	Coulombic efficiency (%)	IR drop (mV)
0.5	33.6	89	9	29.76	87	19
1	30.2	91	16	28.4	89	27
2	26.8	90	39	24	87	59
3	24.6	86	57	21.6	84	82
4	24	84	62	19.2	77	109
5	22	79	94	18	74	137

The GCD performance data at varying current densities are presented in Table 3.5. At 0.5 mA cm⁻², EDLC-0.5M shows an areal capacitance of 33.6 mF cm⁻² and a Coulombic efficiency of 89%, while EDLC-3M has a lower areal capacitance of 29.76 mF cm⁻² and a Coulombic efficiency of 87%. As the current density increased, the capacitance decreased for both devices. However, EDLC-0.5M consistently demonstrated higher values, retaining better performance. At lower current densities, electrolyte ions have more time to penetrate the internal structure of the electrode

material, allowing for more effective diffusion. This enhanced ion accessibility enables a greater portion of the carbon material to utilize in EDL formation, thereby improving the supercapacitor performance [73]. At higher current densities, the limited interaction time restricts ion access primarily to the exterior of electrode, thereby reducing overall accessibility [74]. Additionally, EDLC-0.5M maintained lower IR drop values as compared to EDLC-3M, which further supports its better charge transport properties. The more pronounced voltage drops and less symmetrical charge-discharge curves reflect increased internal resistance and lower ionic conductivity, attributed to the denser cross-linked network of the GCCHME-3M.

The charge transport process occurring in the EDLCs has been investigated by EIS. The Nyquist plots obtained from EIS are given in Fig.3.8 (G) shows a semi-circle in the high frequency region and a straight line in the low frequency region. The insets in Fig.3.8 (G) depict expanded views of the semi-circles in the high frequency regions. The Nyquist plots for EDLC-0.5M and EDLC-3M exhibited a distinct semi-circular feature in the high-frequency region followed by a linear region in the low-frequency region, which is indicative of the capacitive and resistive behaviour of the systems. The EECs for EDLC-0.5M and EDLC-3M are shown in Fig.3.8 (H) and 3.8 (I). The EIS fitting approach to obtain the EECs employs a non-linear least square algorithm to optimize the match between the experimental measurement and theoretical model. This is achieved by minimizing the difference in observed and resulted impedance values, as reflected by the lowest value of chi-squared (χ^2) [75]. The χ^2 value serves as a statistical measure of how accurately the EEC model represents the impedance data. A lower the χ^2 value indicates a better fit, signifying the effectiveness of the model in describing the electrochemical behaviour of the hydrogel electrolyte [76]. The fitted parameters comprised R_s , R_{ct} , a CPE, and W. In the Nyquist plot, R_s is identified as the distance from the origin to the point where the intersects the real axis. The semicircle diameter obtained in the higher-frequency region corresponds to the R_{ct} [77,78]. R_s reflects the resistance of the bulk electrolyte, which is linked to ion movement within the electrolyte. A reduction in ion mobility or an increase in electrolyte thickness leads to rise in R_s . The R_s can be divided into electronic and the ionic resistances. Electronic resistance is attributed to the intrinsic resistance of the electrode material and contact

resistance of current collector and the active material. In contrast, ionic resistance emerges from the resistance to the transport of ions in the electrolyte and through the pores of the electrodes [79]. The R_{ct} signifies the resistance at the interface between the electrode and electrolyte. The CPE is employed to represent the non-ideal capacitive behaviour of the EDLCs, while W characterizes the ideal capacitive behaviour signified by the linear part of the lower frequency [80]. EDLC-0.5M shows a significantly smaller semicircle compared to EDLC-3M. The R_s value of EDLC-0.5M has been found to be 232 m Ω , which is smaller than that of 267 m Ω obtained for EDLC-3M. This indicates high ionic conductivity within the bulk polymer hydrogel electrolyte in EDLC-0.5M, ensuring efficient ion mobility and minimizing resistive losses across the system. The R_{ct} for EDLC-0.5M of 1.95 Ω , is also found to be smaller than that of 3.63 Ω for EDLC-3M, which also reflects the efficiency of charge-transfer at the interface of electrode and electrolyte, a key factor in sustaining high power density and rapid response in supercapacitor.

An important parameter in EIS analysis is the relaxation time constant (τ), which is determined through a detailed analysis of how the real and imaginary components of capacitance vary with frequency. The τ delineates the threshold at which an EDLC shifts from exhibiting capacitive characteristics to resistive ones [81]. Fig.3.8 (J) and 3.8 (K) are Bode plots of the frequency dependence phase angle obtained for EDLC-0.5M and EDLC-3M, respectively. It is seen that both the EDLCs exhibit nearly identical phase angle of 60°, which indicates their capacitive nature [82]. The τ values for EDLC-0.5M and EDLC-3M are 1.2 and 28 ms, respectively. As the EDLC-0.5M exhibited lower τ value, it is capable of delivering its stored energy more rapidly than the EDLC-3M.

Fig.3.8 (L) Displays the Bode plots corresponding to real components of capacitance (C') obtained from EIS for EDLC-0.5M and EDLC-3M. The Bode plots depicting the imaginary components of capacitance (C'') for EDLC-0.5M and EDLC-3M are presented in Fig.3.8 (M). The sharp increase in C' and C'' in low frequency region indicates the relaxation-type behaviour of both EDLCs. In the lower frequency region, the C' values for both the EDLCs exhibited a pronounced frequency dependence, a

typical behaviour seen in capacitors utilizing porous carbon materials [37]. It can be seen that the C' and C'' of EDLC-0.5M at the low frequency are higher than that of EDLC-3M. This means that EDLC-0.5M displays superior performance over EDLC-3M. For both EDLCs, C' calculated at minimum closely match the result derived from GCD.

To investigate real-life applicability, both the EDLCs were subjected to repeated GCD cycling at 1 mA cm^{-2} . After an interval of 1000 cycles, the areal capacitances, Coulombic efficiencies, resistances viz., R_s , R_{ct} , ESR, and IR drop values were calculated. EDLC-0.5M and EDLC-3M exhibited lifespans of 57,000 and 26,000 cycles, corresponding to about 1274 and 560 hours of operation, respectively, until failure.

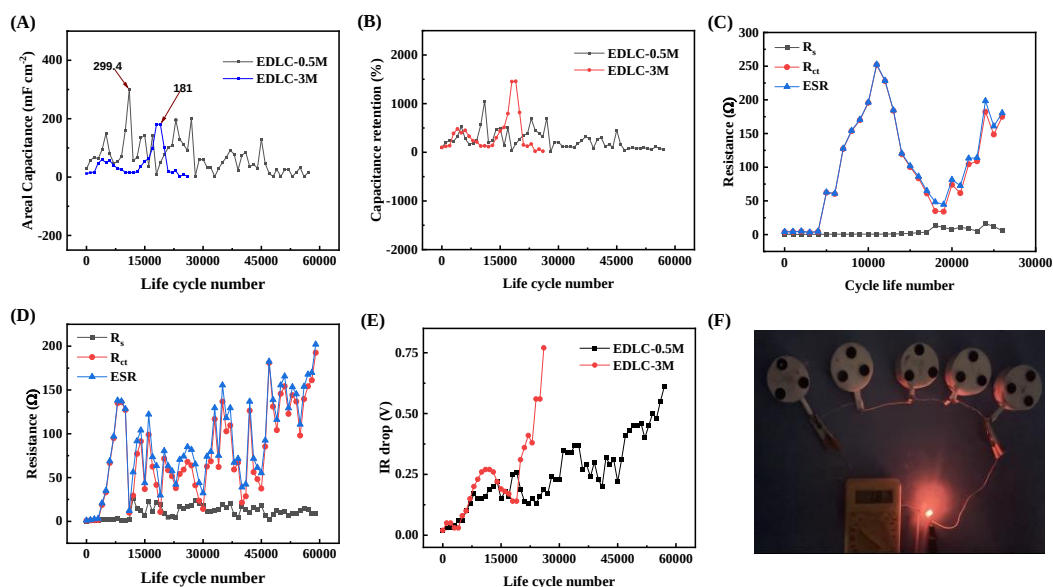


Fig.3.9 (A) Plots of areal capacitance of EDLC-0.5M and EDLC-3M as a function of cycle life number; (B) Plots of capacitance retention of EDLC-0.5M and EDLC-3M as a function of cycle life number; (C) Plots of R_s , R_{ct} , and ESR of the EDLC-0.5M as a function of cycle life number; (D) Plots of R_s , R_{ct} , and ESR of the EDLC-0.5M as a function of cycle life number; (E) Plots of IR drop values of EDLC-0.5M and EDLC-3M as a function of cycle life number; (F) Picture of illumination of a red LED by a prototype power device containing five EDLCs assembled using GCCHME-0.5M.

Fig.3.9 (A) shows the plots of areal capacitances versus cycle number for EDLC-0.5M and EDLC-3M. It reveals critical insights into the long-term performance and stability of EDLC-0.5M and EDLC-3M. Initially, both devices demonstrated a gradual increase in capacitance, which can be attributed to the stabilization and optimization of ion transport pathways within the membrane over the early cycles. Many other studies on electrochemical systems with polymer hydrogel electrolytes have shown similar trends, with the enhanced areal capacitance often linked to the slow diffusion of electrolytes into the porous matrix of the electrodes [83,84]. EDLC-0.5M achieved a peak areal capacitance of 299.4 mF cm^{-2} at 11,000 cycles, and a peak areal capacitance of EDLC-3M of 181 mF cm^{-2} at 19,000 cycles. EDLC-0.5M and EDLC-3M exhibited peak energy densities of 41.58 and $25.14 \text{ } \mu\text{Wh cm}^{-2}$, respectively. The power density of both the EDLCs remained constant at $1000 \text{ } \mu\text{W cm}^{-2}$ during the cycle life test. In EDLC-0.5M, the lower crosslinking density allows for enhanced ion mobility, facilitating better charge accumulation and storage within the electrode. In contrast, EDLC-3M showed consistently lower capacitance values throughout its lifecycle. Tables 3.6 and 3.7 present the electrochemical performance results obtained from EDLC-0.5M and EDLC-3M, respectively, at 1000 -cycles intervals during cyclic stability test. Representative CVs, GCDs, and FRA of some selected cycles during cycle life test for both EDLCs are given in Fig.3.10 (A-F).

Table 3.6: Summary of capacitive performance data for EDLC-0.5M employing GCCHME-0.5M in GCD current density of 1 mA cm^{-2} , that performed 57,000 charge-discharge cycles.

Cycle number	Areal Capacitance (mF cm^{-2})	Energy density ($\mu\text{Wh cm}^{-2}$)	R_s (Ω)	R_{ct} (Ω)	ESR (Ω)	Capacitance retention (%)	Coulombic efficiency (%)
1	28.4	3.94	0.31	0.79	1.1	100	88.19
1000	57.2	7.94	0.48	1.12	1.6	201.40	85.88
2000	68.2	9.47	1.3	1.31	2.61	240.14	88.11
3000	62.8	8.72	1.62	1.54	3.16	221.12	89.97
4000	93.6	13	2.16	18.7	20.86	329.57	94.73
5000	149.4	20.75	1.9	33.22	35.12	526.05	78.88

6000	79.4	11.02	2.17	66.68	68.85	279.57	92.97
7000	67.8	9.41	2.06	94.98	97.04	238.73	89.68
8000	47.8	6.63	3.01	135.11	138.12	168.30	91.57
9000	52.6	7.30	1.23	136.01	137.24	185.21	73.46
10000	70.8	9.83	1.24	127.19	128.43	249.29	63.44
11000	299.4	41.58	2.33	9.862	12.192	1054.22	87.74
12000	9	1.25	26.73	29.49	56.22	31.69	34.09
13000	56.2	7.80	14.61	77.09	91.7	197.88	73.56
14000	67.8	9.41	12.59	91.44	104.03	238.73	72.12
15000	135.2	18.77	6.94	36.92	43.86	476.05	79.15
16000	36.4	5.05	23.18	99.01	122.19	128.16	55.65
17000	142.8	19.83	11.16	62.48	73.64	502.81	82.54
18000	9.8	1.36	21.83	41.65	63.48	34.50	81.66
19000	49.4	6.86	19.08	10.73	29.81	173.94	90.80
20000	76.2	10.58	8.92	71.55	80.47	268.30	90.714
21000	100.4	13.94	4.81	58.44	63.25	353.52	96.72
22000	107.8	14.97	5.91	51.56	57.47	379.57	94.06
23000	195.4	27.13	4.23	37.98	42.21	688.02	85.92
24000	129.6	18	16.48	54.121	70.601	456.33	96.57
25000	82.6	11.47	15.22	59.02	74.24	290.84	72.83
26000	90.2	12.52	17	68.05	85.05	317.60	98.04
27000	199.8	27.75	18.1	63.88	81.98	703.52	81.21
28000	3.4	0.47	24.17	41.17	65.34	11.971	15.74
29000	59.4	8.25	20.26	23.7	43.96	209.15	96.11
30000	60.2	8.36	18.06	14.22	32.28	211.97	95.85
31000	34.6	4.80	11.46	62.66	74.12	121.83	94.53
32000	32.2	4.47	11	68.56	79.56	113.38	93.06
33000	3.8	0.52	12.72	116.78	129.5	13.38	27.53
34000	29.6	4.11	13.1	62.06	75.16	104.22	93.08
35000	50.2	6.97	18.78	136.76	155.54	176.76	92.27
36000	68.2	9.47	15.35	102.79	118.14	240.14	93.68
37000	91.8	12.75	20	109.53	129.53	323.23	62.87
38000	78	10.83	8	59.2	67.2	274.64	70.27
39000	24.2	3.36	4.56	67.07	71.63	85.21	33.06
40000	74.8	10.38	17.45	21.47	38.92	263.38	93.73
41000	85	11.80	13.61	28.63	42.24	299.29	96.59
42000	35.8	4.97	10.49	126.42	136.91	126.05	38.74

43000	43.8	6.08	15.46	56.24	71.7	154.22	95.63
44000	30.8	4.27	13.17	48.17	61.34	108.45	46.66
45000	129.6	18	17.73	37.49	55.22	456.33	71.20
46000	44.2	6.13	7.04	85.43	92.47	155.63	93.64
47000	13.2	1.83	1.65	180.95	182.6	46.47	89.18
48000	0.6	0.08	7.74	131.06	138.8	2.112	3.896
49000	26.4	3.66	11.99	104.19	116.18	92.95	91.03
50000	4.4	0.61	9.86	145.67	155.53	15.49	30.55
51000	25.2	3.5	11.47	154.25	165.72	88.73	86.30
52000	26.8	3.72	6.65	122.76	129.41	94.36	90.54
53000	2.4	0.33	9.41	144.1	153.51	8.450	19.04
54000	16.6	2.30	8.54	136.84	145.38	58.45	91.20
55000	31.8	4.41	12.67	98.05	110.72	111.9	45.17
56000	2.4	0.33	14.34	139.64	153.98	8.450	14.45
57000	14.8	2.05	13.56	154.21	167.77	52.11	91.35

Table 3.7: Summary of capacitive performance data for EDLC-3M employing GCCHME-3M in GCD current density of 1 mA cm^{-2} , that performed 26,000 charge discharge-cycles.

Cycle number	Areal Capacitance (mF cm^{-2})	Energy density ($\mu\text{Wh cm}^{-2}$)	R_s (Ω)	R_{ct} (Ω)	ESR (Ω)	Capacitance retention (%)	Coulombic efficiency (%)
1	13	1.80	0.31	3.9	4.2	100	70.6
1000	15.4	2.13	0.34	4.1	4.4	118.4	73.3
2000	16.8	2.33	0.29	4.8	5.0	129.2	69.4
3000	48	6.66	0.36	3.0	3.4	369.2	71.8
4000	59.6	8.27	0.33	4.3	4.7	458.4	52.3
5000	49.8	6.91	0.54	62.3	62.9	383.0	49.4
6000	56	7.77	0.64	60.4	61.0	430.7	53.1
7000	40.8	5.66	0.63	127.1	127.8	313.8	48.6
8000	29.6	4.11	0.69	153.7	154.4	227.6	40.8
9000	26.4	3.66	0.8	169.9	170.7	203	42.4
10000	16	2.22	0.68	195.7	196.3	123	18.9
11000	16.4	2.27	0.79	251.8	252.6	126.1	23
12000	14.4	2	0.79	227.7	228.5	110.7	18.5

13000	17.8	2.4	0.91	183.8	184.7	136.9	25
14000	37.2	5.16	1.33	119.2	120.6	286.1	44
15000	54.6	7.58	1.8	100.1	101.9	420	57.4
16000	63.6	8.83	2.82	83.5	86.33	489.2	59.8
17000	98.6	13.69	3.83	61	64.9	758.4	64.6
18000	180.2	25.02	13.32	34.9	48.2	1386.1	76.1
19000	181	25.13	10.59	34.1	44.71	1392.3	70.3
20000	101.6	14.11	7.61	74	81.6	781.5	56
21000	18.8	2.611	10.92	61.6	72.59	144.6	66.1
22000	15.6	2.16	8.79	104.4	113.1	120	68.4
23000	21	2.91	5.21	108.8	114	161.5	75.5
24000	2.6	0.36	16.21	182.2	198	20	13.4
25000	8	1.11	12.25	148.6	160.8	61.5	63.4
26000	2.8	0.38	5.68	174.9	180.6	21.5	13.4

The capacitance retention values obtained during cycle life test of EDLC-0.5M and EDLC-3M are plotted in Fig.3.9 (B), which reveals notable differences in stability and performance over extended cycling. Initially, both EDLCs exhibited considerable fluctuations, with EDLC-0.5M exhibiting a particularly pronounced spike in capacitance retention, exceeding 1054% at the 11,000th cycle, and EDLC-3M exceeding 1459 % at the 19,000th cycle. Fig.3.9 (C) and 3.9 (D) present the trends in R_s , R_{ct} , and ESR over successive charge-discharge cycles for EDLC-0.5M and EDLC-3M, respectively. The values of R_s , R_{ct} , and ESR of the EDLC-0.5M and EDLC-3M observed throughout the cycle life tests are summarized in Tables 3.6 and 3.7, respectively. It is seen in Fig.3.9 (B) corresponding to EDLC-0.5M, R_s remains relatively stable throughout the cycle life, indicating minimal changes in the ionic conductivity of the electrolyte. However, both R_{ct} and ESR show periodic fluctuations, with the ESR experiencing a more pronounced increase over time. The observed rise in R_{ct} and ESR with cycle numbers could be attributed to the continuous development of interfacial resistance [85]. Nonetheless, the relatively stable R_s suggest that GCCHME-0.5M maintains efficient ion transport and charge transfer, which is likely due to its optimal WU and ionic conductivity. Similarly, in Fig.3.9 (D) corresponding to EDLC-3M, R_s remains stable, both R_{ct} and ESR display a more pronounced increases and fluctuations, particularly during the early cycles. The higher ESR values,

compared to EDLC-0.5M, indicate that the increased crosslinker concentration in GCCHME-3M has resulted in a denser membrane structure, which might restrict ion mobility, leading to higher resistance.

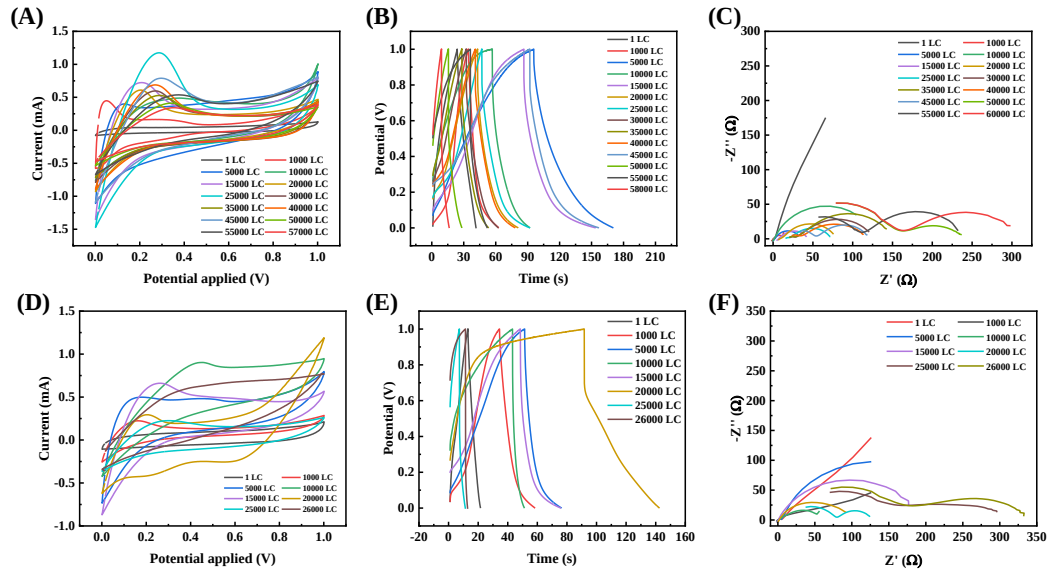


Fig.3.10 (A) Plots of CVs during life cycle studies of EDLC-0.5M; (B) Plots of GCDs during life cycle studies of EDLC-0.5M; (C) Plots of FRAs during life cycle studies of EDLC-0.5M; (D) Plots of CVs during life cycle studies of EDLC-3M; (E) Plots of GCDs during life cycle studies of EDLC-3M; (F) Plots of FRAs during life cycle studies of EDLC-3M.

Nyquist plots for EDLC-0.5M and EDLC-3M, recorded at selected life cycle intervals are presented in Fig.3.10 (C) and (F), respectively. During the initial cycling, a single semicircle appeared in the low-frequency portion. As cycling progressed, a second semicircle emerged, accompanied by a compression of W region. This behaviour suggests a progressive increased in internal resistance and degradation of porous architecture of the electrodes [86].

Fig.3.9 (E) shows the change of IR drops over successive cycles for both the EDLCs. EDLC-0.5M, exhibited a relatively low IR drop over the entire cycling range as compared to EDLC-3M, with only a gradual increase toward the end of its operational lifespan. On the other hand, EDLC-3M, which employs the more densely cross-linked membrane, shows a sharp and significant increase in IR drop after approximately

15,000 cycles, with a pronounced spike near 30,000 cycles. This rapid rise suggests higher internal resistance, likely caused by restricted ion movement because of the rigid structure of GCCHME-3M.

The superior characteristics and performance of the EDLCs motivated the assembly of a prototype devices cell using the better performing GCCHME-0.5M. As shown in Fig.3.9 (F), A series connection of five identical EDLCs prepared using GCCHME-0.5M were taken to light a red LED. Each device underwent charging at 1 mA cm^{-2} . The prototype lit the red LED intensely for around 95 seconds by delivering a voltage output of 1.87 V.

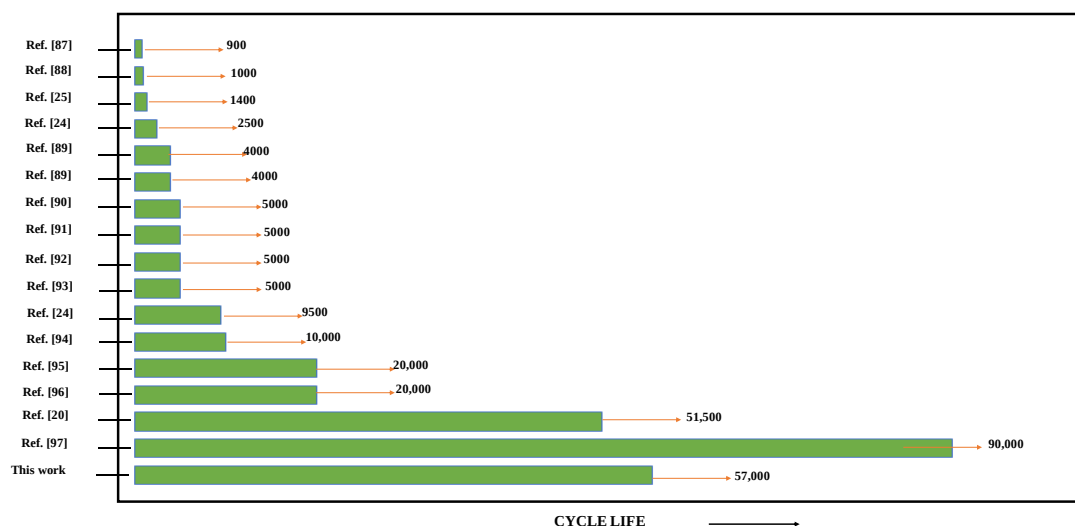


Fig.3.11 Bar diagram comparing the numbers of cycle life for various EDLCs with different hydrogel electrolytes from literature.

Fig.11 illustrates a comparative overview of life cycle data for various EDLCs incorporating different hydrogel electrolytes, as reported in literature [20,24,25,87–97]. Notably, the highest cycle life among all the hydrogels was reported for a redox-active PVA/H₂SO₄/FeCl₃·6H₂O hydrogel electrolyte with microporous electrodes [97]. This impressive performance may be due to the electrode material used, which significantly influenced the durability of the cell, but the preparation process of both the electrolyte and electrode materials are complicated. Our preceding study reported a cycle life of 51,500 cycles [20]. The current research being reported herein, however,

demonstrated a remarkably high life cycle of 57,000. This advancement is particularly relevant for portable electronic devices. Importantly, the materials employed, viz. chitosan, Na_2CO_3 , and water, are not only low-cost and eco-friendly. Additionally, the synthesis process for the electrolyte is straightforward and economical.

Table 3.8: Comparison of results obtained from the previously reported ICCHME [20] and GCCHME (current work).

Properties	ICCHME [20]	GCCHME (Current work)
Crosslinker used	Na_2CO_3	Na_2CO_3
Optimal concentration (M)	0.5	0.5
Optimal crosslinker volume (mL)	2	Not required
WU (%)	226	112
DR (%)	18.24	20.74
Ionic conductivity (mS cm^{-1})	7.89	0.541
Breakdown Voltage (V)	2.32	2.12
Maximum areal capacitance (mF cm^{-2}) at 2 mA cm^{-2}	260.40	182.8
R_s (Ω)	0.23	0.21
R_{ct} (Ω)	0.71	3.05
ESR (Ω)	0.94	3.26
Cyclic life	51,500 (at 2 mA cm^{-2})	22,500 (at 2 mA cm^{-2}) 57,000 (at 1 mA cm^{-2})

The physicochemical electrochemical properties of isotropic ICCHME [20] prepared in Chapter 2 and GCCHME (current work) were systematically compared in Table 3.8 to elucidate the influence of different crosslinking strategies on the hydrogel membrane structures and properties. In the previously reported ICCHME synthesis [20], chitosan solution was mixed directly with Na_2CO_3 , leading to CO_2 bubbles evolution during ionic crosslinking. This process resulted in the formation of numerous bubbles inside the hydrogel matrix, and considerable effort was needed to optimize the

crosslinker concentration, volume, and reaction time to minimize bubble retention and ensure a uniform hydrogel structure. Despite these challenges, the ICCHME exhibited remarkably superior performances across multiple parameters, likely due to the development of an interconnected hydrogel void structure formed inside through CO₂ bubble evolution. In terms of WU, the ICCHME demonstrated a significantly higher uptake compared to GCCHME. This enhancement is attributed to the porous architecture of the ICCHMEs, which provided greater internal free volume for water absorption. In contrast, less porous architecture in GCM restricted their WU capacity. GCCHME exhibited a higher DR value compared to the ICCHME. In the isotropic crosslinking, most of the NH₃⁺ of chitosan chains involved in crosslinking with the CO₃²⁻, leading to the development of a highly interconnected network. As a result, the membrane becomes more resistant to solubility in water, and the extent of dissolution is significantly reduced. In gradient crosslinking, the ionic interaction between the chitosan matrix and the Na₂CO₃ crosslinker predominantly occurs at the membrane surface, resulting in a cross-linked layer confined primarily to the outer surface. Due to the absence of bulk mixing, the crosslinker does not penetrate deeply into the polymer matrix, leaving the core region insufficiently cross-linked. During the accelerated dissolution tests, these uncross-linked or loosely bound chitosan chains within the hydrogel membrane were more prone to dissolution in the aqueous medium, thereby contributing to the slightly elevated DR. Ionic conductivity was notably higher in ICCHME compared to GCCHME. The interconnected void structure in bulk membranes facilitated efficient ion transport, while the compact and dense structure in GCCHME limited the formation of continuous ionic pathways, severely restricting ion mobility. Similarly, the breakdown voltage of ICCHME was slightly higher compared to GCCHME, reflecting better stability against electrochemical decomposition, although the difference was modest. The maximum areal capacitance at 2 mA cm⁻² was also significantly higher for ICCHME relative to the GCCHME. R_s values were relatively close for both the electrolytes. However, R_{ct} and ESR were substantially lower in the ICCHME. The lower resistances in ICCHME again highlight the role of internal voids in facilitating faster ion mobility within the interface of electrode and electrolyte. In terms of cyclic stability, the EDLC fabricated using ICCHME demonstrated excellent stability, maintaining performance for 51,500 cycles at 2 mA

cm^{-2} , while EDLC employing the GCCHME exhibited 22,500 cycles at the same current density. However, at 1 mA cm^{-2} , the GCCHME based EDLC exhibited impressively long cycle life of 57,000 cycles. This suggests that although their ionic transport properties are limited, they maintain structural integrity under milder operational conditions.

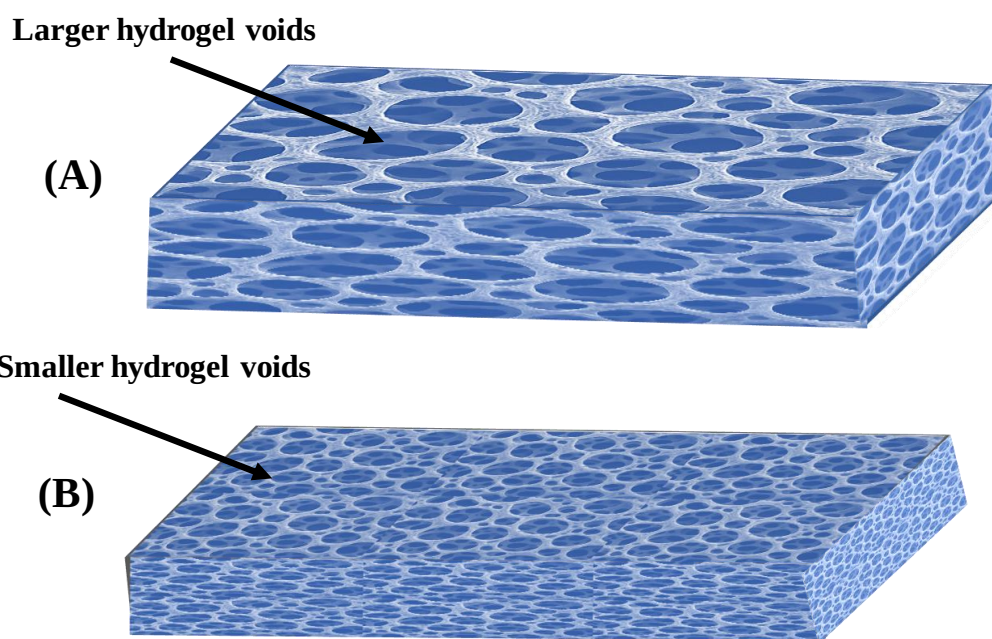


Fig.3.12 Schematic illustration of internal hydrogel void structure in (A) ICCHME; and (B) GCCHME.

To further illustrate the structural difference, schematic representations of the hydrogel void morphology in chitosan hydrogel membranes prepared by both isotropic and gradient crosslinking are shown in Fig.3.12 (A) as well as 3.12 (B), respectively. As presented in Fig.3.12 (A), In ICCHME, CO_2 bubble evolutions leads to formation of larger hydrogel voids in both the surface and core of the hydrogel matrix. These voids are not only increasing internal free volume but also act as continuous channels for water retention and ion diffusion, contribution to its higher performance. In contrast, GCCHMEs, as shown in Fig.3.12 (B), show smaller and compact hydrogel voids due to limited surface crosslinking and absent of any bulk gas evolution. Also, the core of the matrix remains uncross-linked. Thus, by carefully analysing the results obtained in the current study, we can strongly validate the assumption made in our previous work

[20], the superior electrochemical performances of the isotropic ICCHME were primarily due to the formation of an internal hydrogel voids, developed through CO₂ bubble evolution during the crosslinking process. The GCCHME, which were prepared without any direct bulk mixing or bubble formation, inherently lacked such internal large void structures, resulting in comparatively lower ionic conductivity, capacitance, and overall electrochemical performances. This clear contrast between the two methods provides compelling evidence supporting the pivotal role of void formation in enhancing ion transport and electrochemical stability in ICCH-based electrolytes. Nevertheless, it is important to emphasize that the GCCHME offer considerable advantage in terms of facile synthesis. The elimination of complex optimization step for bubble removal, and lengthy preparation process marks a significant improvement in the practical applicability of GCCHMEs. Therefore, while the gradient crosslinking method leads to a denser membrane structure and slightly reduced electrochemical properties compared to isotropic crosslinking method, it represents a valuable advancement towards the development of easily manufacturable, environmentally friendly, and reliable hydrogel electrolyte materials suitable for large-scale applications. This study not only introduces a new and facile fabrication route for chitosan hydrogel membranes but also fundamentally confirms that the formation of an internal hydrogel voids during crosslinking is critical to achieving high-performance hydrogel electrolytes.

3.4 Conclusions

In this work, gradient cross-linked membrane electrolytes (GCCHMEs) were synthesized via a facile ionic crosslinking approach using Na_2CO_3 crosslinker. The formation of ionic linkages between chitosan and carbonate ions was confirmed by FTIR spectroscopy. The resulting GCCHME-0.5M was transparent, mechanically robust, and flexible, with high WU of 112 % and a DR of 20.74 %. Among the samples, GCCHME-0.5M exhibited the most favorable performance, achieving an ionic conductivity of $5.41 \times 10^{-4} \text{ S cm}^{-1}$, ionic mobility of $4.30 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$, and an ion number density of $1.65 \times 10^{22} \text{ m}^{-3}$. The high ion transference number of 0.983 confirmed the dominance of ionic charge transport. EDLC fabricated with GCCHME-0.5M demonstrated an areal capacitance of $299.40 \text{ mF cm}^{-2}$ at 1 mA cm^{-2} , energy and power densities of $41.58 \text{ } \mu\text{Wh cm}^{-2}$ and $1000 \text{ } \mu\text{W cm}^{-2}$, and a minimal R_s of $0.23 \text{ } \Omega$. Excellent cycling stability was observed, with 57,000 charge–discharge cycles retained at 1 mA cm^{-2} . A prototype module comprising five GCCHME-based EDLCs successfully powered a red LED for 96 seconds, demonstrating practical device feasibility. A detailed comparison with ICCHMEs, synthesized using identical chemical components in Chapter 2, confirmed that while ICCHMEs exhibit greater conductivity and areal capacitance due to the formation of internal hydrogel voids from CO_2 bubble evolution, GCCHMEs offer critical advantages in fabrication. The gradient membranes eliminate the need for bulk mixing and bubble removal steps, reduce processing complexity, and maintain sufficient electrochemical performance for flexible energy storage applications. Overall, this study introduces a scalable, environmentally friendly membrane fabrication strategy and establishes a structure–property–performance correlation between crosslinking architecture and electrochemical behavior. These results open new directions for rational design of hydrogel electrolytes in supercapacitors, batteries, and other next-generation solid-state energy systems.

3.4 References

- [1] J. Wang, W. Azam, Natural resource scarcity, fossil fuel energy consumption, and total greenhouse gas emissions in top emitting countries, *Geoscience Frontiers* 15 (2024) 101757. <https://doi.org/10.1016/j.gsf.2023.101757>.
- [2] S. Chu, A. Majumdar, Opportunities and challenges for a sustainable energy future, *Nature* 488 (2012) 294–303. <https://doi.org/10.1038/nature11475>.
- [3] T.M. Gür, Review of electrical energy storage technologies, materials and systems: challenges and prospects for large-scale grid storage, *Energy Environ Sci* 11 (2018) 2696–2767. <https://doi.org/10.1039/C8EE01419A>.
- [4] S.M. Benoy, M. Pandey, D. Bhattacharjya, B.K. Saikia, Recent trends in supercapacitor-battery hybrid energy storage devices based on carbon materials, *J Energy Storage* 52 (2022) 104938. <https://doi.org/10.1016/j.est.2022.104938>.
- [5] J. Zhang, M. Gu, X. Chen, Supercapacitors for renewable energy applications: A review, *Micro and Nano Engineering* 21 (2023) 100229. <https://doi.org/10.1016/j.mne.2023.100229>.
- [6] S.T. Senthilkumar, R.K. Selvan, J.S. Melo, Redox additive/active electrolytes: a novel approach to enhance the performance of supercapacitors, *J Mater Chem A Mater* 1 (2013) 12386. <https://doi.org/10.1039/c3ta11959a>.
- [7] N.A. Choudhury, S. Sampath, A.K. Shukla, Hydrogel-polymer electrolytes for electrochemical capacitors: an overview, *Energy Environ. Sci.* 2 (2009) 55–67. <https://doi.org/10.1039/B811217G>.
- [8] N.A. Choudhury, A.K. Shukla, S. Sampath, S. Pitchumani, Cross-Linked Polymer Hydrogel Electrolytes for Electrochemical Capacitors, *J Electrochem Soc* 153 (2006) A614. <https://doi.org/10.1149/1.2164810>.
- [9] S.B. Aziz, M.A. Brza, M.M. Nofal, R.T. Abdulwahid, S.A. Hussien, A.M. Hussein, W.O. Karim, A Comprehensive Review on Optical Properties of Polymer Electrolytes and Composites, *Materials* 13 (2020) 3675. <https://doi.org/10.3390/ma13173675>.
- [10] Md.M.H. Rumon, Md.S. Rahman, A.A. Akib, Md.S. Sohag, Md.R.A. Rakib, Md.A.R. Khan, F. Yesmin, M.S. Shakil, M.M. Rahman Khan, Progress in hydrogel toughening: addressing structural and crosslinking challenges for

- biomedical applications, *Discov Mater* 5 (2025) 5. <https://doi.org/10.1007/s43939-025-00178-x>.
- [11] S. Bashir, M. Hina, J. Iqbal, A.H. Rajpar, M.A. Mujtaba, N.A. Alghamdi, S. Wageh, K. Ramesh, S. Ramesh, Fundamental Concepts of Hydrogels: Synthesis, Properties, and Their Applications, *Polymers (Basel)* 12 (2020) 2702. <https://doi.org/10.3390/polym12112702>.
- [12] K. Sun, F. Ran, G. Zhao, Y. Zhu, Y. Zheng, M. Ma, X. Zheng, G. Ma, Z. Lei, High energy density of quasi-solid-state supercapacitor based on redox-mediated gel polymer electrolyte, *RSC Adv* 6 (2016) 55225–55232. <https://doi.org/10.1039/C6RA06797B>.
- [13] S. Zallouz, J.-M. Le Meins, C. Matei Ghimbeu, Alkaline hydrogel electrolyte from biosourced chitosan to enhance the rate capability and energy density of carbon-based supercapacitors, *Energy Advances* 1 (2022) 1051–1064. <https://doi.org/10.1039/D2YA00250G>.
- [14] N. Patra, P. Ramesh, V. Donthu, A. Ahmad, Biopolymer-based composites for sustainable energy storage: recent developments and future outlook, *Journal of Materials Science: Materials in Engineering* 19 (2024) 34. <https://doi.org/10.1186/s40712-024-00181-9>.
- [15] G. Gopinath, S. Ayyasamy, P. Shanmugaraj, R. Swaminathan, K. Subbiah, S. Kandasamy, Effects of biopolymers in energy storage applications: A state-of-the-art review, *J Energy Storage* 70 (2023) 108065. <https://doi.org/10.1016/j.est.2023.108065>.
- [16] J. Sun, Y. Deng, J. Jiang, Y. Hu, Q. Cui, Z. Lou, Y. Hou, F. Teng, Cationic effects on solid polymer electrolyte-gated organic transistors, *Org Electron* 106 (2022) 106529. <https://doi.org/10.1016/j.orgel.2022.106529>.
- [17] F. Hong, P. Qiu, Y. Wang, P. Ren, J. Liu, J. Zhao, D. Gou, Chitosan-based hydrogels: From preparation to applications, a review, *Food Chem X* 21 (2024) 101095. <https://doi.org/10.1016/j.fochx.2023.101095>.
- [18] M. Qu, D. Lei, H. Zhang, X. Zhang, Z. Shang, R. Wang, L. Wan, Z. Li, C. Si, One-pot method for in situ synthesis of triple cross-linked hydrogel electrolytes for flexible supercapacitors with high mechanical and electrochemical

- properties, *J Energy Storage* 72 (2023) 108644. <https://doi.org/10.1016/j.est.2023.108644>.
- [19] L. Dai, Y. Wang, Z. Li, X. Wang, C. Duan, W. Zhao, C. Xiong, S. Nie, Y. Xu, Y. Ni, A multifunctional self-crosslinked chitosan/cationic guar gum composite hydrogel and its versatile uses in phosphate-containing water treatment and energy storage, *Carbohydr Polym* 244 (2020) 116472. <https://doi.org/10.1016/j.carbpol.2020.116472>.
- [20] D. Hazarika, D. Kamei, N. Shijoh, N.A. Choudhury, An ionically cross-linked chitosan hydrogel membrane electrolyte for long-lived electrical double layer capacitors, *J Power Sources* 629 (2025) 236037. <https://doi.org/10.1016/j.jpowsour.2024.236037>.
- [21] N.A. Choudhury, J. Ma, Y. Sahai, High performance and eco-friendly chitosan hydrogel membrane electrolytes for direct borohydride fuel cells, *J Power Sources* 210 (2012) 358–365. <https://doi.org/10.1016/j.jpowsour.2012.03.013>.
- [22] I.A. Fadzallah, S.R. Majid, M.A. Careem, A.K. Arof, A study on ionic interactions in chitosan–oxalic acid polymer electrolyte membranes, *J Memb Sci* 463 (2014) 65–72. <https://doi.org/10.1016/j.memsci.2014.03.044>.
- [23] A. GhavamiNejad, N. Ashammakhi, X.Y. Wu, A. Khademhosseini, Crosslinking Strategies for 3D Bioprinting of Polymeric Hydrogels, *Small* 16 (2020). <https://doi.org/10.1002/sml.202002931>.
- [24] D. Kamei, N.A. Choudhury, KI-doped redox-active gelatin chemical hydrogel membrane electrolytes for solid-state electrical double layer capacitors, *Mater Today Chem* 37 (2024) 101891. <https://doi.org/10.1016/j.mtchem.2023.101891>.
- [25] N.A. Choudhury, P.W.C. Northrop, A.C. Crothers, S. Jain, V.R. Subramanian, Chitosan hydrogel-based electrode binder and electrolyte membrane for EDLCs: experimental studies and model validation, *J Appl Electrochem* 42 (2012) 935–943. <https://doi.org/10.1007/s10800-012-0469-2>.
- [26] A. Shahab Marf, R. M. Abdullah, S. B. Aziz, Structural, Morphological, Electrical and Electrochemical Properties of PVA: CS-Based Proton-Conducting Polymer Blend Electrolytes, *Membranes (Basel)* 10 (2020) 71. <https://doi.org/10.3390/membranes10040071>.

-
- [27] S.B. Aziz, S. Al-Zangana, M.A. Brza, S.R. Saeed, R.T. Abdulwahid, M.F.Z. Kadir, Study of Dielectric Properties and Ion Transport Parameters in Chitosan-Barium Nitrate Based Solid Polymer Electrolytes, *Int J Electrochem Sci* 14 (2019) 10580–10595. <https://doi.org/10.20964/2019.12.39>.
- [28] S.B. Aziz, M.F.Z. Kadir, M.H. Hamsan, H.J. Woo, M.A. Brza, Development of Polymer Blends Based on PVA:POZ with Low Dielectric Constant for Microelectronic Applications, *Sci Rep* 9 (2019) 13163. <https://doi.org/10.1038/s41598-019-49715-8>.
- [29] A.K. Arof, S. Amirudin, S.Z. Yusof, I.M. Noor, A method based on impedance spectroscopy to determine transport properties of polymer electrolytes, *Phys. Chem. Chem. Phys.* 16 (2014) 1856–1867. <https://doi.org/10.1039/C3CP53830C>.
- [30] R.T. Abdulwahid, S.B. Aziz, M.F.Z. Kadir, N.M. Sadiq, N.A. Halim, M.H. Hamsan, S.R. Saeed, H.J. Woo, Biodegradable polymer membrane K⁺ ion conductor for electrochemical device application, *J Mater Sci* 57 (2022) 19902–19923. <https://doi.org/10.1007/s10853-022-07825-1>.
- [31] H. Nagahama, H. Maeda, T. Kashiki, R. Jayakumar, T. Furuike, H. Tamura, Preparation and characterization of novel chitosan/gelatin membranes using chitosan hydrogel, *Carbohydr Polym* 76 (2009) 255–260. <https://doi.org/10.1016/j.carbpol.2008.10.015>.
- [32] A.S.F.M. Asnawi, S.B. Aziz, I. Brevik, M.A. Brza, Y.M. Yusof, S.M. Alshehri, T. Ahamad, M.F.Z. Kadir, The Study of Plasticized Sodium Ion Conducting Polymer Blend Electrolyte Membranes Based on Chitosan/Dextran Biopolymers: Ion Transport, Structural, Morphological and Potential Stability, *Polymers (Basel)* 13 (2021) 383. <https://doi.org/10.3390/polym13030383>.
- [33] R. Deivanayagam, R. Shahbazian-Yassar, Electrochemical Methods and Protocols for Characterization of Ceramic and Polymer Electrolytes for Rechargeable Batteries, *Batter Supercaps* 4 (2021) 596–606. <https://doi.org/10.1002/batt.202000221>.
- [34] A.K. Arof, N.E.A. Shuhaimi, S. Amirudin, M.Z. Kufian, H.J. Woo, M.A. Careem, Polyacrylonitrile-lithium bis(oxalato) borate polymer electrolyte for

- electrical double layer capacitors, *Polym Adv Technol* 25 (2014) 265–272. <https://doi.org/10.1002/pat.3231>.
- [35] R. Na, Y. Liu, N. Lu, S. Zhang, F. Liu, G. Wang, Mechanically robust hydrophobic association hydrogel electrolyte with efficient ionic transport for flexible supercapacitors, *Chemical Engineering Journal* 374 (2019) 738–747. <https://doi.org/10.1016/j.cej.2019.06.004>.
- [36] S. Mahmoudi-Qashqay, M.-R. Zamani-Meymian, A. Maleki, A simple method of fabrication hybrid electrodes for supercapacitors, *Sci Rep* 14 (2024) 29105. <https://doi.org/10.1038/s41598-024-80243-2>.
- [37] N. Yadav, N. Yadav, S.A. Hashmi, Ionic liquid incorporated, redox-active blend polymer electrolyte for high energy density quasi-solid-state carbon supercapacitor, *J Power Sources* 451 (2020) 227771. <https://doi.org/10.1016/j.jpowsour.2020.227771>.
- [38] S. Yeasmin, M. Bora, B.K. Saikia, D. Mahanta, Binder mediated enhanced electrochemical capacitance in sodium silicate-graphite paint coated filter paper electrodes for all-solid-state symmetric electrochemical capacitors, *J Energy Storage* 73 (2023) 108945. <https://doi.org/10.1016/j.est.2023.108945>.
- [39] X. He, T. Zhuang, S. Ruan, X. Xia, Y. Xia, J. Zhang, H. Huang, Y. Gan, W. Zhang, An innovative poly(ionic liquid) hydrogel-based anti-freezing electrolyte with high conductivity for supercapacitor, *Chemical Engineering Journal* 466 (2023) 143209. <https://doi.org/10.1016/j.cej.2023.143209>.
- [40] H. El Knidri, R. Belaabed, A. Addaou, A. Laajeb, A. Lahsini, Extraction, chemical modification and characterization of chitin and chitosan, *Int J Biol Macromol* 120 (2018) 1181–1189. <https://doi.org/10.1016/j.ijbiomac.2018.08.139>.
- [41] C. Torres, O. Valerio, R.T. Mendonça, M. Pereira, Influence of chitosan protonation degree in nanofibrillated cellulose/chitosan composite films and their morphological, mechanical, and surface properties, *Int J Biol Macromol* 267 (2024) 131587. <https://doi.org/10.1016/j.ijbiomac.2024.131587>.
- [42] J. Qian, X. Wang, J. Shu, C. Su, J. Gong, Z. Xu, J. Jin, J. Shi, A Novel Complex of Chitosan–Sodium Carbonate and Its Properties, *Mar Drugs* 16 (2018) 416. <https://doi.org/10.3390/md16110416>.

-
- [43] M. Al-Remawi, N. Jaber, A. Elsayed, D. Alsafadi, K.A. Salah, Stabilization of insulin using low molecular weight chitosan carbonate nanocarrier, *Carbohydr Polym* 291 (2022) 119579. <https://doi.org/10.1016/j.carbpol.2022.119579>.
- [44] S. Gupta, T.J. Webster, A. Sinha, Evolution of PVA gels prepared without crosslinking agents as a cell adhesive surface, *J Mater Sci Mater Med* 22 (2011) 1763–1772. <https://doi.org/10.1007/s10856-011-4343-2>.
- [45] T.N.T. Tran, M.P. Clark, H. Chung, D.G. Ivey, Effects of Crosslinker Concentration in Poly(Acrylic Acid)-KOH Gel Electrolyte on Performance of Zinc-Air Batteries, *Batter Supercaps* 3 (2020) 409–416. <https://doi.org/10.1002/batt.201900199>.
- [46] D. Kumar, K. Gohel, D.K. Kanchan, K. Mishra, Dielectrics and battery studies on flexible nanocomposite gel polymer electrolyte membranes for sodium batteries, *Journal of Materials Science: Materials in Electronics* 31 (2020) 13249–13260. <https://doi.org/10.1007/s10854-020-03877-8>.
- [47] S.B. Aziz, M.H. Hamsan, M.F.Z. Kadir, W.O. Karim, R.M. Abdullah, Development of Polymer Blend Electrolyte Membranes Based on Chitosan: Dextran with High Ion Transport Properties for EDLC Application, *Int J Mol Sci* 20 (2019) 3369. <https://doi.org/10.3390/ijms20133369>.
- [48] S.B. Aziz, M.F.Z. Kadir, M.H. Hamsan, H.J. Woo, M.A. Brza, Development of Polymer Blends Based on PVA:POZ with Low Dielectric Constant for Microelectronic Applications, *Sci Rep* 9 (2019) 13163. <https://doi.org/10.1038/s41598-019-49715-8>.
- [49] B. Louati, F. Hlel, K. Guidara, Ac electrical properties and dielectric relaxation of the new mixed crystal (Na_{0.8}Ag_{0.2})₂PbP₂O₇, *J Alloys Compd* 486 (2009) 299–303. <https://doi.org/10.1016/j.jallcom.2009.06.148>.
- [50] A.A. Kaufman, B.I. Anderson, Coulomb’s Law and Stationary Electric Field, in: 2010: pp. 3–78. [https://doi.org/10.1016/S0076-6895\(10\)44001-9](https://doi.org/10.1016/S0076-6895(10)44001-9).
- [51] H. Xu, L. Huang, W. Li, S. Gu, D. Zeng, Y. Zhang, Y. Sun, H. Cheng, Shielding the electrostatic attraction by design of zwitterionic single ion conducting polymer electrolyte with high dielectric constant, *J Memb Sci* 651 (2022) 120452. <https://doi.org/10.1016/j.memsci.2022.120452>.

-
- [52] J. M. Hadi, S. B. Aziz, M. M. Nofal, S.A. Hussein, M.H. Hafiz, M.A. Brza, R.T. Abdulwahid, M.F.Z. Kadir, H.J. Woo, Electrical, Dielectric Property and Electrochemical Performances of Plasticized Silver Ion-Conducting Chitosan-Based Polymer Nanocomposites, *Membranes* (Basel) 10 (2020) 151. <https://doi.org/10.3390/membranes10070151>.
- [53] S.B. Aziz, S.M. Mamand, The Study of Dielectric Properties and Conductivity Relaxation of Ion Conducting Chitosan:NaTf Based Solid Electrolyte, *Int J Electrochem Sci* 13 (2018) 10274–10288. <https://doi.org/10.20964/2018.11.05>.
- [54] H.L. Yeager, B. Kipling, Ionic diffusion and ion clustering in a perfluorosulfonate ion-exchange membrane, *J Phys Chem* 83 (1979) 1836–1839. <https://doi.org/10.1021/j100477a008>.
- [55] R.J. Klein, S. Zhang, S. Dou, B.H. Jones, R.H. Colby, J. Runt, Modeling electrode polarization in dielectric spectroscopy: Ion mobility and mobile ion concentration of single-ion polymer electrolytes, *J Chem Phys* 124 (2006). <https://doi.org/10.1063/1.2186638>.
- [56] E.M.A. Dannoun, S.B. Aziz, S.N. Abdullah, M.M. Nofal, K.H. Mahmoud, A.R. Murad, R.M. Abdullah, Mohd.F.Z. Kadir, Characteristics of Plasticized Lithium Ion Conducting Green Polymer Blend Electrolytes Based on CS: Dextran with High Energy Density and Specific Capacitance, *Polymers* (Basel) 13 (2021) 3613. <https://doi.org/10.3390/polym13213613>.
- [57] Y. Xiao, Y. Xiang, R. Xiu, S. Lu, Development of cesium phosphotungstate salt and chitosan composite membrane for direct methanol fuel cells, *Carbohydr Polym* 98 (2013) 233–240. <https://doi.org/10.1016/j.carbpol.2013.06.017>.
- [58] D.M. Correia, M.A. Gámiz-González, G. Botelho, A. Vidaurre, J.L. Gomez Ribelles, S. Lanceros-Mendez, V. Sencadas, Effect of neutralization and cross-linking on the thermal degradation of chitosan electrospun membranes, *J Therm Anal Calorim* 117 (2014) 123–130. <https://doi.org/10.1007/s10973-014-3707-5>.
- [59] T. Mitra, G. Sailakshmi, A. Gnanamani, A.B. Mandal, Studies on Cross-linking of succinic acid with chitosan/collagen, *Materials Research* 16 (2013) 755–765. <https://doi.org/10.1590/S1516-14392013005000059>.

-
- [60] J. Ma, Y. Sahai, R.G. Buchheit, Evaluation of multivalent phosphate cross-linked chitosan biopolymer membrane for direct borohydride fuel cells, *J Power Sources* 202 (2012) 18–27. <https://doi.org/10.1016/j.jpowsour.2011.11.003>.
- [61] V. Cyriac, Ismayil, K. Mishra, Y.N. Sudhakar, Z.E. Rojudi, S.P. Masti, I.M. Noor, Suitability of NaI complexed sodium alginate-polyvinyl alcohol biodegradable polymer blend electrolytes for electrochemical device applications: Insights into dielectric relaxations and scaling studies, *Solid State Ion* 411 (2024) 116578. <https://doi.org/10.1016/j.ssi.2024.116578>.
- [62] P.G. Gan, S.T. Sam, A.M. Faiq, Tensile Properties and Crystallinity of Crosslinked Nanocrystalline Cellulose/Chitosan Composite, *IOP Conf Ser Mater Sci Eng* 429 (2018) 012042. <https://doi.org/10.1088/1757-899X/429/1/012042>.
- [63] N. Sankararamakrishnan, R. Sanghi, Preparation and characterization of a novel xanthated chitosan, *Carbohydr Polym* 66 (2006) 160–167. <https://doi.org/10.1016/j.carbpol.2006.02.035>.
- [64] T.B. Fideles, J.L. Santos, H. Tomás, G.T.F.S. Furtado, D.B. Lima, S.M.P. Borges, M.V.L. Fook, Characterization of Chitosan Membranes Crosslinked by Sulfuric Acid, *OALib* 05 (2018) 1–13. <https://doi.org/10.4236/oalib.1104336>.
- [65] S. Valizadeh, M. Naseri, S. Babaei, S.M.H. Hosseini, A. Imani, Development of bioactive composite films from chitosan and carboxymethyl cellulose using glutaraldehyde, cinnamon essential oil and oleic acid, *Int J Biol Macromol* 134 (2019) 604–612. <https://doi.org/10.1016/j.ijbiomac.2019.05.071>.
- [66] F. Jahan, R.D. Mathad, S. Farheen, Effect of mechanical strength on chitosan-pva blend through ionic crosslinking for food packaging application, *Mater Today Proc* 3 (2016) 3689–3696. <https://doi.org/10.1016/j.matpr.2016.11.014>.
- [67] J. Ma, Y. Sahai, R.G. Buchheit, Evaluation of multivalent phosphate cross-linked chitosan biopolymer membrane for direct borohydride fuel cells, *J Power Sources* 202 (2012) 18–27. <https://doi.org/10.1016/j.jpowsour.2011.11.003>.
- [68] C. Tang, M.L. Bruening, Ion separations with membranes, *Journal of Polymer Science* 58 (2020) 2831–2856. <https://doi.org/10.1002/pol.20200500>.
- [69] S.B. Aziz, A.S.F.M. Asnawi, P.A. Mohammed, R.T. Abdulwahid, Y.M. Yusof, R.M. Abdullah, M.F.Z. Kadir, Impedance, circuit simulation, transport

- properties and energy storage behavior of plasticized lithium ion conducting chitosan based polymer electrolytes, *Polym Test* 101 (2021) 107286. <https://doi.org/10.1016/j.polymertesting.2021.107286>.
- [70] R. Kant, M.B. Singh, Theory of the Electrochemical Impedance of Mesoporous Electrodes Embedded with Heterogeneous Micropores, *The Journal of Physical Chemistry C* 121 (2017) 7164–7174. <https://doi.org/10.1021/acs.jpcc.7b01287>.
- [71] X. Zhang, M. Kar, T.C. Mendes, Y. Wu, D.R. MacFarlane, Supported Ionic Liquid Gel Membrane Electrolytes for Flexible Supercapacitors, *Adv Energy Mater* 8 (2018). <https://doi.org/10.1002/aenm.201702702>.
- [72] C.-W. Liew, S. Ramesh, Electrical, structural, thermal and electrochemical properties of corn starch-based biopolymer electrolytes, *Carbohydr Polym* 124 (2015) 222–228. <https://doi.org/10.1016/j.carbpol.2015.02.024>.
- [73] B. Pal, S. Yang, S. Ramesh, V. Thangadurai, R. Jose, Electrolyte selection for supercapacitive devices: a critical review, *Nanoscale Adv* 1 (2019) 3807–3835. <https://doi.org/10.1039/C9NA00374F>.
- [74] C.-C. Hu, E. Chen, J.-Y. Lin, Capacitive and textural characteristics of polyaniline-platinum composite films, *Electrochim Acta* 47 (2002) 2741–2749. [https://doi.org/10.1016/S0013-4686\(02\)00139-1](https://doi.org/10.1016/S0013-4686(02)00139-1).
- [75] Metrohm, Electrochemical Impedance Spectroscopy (EIS) on battery electrodes using NOVA, Application Note AN-EIS-005 (2014).
- [76] A.Ch. Lazanas, M.I. Prodromidis, Electrochemical Impedance Spectroscopy—A Tutorial, *ACS Measurement Science Au* 3 (2023) 162–193. <https://doi.org/10.1021/acsmeasuresciau.2c00070>.
- [77] C. Portet, P.L. Taberna, P. Simon, C. Laberty-Robert, Modification of Al current collector surface by sol–gel deposit for carbon–carbon supercapacitor applications, *Electrochim Acta* 49 (2004) 905–912. <https://doi.org/10.1016/j.electacta.2003.09.043>.
- [78] I. Yang, S.-G. Kim, S.H. Kwon, M.-S. Kim, J.C. Jung, Relationships between pore size and charge transfer resistance of carbon aerogels for organic electric double-layer capacitor electrodes, *Electrochim Acta* 223 (2017) 21–30. <https://doi.org/10.1016/j.electacta.2016.11.177>.

-
- [79] S.H. Kwon, E. Lee, B.-S. Kim, S.-G. Kim, B.-J. Lee, M.-S. Kim, J.C. Jung, Preparation of activated carbon aerogel and its application to electrode material for electric double layer capacitor in organic electrolyte: Effect of activation temperature, *Korean Journal of Chemical Engineering* 32 (2015) 248–254. <https://doi.org/10.1007/s11814-014-0215-z>.
- [80] M.E. Orazem, B. Tribollet, *Electrochemical Impedance Spectroscopy*, Wiley, 2008. <https://doi.org/10.1002/9780470381588>.
- [81] I. Stepniak, A. Ciszewski, Electric double layer capacitors with polymer hydrogel electrolyte based on poly(acrylamide) and modified electrode and separator materials, *Electrochim Acta* 54 (2009) 7396–7400. <https://doi.org/10.1016/j.electacta.2009.07.072>.
- [82] E. Cevik, S.T. Gunday, A. Bozkurt, A. Iqbal, S.M. Asiri, A.N. Alqarni, A. Almofleh, Scalable, Quasi-Solid-State Bio-polymer Hydrogel Electrolytes for High-Performance Supercapacitor Applications, *ACS Sustain Chem Eng* 10 (2022) 10839–10848. <https://doi.org/10.1021/acssuschemeng.2c02281>.
- [83] N. Anjum, N. Joyal, J. Iroegbu, D. Li, C. Shen, Humidity-modulated properties of hydrogel polymer electrolytes for flexible supercapacitors, *J Power Sources* 499 (2021) 229962. <https://doi.org/10.1016/j.jpowsour.2021.229962>.
- [84] C. Shen, Y. Xie, M. Sanghadasa, Y. Tang, L. Lu, L. Lin, Ultrathin Coaxial Fiber Supercapacitors Achieving High Energy and Power Densities, *ACS Appl Mater Interfaces* 9 (2017) 39391–39398. <https://doi.org/10.1021/acsami.7b12047>.
- [85] R. Kötz, P.W. Ruch, D. Cericola, Aging and failure mode of electrochemical double layer capacitors during accelerated constant load tests, *J Power Sources* 195 (2010) 923–928. <https://doi.org/10.1016/j.jpowsour.2009.08.045>.
- [86] P. Forouzandeh, V. Kumaravel, S.C. Pillai, Electrode Materials for Supercapacitors: A Review of Recent Advances, *Catalysts* 10 (2020) 969. <https://doi.org/10.3390/catal10090969>.
- [87] N.A. Choudhury, S. Sampath, A.K. Shukla, Gelatin Hydrogel Electrolytes and Their Application to Electrochemical Supercapacitors, *J Electrochem Soc* 155 (2008) A74. <https://doi.org/10.1149/1.2803501>.

-
- [88] S. Sampath, N.A. Choudhury, A.K. Shukla, Hydrogel membrane electrolyte for electrochemical capacitors, *Journal of Chemical Sciences* 121 (2009) 727–734. <https://doi.org/10.1007/s12039-009-0087-7>.
- [89] D. Kamei, D. Hazarika, N.A. Choudhury, Pure and KI-doped glyoxal-crosslinked gelatin hydrogel membrane electrolytes for solid-state EDLCs, *Mater Today Chem* 43 (2025) 102470. <https://doi.org/10.1016/j.mtchem.2024.102470>.
- [90] G. Li, X. Zhang, M. Sang, X. Wang, D. Zuo, J. Xu, H. Zhang, A supramolecular hydrogel electrolyte for high-performance supercapacitors, *J Energy Storage* 33 (2021) 101931. <https://doi.org/10.1016/j.est.2020.101931>.
- [91] X. Gao, Q. Hu, K. Sun, H. Peng, X. Xie, H.A. Hamouda, G. Ma, A novel all-in-one integrated flexible supercapacitor based on self-healing hydrogel electrolyte, *J Alloys Compd* 888 (2021) 161554. <https://doi.org/10.1016/j.jallcom.2021.161554>.
- [92] G. Zhou, L. Yang, W. Li, C. Chen, Q. Liu, A Regenerable Hydrogel Electrolyte for Flexible Supercapacitors, *IScience* 23 (2020) 101502. <https://doi.org/10.1016/j.isci.2020.101502>.
- [93] H. Li, T. Lv, N. Li, Y. Yao, K. Liu, T. Chen, Ultraflexible and tailorable all-solid-state supercapacitors using polyacrylamide-based hydrogel electrolyte with high ionic conductivity, *Nanoscale* 9 (2017) 18474–18481. <https://doi.org/10.1039/C7NR07424G>.
- [94] C. Lu, X. Chen, All-Temperature Flexible Supercapacitors Enabled by Antifreezing and Thermally Stable Hydrogel Electrolyte, *Nano Lett* 20 (2020) 1907–1914. <https://doi.org/10.1021/acs.nanolett.9b05148>.
- [95] Q. Liu, D. Wu, T. Wang, Y. Guo, Polysaccharide of agar based ultra-high specific surface area porous carbon for superior supercapacitor, *Int J Biol Macromol* 228 (2023) 40–47. <https://doi.org/10.1016/j.ijbiomac.2022.12.126>.
- [96] H. Wada, S. Nohara, N. Furukawa, H. Inoue, N. Sugoh, H. Iwasaki, M. Morita, C. Iwakura, Electrochemical characteristics of electric double layer capacitor using sulfonated polypropylene separator impregnated with polymer hydrogel electrolyte, *Electrochim Acta* 49 (2004) 4871–4875. <https://doi.org/10.1016/j.electacta.2004.05.041>.

-
- [97] M.S. Lal, A. Arjunan, V. Balasubramanian, R. Sundara, Redox-active polymer hydrogel electrolyte in biowaste-derived microporous carbon-based high capacitance and energy density ultracapacitors, *Journal of Electroanalytical Chemistry* 870 (2020) 114236. <https://doi.org/10.1016/j.jelechem.2020.114236>.

CHAPTER 4

Sustainable and Robust Oxalate Cross-linked Quasi-Solid Chitosan Hydrogel Membrane Electrolyte for Durable Solid-State Electrical Double Layer Capacitors

This chapter presents the synthesis, characterizations of OCCHMEs for application as electrolyte cum separator in EDLCs. OCCHMEs were fabricated by ionic crosslinking of chitosan with potassium oxalate, and their physicochemical properties such as WU, dissolution stability, crystallinity, and mechanical strength were examined. Structural and morphological features of the membranes were analysed using FTIR, XRD, FE-SEM, and EDX. Electrochemical techniques, including transference number measurement, LSV, CV, EIS, and GCD were employed to evaluate conductivity, transport parameters, electrochemical stability window, capacitance, resistance, and energy storage performance of the EDLCs utilizing OCCHMEs.

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4.1 Introduction

The global energy sector is undergoing a profound transformation, driven by the urgent imperative to reduce reliance on finite fossil fuel resources and to mitigate the environmental impacts associated with their extraction and use [1]. As global electricity demand continues to rise, particularly sectors such as transportation, communications, and smart grids, the development of efficient and sustainable energy storage technologies has become paramount [2]. Among various electrochemical ESSs, ESs, and particularly EDLCs, have emerged as a critical class of devices offering high power density, ultrafast charge-discharge capability, and exceptional cycle life. EDLC stores energy by the interfacial electrostatic accumulation of ions, avoiding faradaic redox reactions and thus offering long operational life and safety advantages over batteries [3]. However, the effectiveness of EDLCs is strongly influenced by the properties of their internal components, most notably the electrolyte. Electrolytes serve as the medium for ionic conduction between electrodes and critically dictate parameters such as operating voltage window, ion transport kinetics, and overall energy density [4]. Conventional EDLCs predominantly utilize liquid electrolytes viz., aqueous, organic, or ionic liquids for their high ionic conductivity and ease of integration [5]. Nevertheless, liquid-based systems are limited by drawbacks including leakage, evaporation, thermal instability, and potential toxicity, all of which compromise device safety and long-term viability [6,7].

In recent years, GPEs have gained considerable interest as a middle ground between liquid and SSEs [8,9]. Particularly HPEs, where water serves as the plasticizer, offer compelling advantages such as high ionic mobility, biocompatibility, mechanical flexibility, and safer operating process [10–14]. These attributes render HPEs ideal for flexible and wearable supercapacitor platforms. HPEs typically rely on cross-linked polymeric networks that imbibe water and dissolved ions, facilitating ion transport while preventing leakage and ensuring structural coherence [15,16]. While synthetic polymers such as PEO, PAA, and PVA have been traditionally used in hydrogel systems, the increasing emphasis on green chemistry and sustainability has sparked a surge of interest in natural, biodegradable polymers [17].

Natural materials have emerged as promising building blocks for energy storage devices owing to their abundance, sustainability, and intrinsic functional properties. Carbon-rich biomass, for example, can be converted into porous carbons with high surface area and heteroatom functionalities, which are highly effective as electrode materials in supercapacitors and batteries [18]. Similarly, natural polymers have been engineered into membranes, binders, and separators that combine low cost with environmental compatibility [19]. Among these, biopolymers such as cellulose, chitosan, starch, carrageenan, and gelatin have gained particular attention due to their renewable nature, biodegradability, and chemical versatility. Their polar functional groups ($-\text{OH}$, $-\text{NH}_2$, $-\text{COOH}$) enable strong interactions with ionic species and dopants, thereby facilitating enhanced ionic conductivity and improved electrode-electrolyte interfacial contact [20]. In addition, their hydrophilic nature supports efficient ion migration within hydrogel matrices, making them attractive candidates for quasi-solid-state electrolytes in EDLCs and batteries [21]. Beyond electrolytes, biopolymers have also been employed as binders, separators, and electrode modifiers, contributing to safety, flexibility, and sustainability in device configurations [22]. Collectively, natural materials and particularly biopolymer-based systems, represent eco-friendly, multifunctional alternatives to conventional synthetic polymers, with significant potential to advance the performance and sustainability of next-generation energy storage technologies [23].

Chitosan, a natural polymer derived from deacetylation of chitin, is widely favored for hydrogel matrix design owing to its biocompatibility, cationic nature, and functional group diversity [24]. The availability of hydroxyl and amino groups facilitates various crosslinking mechanisms, of which ionic crosslinking is especially attractive due to its mild reaction conditions and environmental friendliness. The ionic association between $-\text{NH}_3^+$ groups on chitosan and multivalent anions forms adaptable, physically stable hydrogel frameworks capable of retaining water and conducting ions efficiently [25]. Crosslinkers like sulfate [26], citrate [27], and carbonate [17,28] have been frequently utilized to tune the swelling, mechanical strength, and conductivity of chitosan-based hydrogels. Oxalate anions, being bidentate and highly soluble in water, offer dual coordination sites that may lead to denser ionic networks and enhanced

matrix uniformity. Their symmetrical geometry, coupled with a high charge density, provides a basis for forming compact and potentially more conductive polymer networks. Although several studies have examined oxalate-based hydrogel systems [29–31], these typically incorporate additional polymers or chemical modifiers, thereby obscuring the intrinsic role of potassium oxalate as a standalone ionic crosslinker. The synthesis of hydrogel membranes composed exclusively of chitosan and potassium oxalate via ionic gelation and their application as SSEs in EDLCs remains unreported. This research gap is particularly significant given the bidentate coordination capacity and high charge density of oxalate dianions, which offer favorable crosslinking within the polycationic framework of chitosan. Furthermore, the distinct physicochemical contributions of oxalate anions and potassium cations to membrane properties such as WU, DR, and WVTR remain largely unexplored. Building upon our prior investigation involving sodium carbonate cross-linked chitosan membranes [17], where the structure–property relationships of ionically cross-linked hydrogels were systematically explored for EDLC applications, the present study shifts focus to oxalate ions as alternative divalent crosslinkers. This comparative trajectory offers deeper mechanistic insights into how different ionic species influence membrane architecture, hydration behavior, and electrochemical performance.

In this study, a novel potassium Oxalate Cross-linked Chitosan Hydrogel Membrane Electrolytes (OCCHMEs) were synthesized by ionic crosslinking, devoid of any additional chemical agents. These membranes were comprehensively evaluated for their structural features, hydration dynamics, ionic conductivity, mechanical robustness, and electrochemical behavior. Key parameters such as WU, DR, WVTR, electrochemical stability window, and long-term cycling performance in real EDLC assemblies were systematically assessed. The findings offer new insights into oxalate-based ionic crosslinking in biopolymer hydrogels, underscoring its viability for next-generation, sustainable SSE applications in high-performance energy storage devices.

4.2 Materials and methods

4.2.1 Materials

Chitosan (CAS No.: 9012-76-4, Loba Chemie Pvt. Ltd., 75 % deacetylation, di-Potassium oxalate monohydrate ($K_2C_2O_4 \cdot H_2O$) (Merck), glacial CH_3COOH (Merck, 90-100 %), Cabot BPC, PVA (Loba Chemie Pvt. Ltd), ethanol (99.9 %), and glutaraldehyde (25 %).

4.2.2 Preparation of aqueous chitosan stock solution

A 2 % (v/v) acetic acid solution was first prepared by adding 2 mL of glacial acetic acid into a 100 mL volumetric flask and diluting to the mark with deionized (DI) water. To prepare 100 mL of 2 % (w/v) chitosan stock solution, 2 g of chitosan flakes were transferred into a clean beaker and the 100 mL freshly prepared 2 % acetic acid solution was added. The mixture was covered to minimize evaporation and stirred magnetically using 450 rpm at room temperature for 24 h to ensure solubilization of the polymer. Subsequently, the solution was further stirred at around 60 °C in water bath for 2 h to enhance homogeneity and solubility. The resulting clear and viscous chitosan stock solution was used only after complete cooling for the preparation of hydrogels, or stored until further use.

4.2.3 Preparation of Oxalate Cross-linked Chitosan Hydrogel

Firstly, potassium oxalate crosslinker solutions of different concentrations (w/v) were freshly prepared by dissolving the calculated amount of potassium oxalate powder in DI water. For the preparation of Oxalate-crosslinked Chitosan Hydrogels, 10 mL of the chitosan stock solution (prepared as described in Section 2.2) was transferred into a 25 mL glass beaker, followed by the addition of 2 mL of potassium oxalate solution of the desired concentration. The mixture was magnetically stirred at ~500 rpm under ambient conditions in a covered beaker. As stirring progressed, the solution gradually increased in viscosity, and visible lump-like hydrogel domains began to form within minutes, indicating the onset of ionic crosslinking between protonated chitosan chains and oxalate ions. Stirring was continued for 2-3 h until a uniform, self-standing hydrogel was obtained. The resulting OCCHs were white and semi-translucent in appearance. Each preparation was performed in triplicate to confirm reproducibility.

4.2.4 Preparation of Oxalate Cross-linked Chitosan Hydrogel Membrane Electrolyte

The synthesis of the oxalate crosslinked chitosan hydrogel membrane electrolyte (OCCHME) was carried out as illustrated in Fig.4.1 The preparation followed the same procedure as described for the synthesis of the OCCH in Section 4.2.3, with a modification in the membrane formation step. Prior to complete hydrogel formation, the crosslinked viscous chitosan-oxalate mixture was carefully cast onto a sterile plastic Petri plate ($90 \times 15 \text{ mm}^2$) to form a uniform film. The cast film was allowed to stand under ambient conditions for 48 hours to ensure solvent evaporation and complete membrane drying in a hot air oven. The dried membrane was then immersed in a freshly prepared potassium oxalate solution for 30 minutes to promote secondary ionic crosslinking, thereby enhancing membrane integrity and mechanical stability. Excess crosslinker was removed by decantation, and the membrane was subsequently rinsed multiple times with deionized (DI) water to eliminate any unbound ions or residual reagents. The resulting OCCHME was stored in DI water at room temperature until further use.

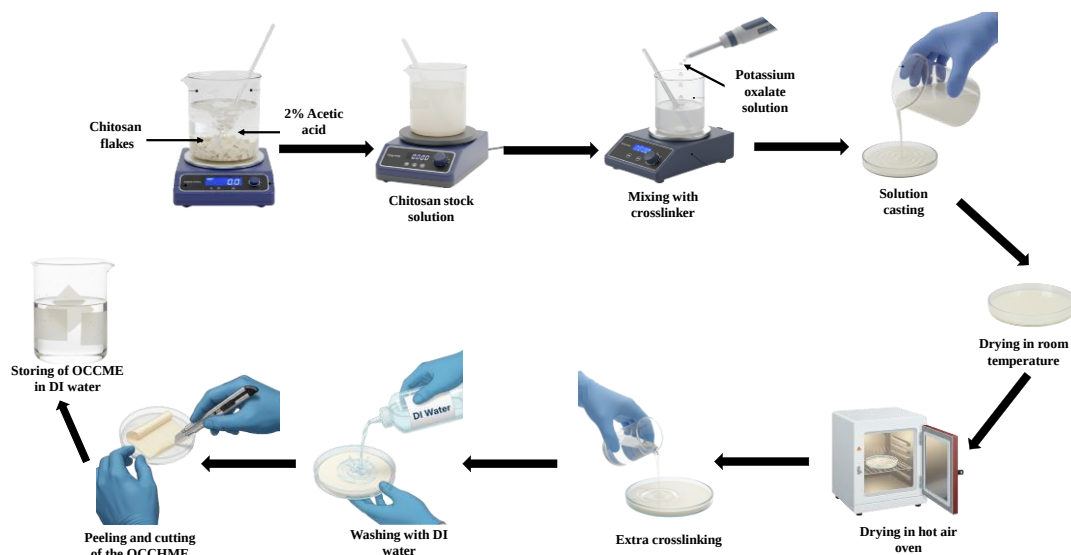


Fig.4.1. Schematic representation of the preparation of OCCHME.

4.2.5 FT-IR spectroscopic studies

A Perkin Elmer Spectrum Two FT-IR spectrometer was employed to record the FTIR spectra of $K_2C_2O_4$ powder, chitosan flakes and OCCHME. All samples were scanned from 4000 to 500 cm^{-1} wavenumber. For chitosan flakes and $K_2C_2O_4$ powder, FTIR pellets were prepared by thoroughly mixing the samples with KBr powder followed by compression under a hydraulic press applying a force of 255 $kg\ cm^{-2}$.

4.2.6 DC and AC ionic conductivity studies

DC and AC ionic conductivities of the OCCHMEs were studied as a function of varying $K_2C_2O_3$ concentration. This was done by placing an OCCHME having an area of 1 cm^2 between two SS electrodes of the same area. This assembly is referred to as the HMEA. EIS was conducted to determine the ionic conductivity employing potential amplitude of 5 mVrms across. To obtain the DC ionic conductivity (σ_{DC}) from the Nyquist plot of EIS, the R_b value was evaluated. Finally, the value of R_b was employed to calculate the conductivity using the equation given below [32,33].

$$\sigma_{DC} = \frac{L}{A \times R_b} \quad (1)$$

where, L and A are the thickness and area of the OCCHME.

AC conductivities (σ_{AC}) of OCCHMEs with varying concentration of potassium oxalate were evaluated by using the following equation [32].

$$\sigma_{AC} = \left[\frac{z'}{z'^2 + z''^2} \right] \times \left(\frac{L}{A} \right) \quad (2)$$

Where, z' and z'' are the real and imaginary parts of the Nyquist plot.

4.2.7 Dielectric studies

Key parameters, including the dielectric constant (ϵ'), dielectric loss (ϵ''), dielectric loss tangent ($\tan(\delta)$), and dielectric modulus of real (M') as well as imaginary (M'') are important to know the ion transport within polymer-based electrolytes. Here, ϵ' , ϵ'' , $\tan(\delta)$, M' and M'' for OCCHMEs were analysed using the following equations [34,35].

$$\epsilon' = \frac{z''}{\omega C_0(z'^2 + z''^2)} \quad (3)$$

$$\epsilon'' = \frac{z'}{\omega C_0(z'^2 + z''^2)} \quad (4)$$

$$\tan(\delta) = \frac{\epsilon''}{\epsilon'} \quad (5)$$

$$M' = \frac{\epsilon'}{\epsilon'^2 + \epsilon''^2} \quad (6)$$

$$M'' = \frac{\epsilon''}{\epsilon'^2 + \epsilon''^2} \quad (7)$$

Here, $\omega = 2\pi f$, where f is frequency; $C_0 = \frac{\epsilon_0 A}{L}$ is vacuum capacitance, where ϵ_0 (equal to $8.85 \times 10^{-14} \text{ F cm}^{-1}$) is the permittivity of free space, L is the membrane thickness, A is blocking electrode area.

4.2.8 Determination of ion transport parameters

EIS method was employed to calculate the ion transport parameters. The diffusion coefficient (D), ionic mobility (μ), and ion number density (n) were calculated based on the following established equations that provide the theoretical framework for interpreting impedance data [36]. The following equation can be used to determine D value [37].

$$D = \left(\frac{(k\epsilon_0\epsilon' A)^2}{\tau} \right) \quad (8)$$

In Eq. (8), k denotes the reciprocal of CPE, while τ represents the reciprocal of the angular frequency (ω), which can be obtained using the frequency (f) from equation $\omega = 2\pi f$. A refers to the geometrical area of OCCHMEs, and ϵ_0 is the vacuum permittivity, valued at $8.85 \times 10^{-12} \text{ Fm}^{-1}$. The dielectric constant (ϵ') is determined using the equation $\epsilon_r = \frac{z''}{\omega C_0(z'^2 + z''^2)}$; where the vacuum capacitance (C_0) is calculated using

$C_0 = \frac{\varepsilon_0 A}{L}$ with L denoting the thickness of OCCHMEs. Furthermore, ionic mobility, μ can be determined employing equation (9) [37].

$$\mu = \left(\frac{eD}{k_B T} \right) \quad (9)$$

Where, T , k_B , and e represents the absolute temperature, Boltzmann constant (valued as $1.38 \times 10^{-23} \text{ JK}^{-1}$), and electric charge (valued as $1.602 \times 10^{-19} \text{ C}$), respectively.

Ion number density, n for the OCCHMEs was obtained employing the Eq. (10) [37].

$$n = \left(\frac{\sigma_{DC} k_B T \tau}{(e k \varepsilon_0 \varepsilon' A)^2} \right) \quad (10)$$

4.2.9 WU studies

WU measurements of OCCHME was conducted on samples cut into $4 \times 4 \text{ cm}^2$ portions. The OCCHME was immersed in DI water within a beaker to ensure complete absorption of water in its polymeric matrices. Following the removal of excess water using filter paper, the hydrated membrane was weighed (W_h). The OCCHME was subjected to drying in an oven for 48 hours at 45°C to eliminate absorbed moisture. The OCCHME was weighted every 12 hours until a consistent dry weight (W_d) was achieved to ensure full evaporation. The percentage of WU was calculated from the dry and wet weights employing the formula shown below [26].

$$\text{WU (\%)} = \left(\frac{W_h - W_d}{W_d} \right) \times 100 \quad (11)$$

4.2.10 DR study

To determine DR (%), OCCHME was initially cut into 2 cm^2 square. The initial wet weights (W_1) of the OCCHMEs were noted prior to testing. To evaluate their dissolution behavior under accelerated conditions, the OCCHMEs were immersed in boiling hot DI water for 6 hours. This was followed by oven-drying the samples at 35°C for 48 hours to get the dry weight (W_2) of the OCCHMEs. The DR % was then calculated using the following equation [38]

$$DR (\%) = \left(\frac{W_1 - W_2}{W_1} \right) \times 100 \quad (12)$$

4.2.11 WVTR study

The WVTR was determined using the Wet Cup Method in accordance with ASTM E-96-95 [39]. A plastic Petri dish containing 30 mL of DI water was sealed with the OCCHME sample, which had an exposed area of $4.29 \times 10^{-3} \text{ m}^2$. After recording the initial mass, the entire setup was placed in an oven maintained at 34°C . Weight measurements were taken every 12 hours. The WVTR ($\text{g m}^{-2} \text{ h}^{-1}$) for the OCCHME was then calculated using the following equation [40,41].

$$WVTR = \frac{G}{t \times A} \quad (13)$$

Here, G represents the mass of water lost in grams, t is the time duration in hours, and A is the surface area of the OCCHME that was exposed to vapor transmission (in m^2).

4.2.12 TGA studies

TGA of UCM and OCCHME was investigated using a TGA4000 PerkinElmer thermogravimetric analyser, with measurements conducted under a controlled N_2 atmosphere. The thermal analysis was performed over a temperature range of room temperature to 800°C , with a uniform heating rate of $10^\circ\text{C min}^{-1}$.

4.2.13 DSC studies

The thermal behavior of UCM and OCCHME was analyzed using a NETZSCH DSC 204F1 Phoenix Differential Scanning Calorimeter, operated under a nitrogen atmosphere to maintain controlled conditions. The thermal analysis spanned from room temperature to 250°C , with a precise heating rate of $10^\circ\text{C min}^{-1}$, enabling a detailed examination of the thermal transitions, melting behaviour, and heat flow properties of these materials.

4.2.14 Polarized Optical Microscopy

UCM and OCCHME were extruded on glass plate and tested under an Olympus BX51 polarized optical microscope. Images were captured by a camera associated with the microscope with shutter speed of 1/320.

4.2.15 XRD studies

The XRD analysis was used to examine the structural characteristics of $K_2C_2O_4$ powder, UCM and OCCHME. The analyses were conducted using a Bruker D8 Advance X-ray diffractometer (Germany), equipped with Cu radiated Ni-filter at 30 mA and 30 kV. Diffraction patterns were recorded over a 2θ range of 5° to 65° . XRD deconvolution for UCM and OCCHMEs were carried out using OriginPro software (2022). Gaussian fitting functions were applied to distinguish and quantify the crystalline (A_c) and amorphous (A_a) regions of the diffraction profiles. The degree of crystallinity (X_c), was then evaluated using the formula [42]

$$X_c = \left[\frac{A_c}{A_c + A_a} \right] \times 100 \% \quad (14)$$

4.2.16 FE-SEM and EDX studies

The surface morphology of the UCM and OCCHME was analyzed using a ZEISS Sigma FE-SEM. Additionally, the elemental composition of the samples was determined through EDX spectroscopy.

4.2.17 Mechanical strength studies

The mechanical integrity of UCM and OCCHME were tested using Universal Testing Machine (Instron, E-3000) set at a stretching rate of 1 mm min^{-1} .

4.2.18 Transference number measurement

The DC polarization technique was employed to determine the ion transference number (t_{ion}). The HMEA was polarized by a constant voltage of 1 V and a current versus time plot was recorded. Initial current (I_0) reflects the contribution from both electronic and ionic charge carriers. Over time, as the current stabilizes, a steady-state

current (I_{ss}) was obtained, which corresponds exclusively to electronic conduction. The t_{ion} was calculated employing the following equation [42].

$$t_{ion} = \frac{I_0 - I_{ss}}{I_0} \quad (15)$$

Anionic and cationic transference numbers are critical parameters for evaluating the efficiency and performance of electrolytes. Accurate determination of the ionic conductivity requires the quantification of individual ion contributions. A widely adopted method for this purpose is the Bruce-Vincent technique, which integrate DC polarization employing AC impedance. AC impedance measurements are performed both before and after the polarization to determine any changes in the interfacial resistances. The cationic transference number (t_{cation}) is quantified by the following equation [43,44].

$$t_{cation} = \frac{I_{ss} (\Delta V - I_0 R_0)}{I_0 (\Delta V - I_{ss} R_{ss})} \quad (16)$$

Where, R_0 is the initial resistance and R_{ss} is the resistance at steady-state.

4.2.19 LSV study

LSV was employed to assess the decomposition voltage of the OCCHME. This was done by sweeping the HMEA with a voltage of 1 to 3 V. A sudden increase in the current during the sweep marks its decomposition.

4.2.20 Electrochemical characterizations of OCCHME

All electrochemical characterizations, excluding cycle life analysis, were performed using the same Metrohm M204 Multi Autolab and cycle life analysis was conducted using a Battery Analyzer (MTI Corporation, USA). The electrode material used for this experiment was prepared using established procedures [5], as shown in the schematic diagram in Fig.4.2. Accordingly, 0.1 g of BPC was dispersed in 1 mL of ethanol and stirred magnetically for 1 hour to form a uniform suspension. Subsequently, 0.83 mL of 3% (w/v) aqueous PVA solution was added dropwise, followed by the gradual addition of 0.83 mL glutaraldehyde solution. Concentrated

sulfuric acid was then introduced dropwise as a catalyst. The resulting mixture was sonicated in a water bath for 3 hours and further stirred for 48 hours to obtain a well-dispersed ink. This electrode ink was coated onto the SS current collectors using a paintbrush maintaining a consistent active material loading of approximately 1 mg cm^{-2} . The solid-state EDLCs were assembled using these electrodes and the OCCHME as electrolytes-cum-separators. The EDLCs were sealed with Teflon tape and secured with Teflon holders as depicted in Fig.4.2. Parafilm was wrapped around the holder to prevent water evaporation or leakage.

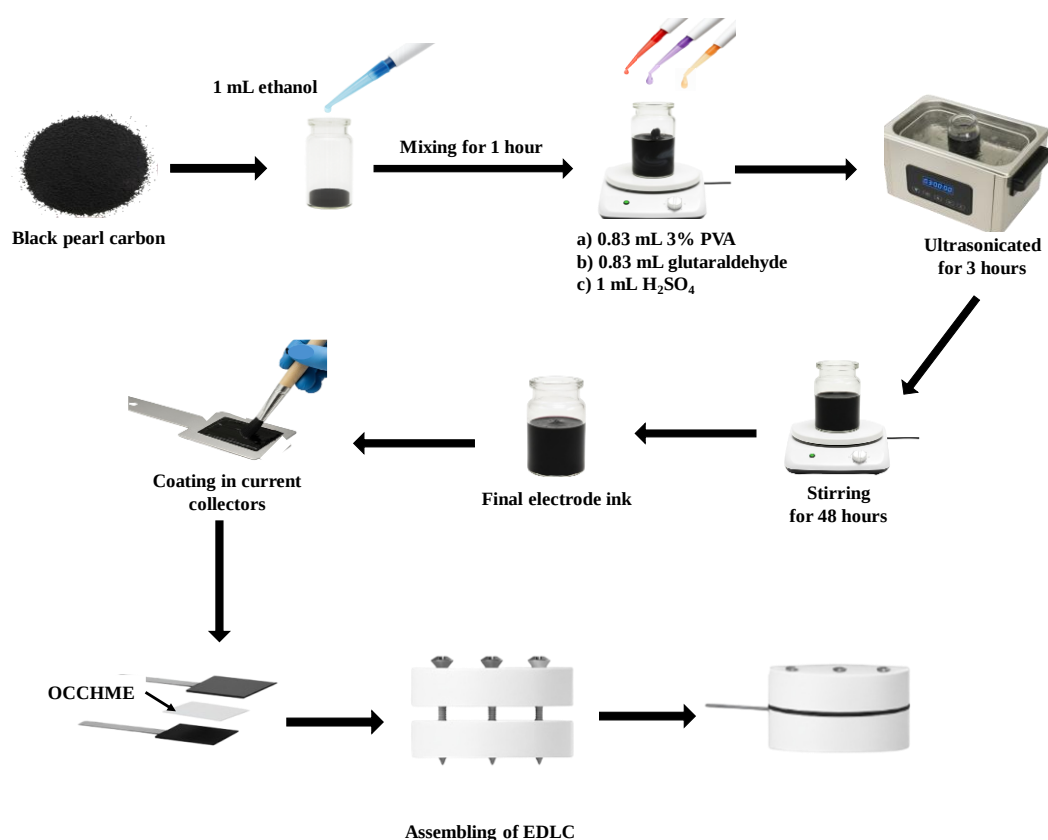


Fig.4.2 Schematic illustration of preparation stages of BPC-based electrode ink and the assembling of EDLC.

Electrochemical performance was evaluated via CV, GCD, and EIS. CV scans were performed within a potential window of 0-1 V at scan rates ranging from 5 to 100 mV s^{-1} . GCD testing was carried out over the same voltage range at current densities between 1 to 5 mA cm^{-2} . EIS measurements were conducted across a frequency range of 1 MHz to 0.1 Hz with a 5 mV rms amplitude [45].

The EEC diagram was derived through a detailed analysis of the EIS data, utilizing the "Fit and Simulation" tool within Nova 2.1 software of the Multi Autolab workstation. This fitting process employed a non-linear least squares algorithm to refine the alignment between the measured EIS data and the theoretical model. The goal was to minimize discrepancies between the experimental and simulated impedance values, with the quality of the fit indicated by the chi-squared (χ^2) statistic [46]. A lower χ^2 value suggests a closer match between the model and the data, reflecting how accurately the circuit model represents the electrochemical behavior of the hydrogel electrolyte [47]. From the Bode plot of phase angle versus frequency, obtained during EIS, the relaxation time constant (τ) was calculated by employing the following equation [48].

$$\tau = \frac{1}{2\pi f^*} \quad (17)$$

Where, f^* is the frequency in Hz corresponds to the phase angle of 45° .

The real and imaginary components (C' and C'') of capacitance obtained from the Bode plot were calculated from the following equations [49].

$$C'(\omega) = \frac{-z''(\omega)}{\omega |z(\omega)|^2} \quad (18)$$

$$C''(\omega) = \frac{z'(\omega)}{\omega |z(\omega)|^2} \quad (19)$$

The b-value analysis was performed for the EDLCs to understand its capacitive contributions. The relationship between peak current (i) and scan rate (v) follows a power-law equation [50,51].

$$i = av^b \quad (20)$$

Where, a is a constant, and b is the slope obtained from the log-log plot.

Thus, equation (20) was linearized as,

$$\log(i) = b \log(v) + \log(a) \quad (21)$$

The slope of the $\log(i)$ versus $\log(v)$ plot provides the b-value.

To further quantify these contributions, the current response at a given potential was separated into capacitive and diffusion-controlled terms using the following relationship [52,53].

$$i(v) = k_1 v + k_2 v^{1/2} \quad (22)$$

where $k_1 v$ represents the surface-controlled capacitive contribution, and $k_2 v^{1/2}$ corresponds to the diffusion-controlled process. Rearranging equation (22) gives the following equation.

$$\frac{iv}{v^{1/2}} = k_1 v^{1/2} + k_2 \quad (23)$$

By plotting $\frac{iv}{v^{1/2}}$ against $v^{1/2}$, k_1 and k_2 can be extracted from the slope and intercept, respectively. The ratio of the capacitive contribution ($k_1 v$) to the total current provides a quantitative measure of capacitive dominance at each scan rate.

The cycle life stability of the EDLC was tested by analysing GCD at the constant current densities of 2 and 5 mA cm⁻², examining their performance till the end of their charge-discharge behaviour.

Areal capacitance C_A (mF cm⁻²), energy density E (μWh cm⁻²), as well as power density P (mW cm⁻²) of EDLCs were mathematically calculated analysing GCD plots employing equations (24), (25), and (26), respectively [54,55].

$$C_A = 2 \times \frac{I \times t_d}{A \times \Delta V} \quad (24)$$

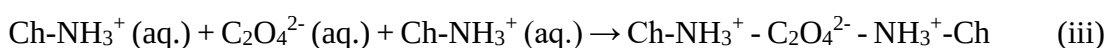
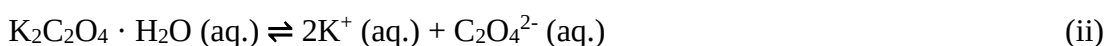
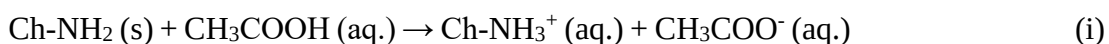
$$E = \frac{1}{2} \times \frac{1000}{3600} C_A \times (\Delta V)^2 \quad (25)$$

$$P = \frac{E}{t_d} \times 3600 \quad (26)$$

Where, I (mA) represents the current density, t_d represents discharge time, A denotes area (cm^2) of electrodes, and ΔV denotes potential window (V).

4.3 Results and discussion

The ionic interaction between chitosan and oxalate anions constitutes the core mechanism underlying the formation of the OCCHME, as mechanistically outlined in Fig.4.3 (A). Chitosan, a naturally occurring cationic polysaccharide, contains primary amine groups ($-\text{NH}_2$) at the C-2 position of the repeating glucosamine units [56]. In its native state, chitosan exhibits limited solubility in water due to the lack of readily ionizable groups. However, in the presence of dilute CH_3COOH , these amino functionalities undergo protonation, yielding positively charged ammonium moieties ($-\text{NH}_3^+$), which enhance solubility through intra- and intermolecular electrostatic repulsion, as depicted in Reaction (i). Simultaneously, the dissolution of dipotassium oxalate in aqueous medium leads to the generation of oxalate dianions ($\text{C}_2\text{O}_4^{2-}$) and potassium cations as shown in reaction (ii). The resulting oxalate anions serve as bidentate ionic linkers, bridging adjacent chitosan chains by interacting with protonated amine groups through electrostatic interactions, as outlined in Reaction (iii). This ionic complexation leads to the formation of a physically cross-linked, three-dimensional hydrogel matrix. The resulting hydrogel network is stabilized by these ionic bonds, enabling structural integrity and flexibility.



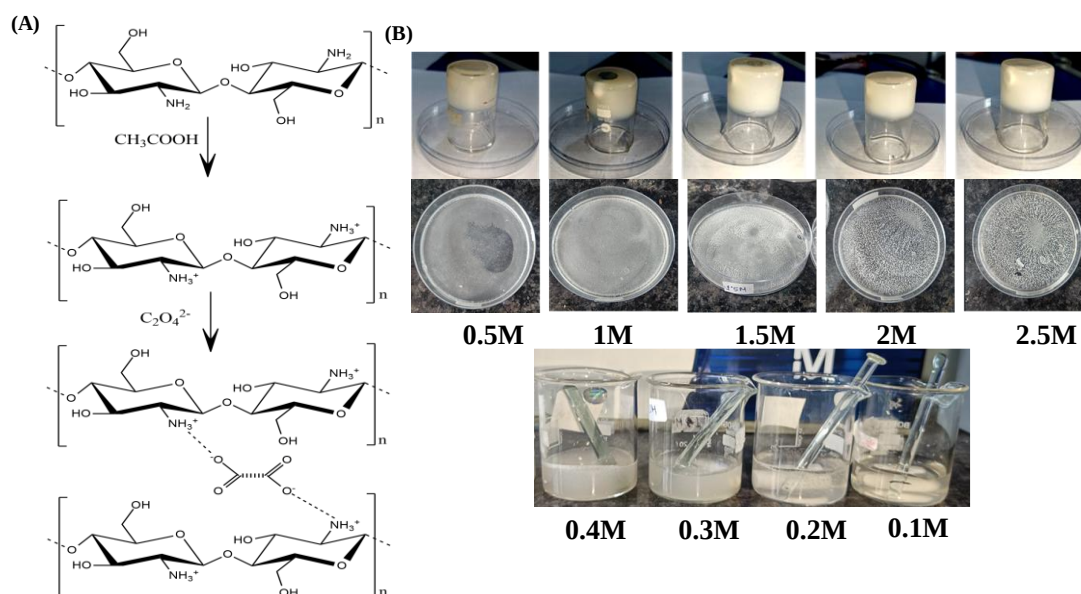


Fig.4.3 (A) Schematic diagram of the ionic crosslinking reaction between protonated chitosan and $K_2C_2O_4$; (B) visual comparison of hydrogel gelation and membrane formation behavior at different potassium oxalate concentrations.

To identify the optimal condition of potassium oxalate for the formation of robust OCCHME, a systematic optimization study was conducted by varying the molar concentration from 0.1-2.5 M and using fixed volume of the crosslinker in 10 mL of chitosan stock solution. The outcomes were recorded based on two key criteria viz., lump gel formation during initial ionic gelation and the physical integrity of the cast membranes after the drying process. The hydrogel lumps formed during gelation appear milky white and semi-translucent, while the corresponding OCCHME membranes exhibit a uniform whitish coloration upon drying. A visual summary of these results is provided in Table 4.1 and Fig.4.3 (B).

Table 4.1: Overview of the optimization procedure for synthesizing OCCHME, utilizing various concentrations and volumes of $K_2C_2O_4$ crosslinker in 10 mL of acidic chitosan solution.

$K_2C_2O_4$ Concentration (M)	$K_2C_2O_4$ Volume (mL)	Observation of OCCH formation behavior	Observation of OCCHME formation behavior

0.1	1	Not formed	Formed
	2	Not formed	Formed
0.2	1	Not formed	Formed
	2	Not formed	Formed
0.3	1	Not formed	Formed
	2	Not formed	Formed
0.4	1	Not formed	Formed
	2	Weak gel formation	Formed
0.5	1	Weak gel formation	Formed
	2	Strong gel formation	Formed
1.0	1	Weak gel formation	Formed but structural disintegration upon drying
	2	Strong gel formation	Formed but structural disintegration upon drying
1.5	1	Strong gel formation	Formed but structural disintegration upon drying
	2	Strong gel formation	Formed but structural disintegration upon drying
2.0	1	Strong gel formation	Formed but structural disintegration upon drying
	2	Strong gel formation	Formed but structural disintegration upon drying
2.5	1	Strong gel formation	Formed but structural disintegration upon drying
	2	Strong gel formation	Formed but structural disintegration upon drying

At higher crosslinker concentrations viz., 1.0 M to 2.5 M, the interaction between the oxalate ions and protonated amine groups ($-\text{NH}_3^+$) of chitosan chains was sufficiently strong to promote rapid and dense gelation, resulting in the formation of rigid hydrogel lumps. However, the corresponding membranes although successfully formed, but underwent structural disintegration upon drying. This failure is attributed to excessive

ionic crosslinking, which leads to internal stress accumulation, reduced polymer flexibility, and phase inhomogeneity during solvent evaporation. Such over-cross-linked networks are highly susceptible to microcrack propagation due to their reduced ability to dissipate mechanical stress. In contrast, when the crosslinker concentration was lowered below 0.5 M, the resulting gels were notably weaker and less cohesive, especially at 0.1 M and 0.2 M. These lower concentrations failed to produce visibly robust lump gels; however, the membranes cast from these solutions demonstrated excellent film-forming ability and mechanical integrity during drying. This observation suggests that at sub-optimal crosslinker concentrations, although complete ionic bridging of polymer chains was not achieved, the flexibility and water-retaining capacity of the membrane matrix were sufficiently preserved, allowing uniform shrinkage and stress relaxation during dehydration [57]. Interestingly, the hydrogel and membrane prepared at 0.5 M $\text{K}_2\text{C}_2\text{O}_4$ achieved an effective balance between ionic crosslinking and network flexibility. The gel exhibited appreciable lump formation during ionic interaction, and most importantly, the membrane retained its integrity upon drying, with no observable structural disintegration. This indicates that 0.5 M serves as a threshold concentration where chitosan chains are sufficiently cross-linked to yield a mechanically stable structure without reaching the brittleness associated with higher crosslinking densities. Thus, this two-step optimization study clearly identifies 0.5 M potassium oxalate with 2 mL volume as the ideal crosslinking condition, achieving a stable, flexible hydrogel membrane with no structural compromise. These insights are critical in the design of quasi-solid electrolytes, where both ion transport properties and mechanical integrity are crucial.

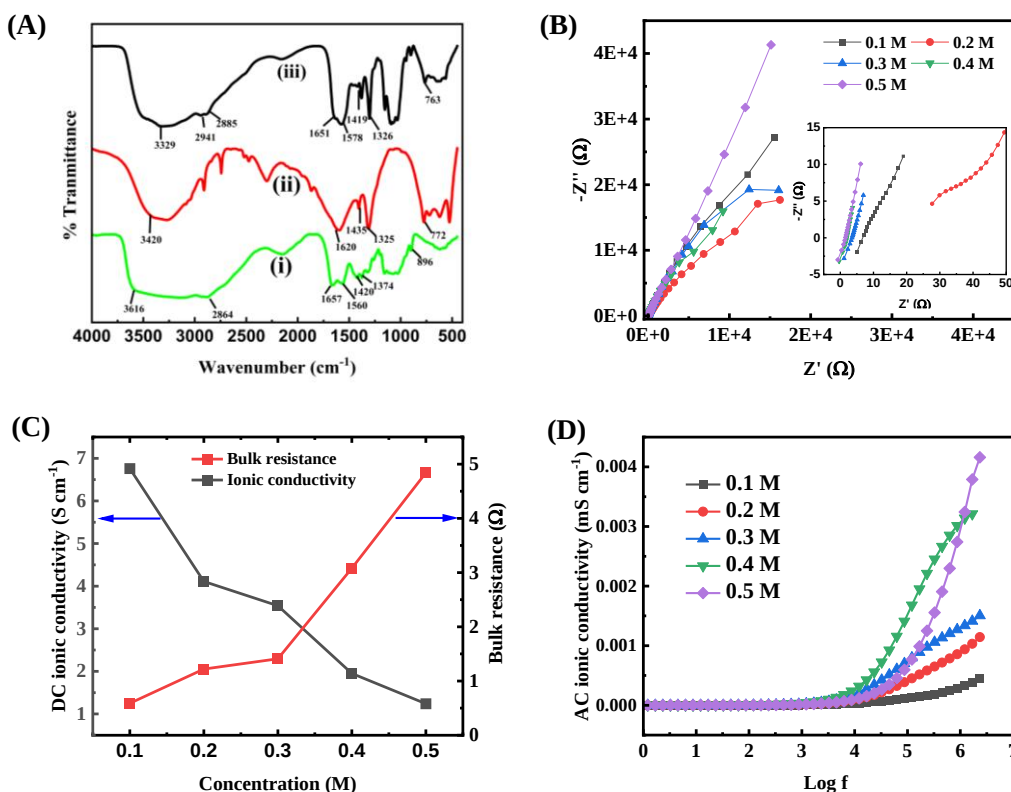


Fig.4.4 (A) FTIR spectra of K₂C₂O₄ powder (i), chitosan flakes (ii), and OCCHME (iii); (B) Nyquist plots obtained during ionic conductivity determination for OCCHMEs with varying crosslinker concentrations (the inserts provide enlarged views of the regions with higher frequencies); (C) Graph of R_b and DC ionic conductivity as a function of K₂C₂O₄ concentrations; (D) Graph of AC ionic conductivity as a function of K₂C₂O₄ concentrations.

The FTIR spectra of chitosan flakes, potassium oxalate powder, and the OCCHME are shown in Fig.4.4 (A). The spectrum of chitosan flakes exhibits a broad absorption band in the 3100–3600 cm^{-1} region, attributed to overlapping O–H and N–H stretching vibrations arising from inter- and intramolecular hydrogen bonding [58,59]. A characteristic aliphatic C–H stretching band appears at 2864 cm^{-1} , confirming the presence of methylene groups. The absorption peaks observed at 1657 cm^{-1} and 1560 cm^{-1} correspond to amide-I (C=O stretching) and amide-II (N–H bending), respectively, which are associated with residual N-acetyl groups from incomplete deacetylation of chitin [60]. Additionally, the presence of a peak at 896 cm^{-1} confirms the β -glycosidic linkages (β -1 $\rightarrow$ 4) within the polysaccharide backbone [61]. Small but

noticeable bands at 1420 cm^{-1} and 1374 cm^{-1} can be attributed to scissoring vibrations of -NH_2 , indicative of interactions within the amino functionality [62]. The FTIR spectrum of potassium oxalate shows a broad band around 3420 cm^{-1} , corresponding to O–H stretching vibrations. Distinct absorption peaks at 1620 cm^{-1} and 1325 cm^{-1} correspond to asymmetric and symmetric stretching of the carboxylate (COO^-) groups, respectively, typical coordination environment of the oxalate dianion [63,64]. A sharp peak near 1435 cm^{-1} is ascribed to C=O stretching, while the absorption at 772 cm^{-1} reflects out-of-plane deformation associated with -COOH scissoring [63]. In the case of the OCCHME, the FTIR spectrum reveals significant spectral shifts and band modifications, confirming successful ionic crosslinking between chitosan and oxalate. The peaks at 2941 cm^{-1} and 2885 cm^{-1} , representing asymmetric and symmetric $\text{-CH}_2\text{-}$ stretching vibrations, are retained but show variations in intensity due to altered backbone dynamics post-crosslinking. Notably, the amide-I and II bands appear at 1651 cm^{-1} and 1578 cm^{-1} , respectively, with subtle shifts suggesting electrostatic interaction between chitosan's -NH_3^+ groups and oxalate's COO^- anions, leading to the formation of a semi-interpenetrated ionic network [65]. Strong absorption bands at 1419 cm^{-1} and 1326 cm^{-1} are clearly visible and closely match the symmetric and asymmetric stretching modes of the oxalate group, confirming the structural incorporation of potassium oxalate within the chitosan matrix [63,64]. Most significantly, the original oxalate band at 772 cm^{-1} is red-shifted to 763 cm^{-1} in the membrane, indicating a change in the vibrational environment of oxalate. This shift strongly supports the occurrence of ionic interaction within the hydrated chitosan matrix. The combination of spectral shifts and new band emergence clearly confirms the successful structural integration of potassium oxalate into the chitosan framework, yielding a cross-linked membrane with modified molecular interactions and improved functional characteristics. Although the observed band shifts (amide I and II, COO^- vibrations, and oxalate deformation band) strongly support $\text{NH}_3^+\text{-C}_2\text{O}_4^{2-}$ electrostatic interactions, similar FTIR features can also arise from hydrogen bonding involving -OH/-NH groups. Indeed, Calderón et al. [62] reported that oxalic acid cross-linked chitosan hydrogels show deformation of the amide II band mainly due to electrostatic $\text{NH}_3^+\text{-C}_2\text{O}_4^{2-}$ interactions, while also noting the coexistence of hydrogen bonding. This

suggests that in the OCCHME, both ionic crosslinking and hydrogen bonding act synergistically to stabilize the network.

Table 4.2: Conductivity related data for the OCCHMEs with varying $K_2C_2O_4$ concentrations.

Concentration (M)	Thickness (mm)	R_b (Ω)	DC Ionic conductivity ($S\ cm^{-1}$)	AC ionic conductivity ($S\ cm^{-1}$)
0.1	0.04	6.76	0.59	0.46
0.2	0.05	4.11	1.22	1.14
0.3	0.05	3.54	1.41	1.51
0.4	0.06	1.95	3.08	3.21
0.5	0.06	1.24	4.84	4.56

The Nyquist plots presented in Fig.4.4 (B) exhibit a typical impedance profile comprising a depressed semicircular arc in the high-frequency region, followed by a linear tail at lower frequencies. The initial intercept of the arc with the real axis denotes the R_b of the membrane, which was found to decline steadily with increasing oxalate concentration, as given in Table 4.2. This trend is further substantiated by Fig.4.4(C), which depicts a pronounced inverse relationship between the crosslinker concentration and R_b , accompanied by a simultaneous increased in DC ionic conductivity upto from $0.46\ S\ cm^{-1}$ at 0.1M to $4.56\ S\ cm^{-1}$ 0.5M. The enhancement in conductivity with increasing crosslinker concentration can be ascribe to the greater availability of mobile ionic species, primarily protons, potassium ions and oxalate dianions, resulting from the progressive dissociation in the hydrogel matrix. The chitosan network, rich in polar functional groups, provides a conductive environment for ion solvation and transport. As oxalate concentration increases, these polar domains become more densely populated with mobile charge carriers, thereby facilitating continuous ion migration pathways.

AC ionic conductivity measurements were carried out to further elucidate the frequency-dependent ion-transport characteristics. The conductivity profiles, shown in

Fig.4.4 (D), reveal two distinct regimes: a low-frequency region marked by interfacial polarization effects, and a high-frequency region where conductivity rises sharply due to increased ion hopping and reduced space charge accumulation [66]. As shown in Table 4.2, among all the OCCHME samples, the membrane prepared with 0.5 M potassium oxalate exhibited the highest AC conductivity. Furthermore, for all concentrations, the AC conductivity values were found to be nearly equal to the corresponding DC conductivity values, indicating consistent ion transport behavior across the frequency range.

The σ_{DC} was determined from the bulk resistance (R_b) at the high-frequency intercept of the Nyquist plot, which represents continuous long-range ion migration across the membrane. In contrast, σ_{AC} is inherently frequency-dependent and captures additional dynamic processes such as localized ion hopping, relaxation events, and interfacial polarization, particularly evident in the low-frequency region. These localized contributions can lead to small deviations between σ_{AC} and σ_{DC} , even though both reflect ionic transport properties of the system. This behavior is well-documented in the literature, where polymer-based electrolytes consistently show σ_{AC} and σ_{DC} values that are close in magnitude but not identical, owing to the inclusion of short-range and interfacial processes in AC measurements [32,67–69].

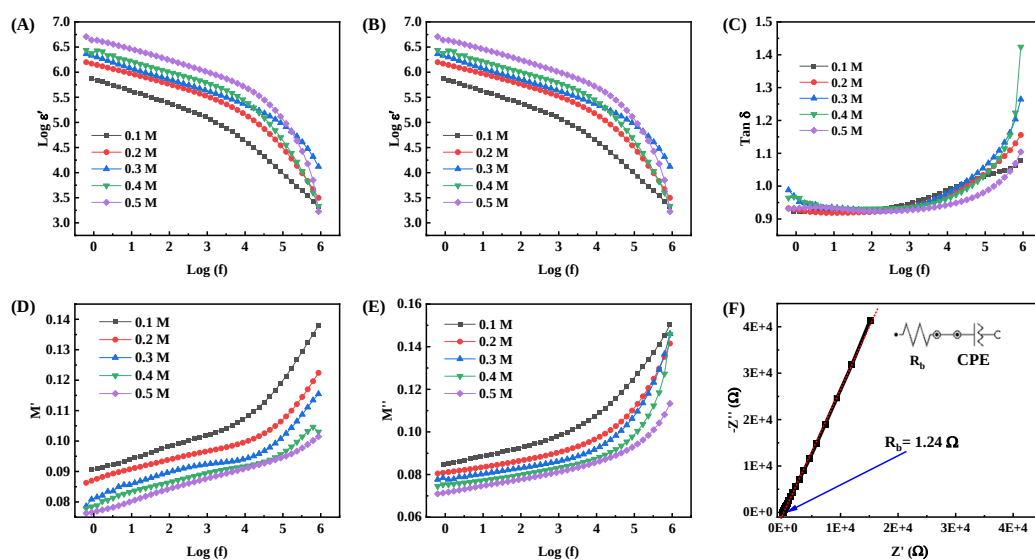


Fig.4.5 (A) Plots of frequency dependent dielectric constant; (B) Plots of frequency dependent dielectric loss; (C) Plots of frequency dependent dielectric loss tangent; (D)

Plots of frequency dependent real modulus; (E) Plots of frequency dependent imaginary modulus; (F) Nyquist plot, its fitting, and the related electrochemical equivalent circuit (shown in the inset) for the optimized OCCHME.

The dielectric behaviour of the OCCHME provides valuable insight into its frequency-dependent electrical properties, crucial for energy storage applications. As shown in Fig.4.5 (A), at low frequencies, the dielectric constant (ϵ') significantly decreases with increasing oxalate concentration, reflecting a typical polar dielectric response where dipoles fail to realign with rapidly oscillating electric fields [70]. This behaviour points to strong interfacial polarization and enhanced charge carrier accumulation, which improve chitosan chain flexibility and conductivity [71]. Similarly, the dielectric loss (ϵ''), as shown in Fig.4.5 (B) shows a decreasing trend with frequency and a rising trend with oxalate concentration, suggesting improved ionic mobility and relaxation dynamics due to structural modifications induced by ionic crosslinking. This frequency-dependent evolution of dielectric properties high ϵ' and ϵ'' at low frequencies and sharp declines at high frequencies confirms typical interfacial and dipolar relaxation behaviour in polymer-based electrolytes [72]. At high frequencies, the dielectric loss tangent ($\tan \delta$), shown in Fig.4.5 (C), reaches towards maximum with increasing oxalate concentrations, indicating optimal ion dissociation and dielectric relaxation [73]. The electric modulus parameters, where real modulus (M') reflects energy storage capability, which is inversely related to the dielectric constant, remains near zero at low frequencies with increase in potassium oxalate concentrations, indicating dominant electrode polarization and high dielectric permittivity due to mobile ion accumulation at the electrode-electrolyte interface [74]. As shown in Fig.4.5 (D), the frequency increases, M' rises gradually, signifying a transition from interfacial to bulk relaxation processes, where ion hopping and polymer chain dynamics begin to dominate [70]. The imaginary modulus (M'') reflects energy dissipation and displays broad, asymmetric peaks at intermediate-to-high frequencies as seen from Fig.4.5 (E), characteristic of non-Debye relaxation behavior with a distribution of relaxation times rather than a single mechanism [75]. These peaks shift toward higher frequencies and slightly decrease in intensity with increased oxalate concentration, suggesting faster ionic relaxation and lower R_b in more effectively

cross-linked systems. This behaviour indicates enhanced ion mobility, improved dielectric response, and optimized free ion density due to potassium oxalate's ability to dissociate more ions and disrupt interchain interactions [72]. The M' and M'' plots confirm that the dielectric response is governed by a combination of ionic transport and polymer crosslinking dynamics, with higher oxalate concentration, specially 0.5 M achieving a favourable balance between conductivity and structural integrity. These findings highlight the system's potential for electrochemical energy storage applications such as EDLCs.

Based on the comparative evaluation of physical integrity, ionic conductivity, and dielectric performance, the membrane synthesized using 0.5 M potassium oxalate was identified as optimal. Therefore, all subsequent physicochemical and electrochemical characterizations were performed using this optimized OCCHME.

The ion transport characteristics of the optimized OCCHME membrane prepared with optimal oxalate concentration, which exhibits the highest ionic conductivity, were examined using EIS and modeled through equivalent circuit fitting via Nova 2.1.5 software. In Fig.4.5 (F), the Nyquist plots exhibit only a spike without a semicircle, indicating capacitive behavior with negligible charge-transfer resistance. Therefore, the EEC, as shown in the inset of Fig.4.5 (F) was modelled with a bulk resistance (R_b) in series with a CPE [17,76]. The R_b corresponds to the bulk resistance of the OCCHME, which was found to be 1.24Ω . The extracted CPE value of $1.06 \times 10^{-5} F$ highlights the capacitive character of the OCCHME and suggests efficient interfacial charge accumulation at the electrode-electrolyte interface.

The values of Z_r and Z_i associated to the EEC can be described as follows [76].

$$Z_r = R_b + \frac{\cos\left(\frac{\pi p}{2}\right)}{C \omega^p}$$

$$Z_i = \frac{\sin\left(\frac{\pi p}{2}\right)}{C \omega^p}$$

And the impedance of CPE can be described by the equation given below [77].

$$Z = R_b + \frac{1}{C\omega^p} [\cos\left(\frac{\pi p}{2}\right) + j \sin\left(\frac{\pi p}{2}\right)]$$

Where, p is the deviation of the tilted spike from the horizontal axis, C represents the capacitance of CPE, and ω is the angular frequency.

Based on the fitted parameters, the diffusion coefficient was calculated to be $5.09 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$, indicating moderate ionic diffusion, which is typical for polymer hydrogels where the network structure influences ion mobility. The ionic mobility was calculated to be $1.98 \times 10^{-5} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$, reflecting the capacity of the mobile ions to respond effectively under an applied electric field, an essential factor for enabling quick ion transport during device operation. Additionally, the ion number density (n) was determined to be $1.53 \times 10^{23} \text{ m}^{-3}$, suggesting a significant population of free charge carriers available for conduction. This high carrier density aligns with the enhanced ionic conductivity observed and indicates the effectiveness of oxalate-mediated crosslinking in maintaining a well-hydrated and ion-conductive environment. These ion transport parameters reinforce the viability of OCCHME as a robust SSE for EDLC applications, where high conductivity and stable ion dynamics are critical.

The WU of the optimal OCCHME was measured to be 208%, reflecting significant swelling capacity. This behavior is primarily governed by the hydrophilic nature of chitosan, which possesses polar functional groups viz., $-\text{NH}_2$, $-\text{OH}$, and $\text{C}-\text{O}-\text{C}$, capable of forming hydrogen bonds with water. The oxalate-based ionic crosslinking introduces interstitial free volume and microporosity within the membrane, facilitating water penetration and retention. As the crosslinks are non-covalent, the network allows for reversible swelling without compromising mechanical stability, thereby supporting hydration while preserving membrane integrity.

The DR is a quantitative indicator used to assess the stability of hydrogel matrices under aqueous conditions. It is defined as the proportion of the polymer network that dissolves in a solvent over a defined immersion period, typically under accelerated

environments. Fig.4.6 (A) displays the DR of OCCHME, subjected to continuous boiling in deionized water for durations ranging from 1 to 6 h. A monotonic increase in DR was observed, reaching a value of 17.8 % after 6 h, suggesting moderate susceptibility of the polymeric network to hydrolytic disruption under thermally stressed conditions. The DR data confirm the presence of an intermediate degree of network stability, rendering the membrane suitable for applications that demand controlled aqueous erosion without rapid disintegration.

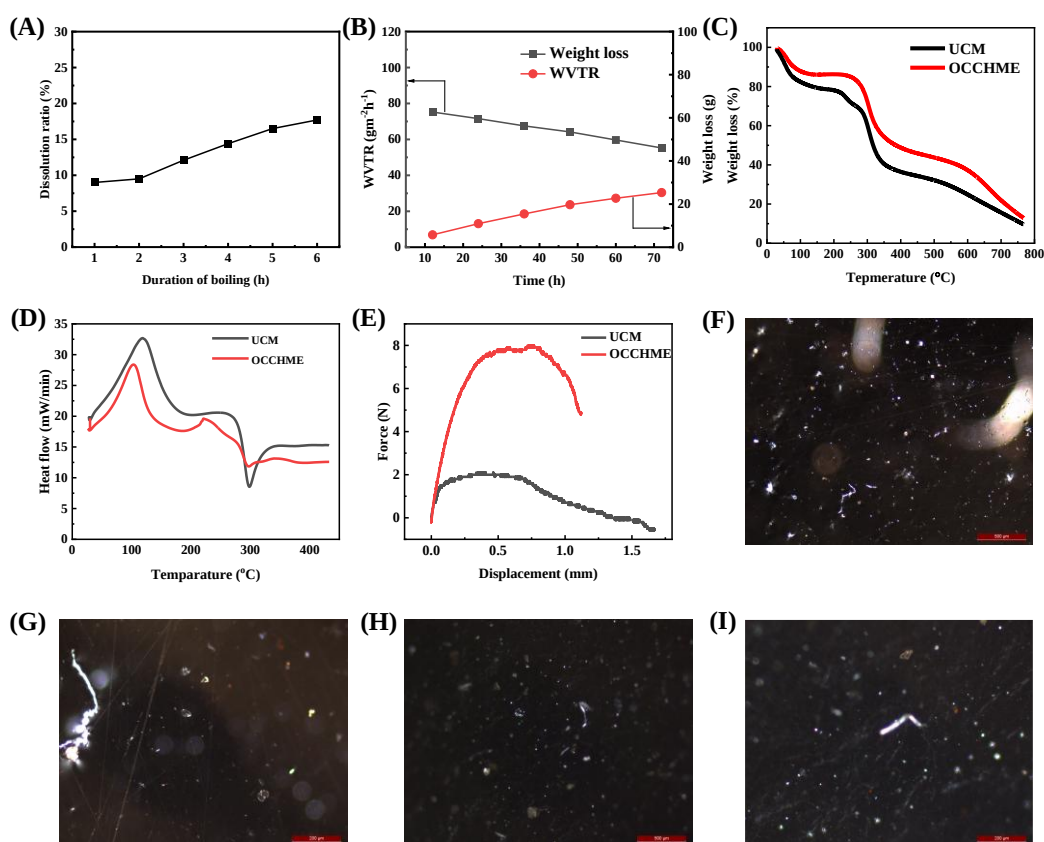


Fig.4.6 (A) Variation of DR for OCCHME with respect to the time of boiling; (B) Variation of weight loss and WVTR for OCCHME; (C) TGA plots of UCM and OCCHME; (D) DSC plots of UCM and OCCHME; (E) Force vs displacement plots of UCM and OCCHME; (F) POM image of UCM at 500 μm ; (G) POM image of UCM at 200 μm ; (H) POM image of OCCHME at 500 μm ; (I) POM image of OCCHME at 200 μm .

The WVTR, a key parameter in characterizing the permeability of hydrogel membranes to moisture vapor, was measured to evaluate membrane porosity and

hydrophilic transport capacity. As shown in Fig.4.6 (B), WVTR increased steadily over the test duration, achieving a maximum value of $29.1 \text{ g m}^{-2}\text{h}^{-1}$ at 72 h, indicating the formation of an interconnected porous microstructure that facilitates vapor diffusion. Simultaneously, the mass loss due to water evaporation exhibited a gradual linear decrease, suggesting sustained yet controlled moisture permeation through the membrane matrix. The moderately low WVTR relative to highly porous synthetic membranes implies that the cross-linked chitosan network possesses limited pore volume and a well-reticulated architecture, which restricts excessive vapor loss while still maintaining sufficient humidity exchange. This balance is critical for the operational stability of hydrogel electrolytes employed in electrochemical and biomedical systems, where excessive dehydration can compromise ionic conductivity and membrane integrity.

TGA was conducted to assess the thermal stability of UCM and OCCHME. From the Fig.4.6 (C), it is clear that the initial weight loss observed below $\sim 100^\circ\text{C}$ for both membranes, starting as early as 25°C , is attributed to the evaporation of physically adsorbed and bound water molecules. This is a common phenomenon in hydrophilic polymers such as chitosan, which can retain moisture due to hydrogen bonding [78]. The second and major weight loss event, occurring around 240°C , corresponds to the thermal degradation of the chitosan backbone. This stage involves the cleavage of glycosidic linkages, depolymerization of polysaccharide chains, and decomposition of the functional groups such as acetylated units [79]. At this temperature, OCCHME retains about 86% of its original weight, while UCM retains only 77%, indicating that ionic crosslinking with oxalate significantly enhances the thermal stability of chitosan. The crosslinking introduces additional ionic interactions that restrict polymer chain mobility, thereby increasing the resistance to thermal decomposition [78]. As the temperature increases beyond 240°C , both membranes continue to degrade. However, UCM exhibits a higher overall weight loss compared to OCCHME throughout the higher temperature range, further confirming the stabilizing effect of ionic crosslinking. A third thermal event is evident at higher temperatures. OCCHME shows a distinct decomposition peak around 560°C , with a residual weight of approximately 41%. This peak may be associated with the breakdown of more thermally stable cross-

linked domains formed via oxalate linkages. In contrast, UCM does not show a pronounced third peak but displays gradual degradation with a residual weight of around 30% at 500 °C. This difference suggests that the ionic network in OCCHME delays the final decomposition phase, reinforcing its superior thermal resistance. The TGA results clearly demonstrate that oxalate crosslinking improves the thermal stability of chitosan membranes. OCCHME resists thermal degradation more effectively across all temperature ranges compared to UCM, primarily due to the formation of an ionically cross-linked network structure that strengthens the polymer matrix [78,80,81]. The incomplete decomposition observed in the TGA thermograms can be attributed to the presence of a thermally stable carbonaceous residue formed during the degradation of the polymer matrix. In particular, the incorporation of carbon-rich components and crosslinking within the polymer structure enhances char formation, which resists complete volatilization even at elevated temperatures up to 750 °C [82]. Such residual mass is a common characteristic of biopolymer and carbon-based systems, where the stable carbon framework prevents total decomposition [83].

The DSC plots of UCM and OCCHME are shown in Fig.4.6 (D). The UCM reveals an exothermic peak at approximately 298 °C, attributed to the degradation of polymer chains. This process involves saccharide ring dehydration, depolymerization, and the decomposition of both deacetylated and acetylated chitosan units. Additionally, an endothermic peak observed at 118 °C corresponds to the dissociation of interchain hydrogen bonds in chitosan. The glass transition temperature (T_g) of chitosan remains a subject of controversy due to its variability as a natural polymer. Factors such as crystallinity, molecular weight, and the degree of deacetylation contribute to inconsistencies in reported T_g values. Ratto et al. [84] reported a T_g of 308 °C, while Sakurai et al. [85] observed it at 203 °C, and Rao et al. [86] at 222 °C. In contrast, Kittur et al. [87] found no evidence of a T_g , suggesting that degradation may occur before the glass transition becomes detectable. In the present study, DSC measurements did not exhibit a significant stepwise increase in specific heat, indicating no clear evidence for the occurrence of a T_g . For the OCCHME, the degradation peak shifted to a lower temperature with a reduced intensity. This shift suggests enhanced thermal stability due to crosslinking interactions between chitosan

and potassium oxalate. Furthermore, an additional endothermic peak at approximately 235 °C was observed in OCCHME, likely corresponding to the decomposition of potassium oxalate within the chitosan matrix. The endothermic event observed at 118 °C is more accurately attributed to the removal of absorbed and bound water molecules from the chitosan matrix, which is closely associated with the disruption and relaxation of intra- and interchain hydrogen bonding. This interpretation is consistent with previous reports, where endothermic peaks in the range of 100-130 °C have been ascribed to dehydration and concomitant weakening of the hydrogen-bond network in chitosan-based systems [88–90]. The endothermic event observed at 118 °C is more accurately attributed to the removal of absorbed and bound water molecules from the chitosan matrix, which is closely associated with the disruption and relaxation of intra- and interchain hydrogen bonding. This interpretation is consistent with previous reports, where endothermic peaks in the range of 100-130 °C have been ascribed to dehydration and concomitant weakening of the hydrogen-bond network in chitosan-based systems.

The force-displacement curves obtained from the mechanical strength characterization of the UCM and OCCHME are presented in Fig.4.6 (E). The UCM exhibited a tensile strength of 30.51 MPa, elongation at break of 6.48 %, and a Young's modulus of 470.84 MPa. Upon crosslinking with potassium oxalate, the tensile strength increased markedly to 55.04 MPa, indicating enhanced intermolecular interactions and improved load-bearing capacity. However, a slight reduction in elongation percentage to 5.60 % was observed, suggesting a decrease in flexibility due to the restricted mobility of polymer chains in the cross-linked network. Moreover, the Young's modulus increased significantly to 982.85 MPa, reflecting a stiffer and more rigid membrane structure. These results confirm that ionic crosslinking with potassium oxalate reinforces the mechanical strength and stiffness of chitosan membranes, making them more suitable for applications requiring mechanical robustness. Similar trends have been observed in previous studies on chitosan-based membranes, where crosslinking contributed to improved tensile properties and overall mechanical performance [81,91,92].

POM was employed to assess the internal microstructure and crystallinity of the UCM and OCCHME. From Fig.4.6 (F) and 4.6 (G), it is seen that the UCM surface exhibited a low degree of birefringence, indicating a mostly amorphous morphology with weak or poorly organized crystalline domains. The absence of distinct interference colours or well-defined spherulitic patterns suggests that chitosan chains in the uncross-linked state are randomly oriented with limited molecular ordering. This observation is consistent with the known semicrystalline nature of chitosan [93,94]. In the uncross-linked state, the polymer chains lack sufficient cohesion to form ordered crystalline structures, resulting in an optically isotropic or weakly anisotropic appearance under cross-polarized light. For the OCCHME, at 500 μm of Fig.4.6 (H), the membrane appears largely amorphous with limited birefringence. This suggests heterogeneity in crosslinker diffusion or phase separation during membrane formation. Only a few isolated bright spots were observed, implying that crystalline domains are sparse or localized in specific regions. At low magnification of 200 μm , as shown in Fig.4.6 (I), the OCCHME surface appeared predominantly dark, interspersed with discrete bright regions indicating localized birefringence. These birefringent streaks are suggestive of oriented or semi-crystalline domains resulting from ionic interactions between the protonated amine groups of chitosan and oxalate anions. The scattered bright spots may also correspond to residual salt microcrystals or early-stage nucleation sites. A higher magnification image (500 μm) reveals the presence of well-defined spherulitic structures exhibiting radial birefringence patterns. These formations are indicative of crystallization centres, likely due to the nucleation and growth of potassium oxalate crystals within the chitosan matrix.

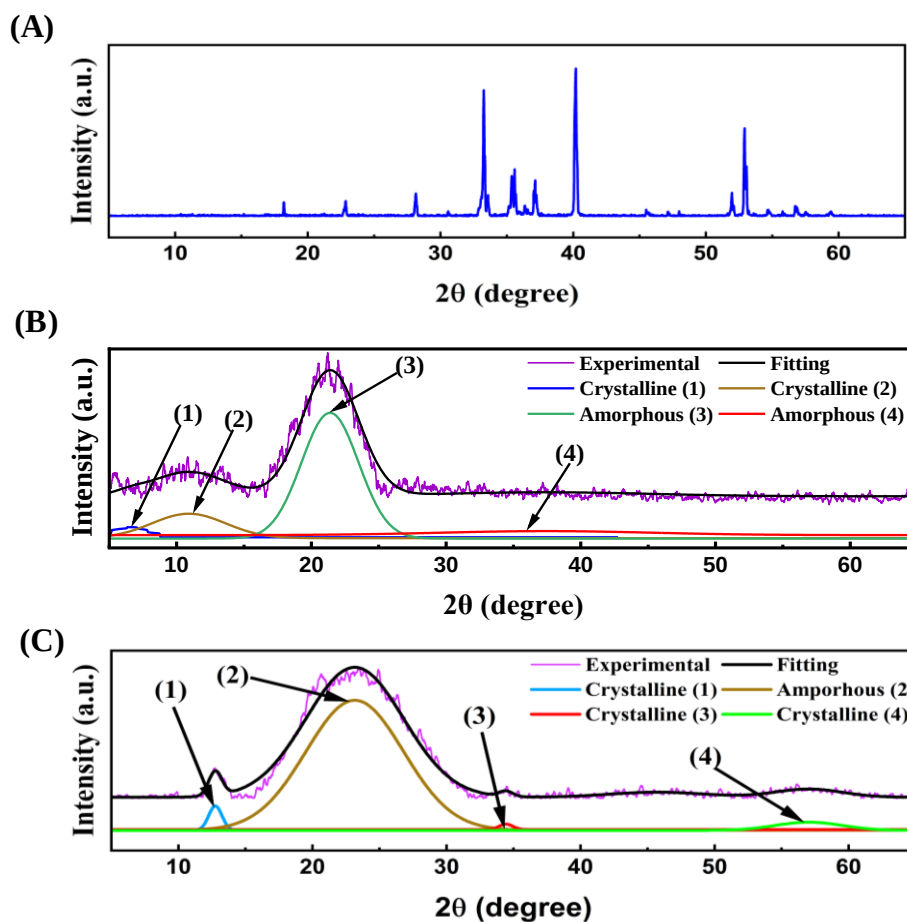


Fig.4.7 (A) XRD pattern of pure $K_2C_2O_4$; (B) Deconvoluted XRD pattern of UCM; (C) Deconvoluted XRD pattern of OCCHME.

XRD patterns of pure $K_2C_2O_4$, the UCM, and the optimized OCCHME are presented in Fig.4.7 (A), (B), and (C), respectively. As observed in Fig.4.7 (A), the diffraction profile of $K_2C_2O_4$ features numerous sharp, intense peaks, indicative of its highly crystalline nature. This pattern confirms the ordered solid-state structure of the salt before incorporation into the polymer matrix. The deconvoluted XRD profile of the UCM, shown in Fig.4.7 (B), reveals two well-defined crystalline peaks centered around $2\theta \approx 6^\circ$ and 11° (bands 1 and 2), along with two broader amorphous bands located near $2\theta \approx 21^\circ$ and 38° (bands 3 and 4). These features are consistent with typical semi-crystalline chitosan and reflect the presence of organized domains stabilized by intermolecular hydrogen bonding. In contrast, the XRD pattern of the OCCHME membrane in Fig.4.7 (C) shows a notable reduction in crystallinity. The deconvoluted spectrum displays crystalline peaks near $2\theta \approx 7^\circ$ and 29° (bands 1 and

4) and two amorphous humps at approximately 13° and 20° (bands 2 and 3), with the latter being substantially broadened compared to the UCM. The calculated degree of crystallinity was 19.50% for the UCM, while for the OCCHME it reduced significantly to 10.19%, confirming a clear transition toward a more disordered, amorphous morphology. This decrease in crystallinity can be attributed to the ionic crosslinking interactions between the oxalate dianions and the protonated amine groups of chitosan. The introduction of oxalate disrupts the pre-existing hydrogen-bonded crystalline domains by forming ionic bridges, which interfere with polymer chain packing and increase chain irregularity. The absence of characteristic crystalline peaks from potassium oxalate in the OCCHME pattern further indicates complete dissolution and molecular dispersion of the salt within the hydrogel matrix.

The birefringence observed in POM images reflects local anisotropy and chain alignment, which can occur even in regions with low long-range crystallinity. As reported by Guo et al. [95], birefringence may arise in order-disorder transition zones with only weak orientation. Also, according to Haji et al. [96], negligible crystallinity demonstrated that birefringence results from both crystalline and amorphous orientation contributions. Therefore, the observed birefringence in OCCHME is consistent with the XRD crystallinity index of 10.19 %, confirming the presence of locally aligned domains within a predominantly amorphous structure.

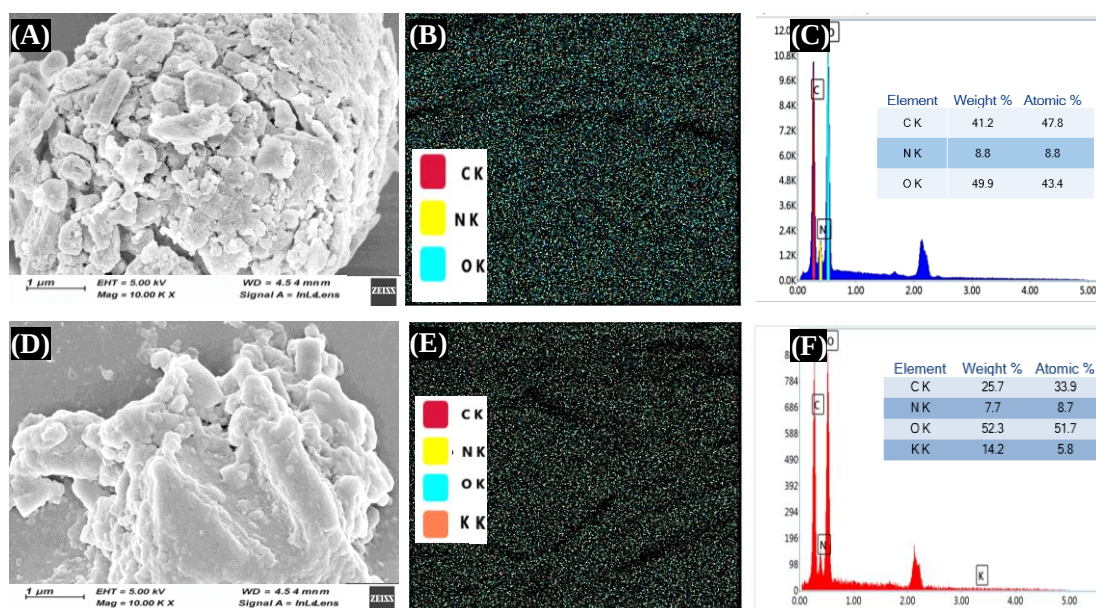


Fig.4.8 (A) FE-SEM image of UCM; (B) EDX mapping of UCM; (C) EDX spectrum and elemental data of UCM; (D) FE-SEM image of OCCHME; (E) EDX mapping of OCCHME; (F) EDX spectrum and elemental data of OCCHME.

The surface morphology and elemental composition of UCM and OCCHME were analyzed using FESEM and EDX, as shown in Fig.4.8. The FESEM image in Fig.4.8 (A) reveals that the UCM exhibits a rough, irregular, and porous surface morphology [97]. The EDX mapping in Fig.4.8 (B) shows a uniform distribution of carbon (C), nitrogen (N), and oxygen (O) elements, confirming the chemical composition typical of pure chitosan. The corresponding EDX spectrum and elemental data in Fig.4.8 (C) indicate weight percentages of C (41.2%), N (8.8%), and O (49.9%), which is consistent with the polysaccharide backbone of chitosan containing amine and hydroxyl functional groups [98–100]. In contrast, the FESEM image in Fig.4.8 (D) demonstrates a significant morphological transformation upon crosslinking with potassium oxalate. The surface appears denser, smoother, and more compact, indicating the formation of a more cohesive and uniform membrane structure. This alteration is due to ionic interactions between oxalate anions and the protonated amino groups of chitosan, which restrict polymer chain movement and enhance the structural integrity of the matrix [101]. The EDX mapping in Fig.4.8 (E) confirms the homogeneous distribution of C, N, O, and K throughout the membrane, verifying successful incorporation of the oxalate crosslinker. The EDX spectrum and compositional data in Fig.4.8 (F) show a decrease in carbon content to 25.7%, and slight reduction in nitrogen to 7.7%, while oxygen increases to 52.3% and potassium appears with a substantial weight percentage of 14.2%. The presence of potassium strongly supports the formation of ionic crosslinks with oxalate groups.

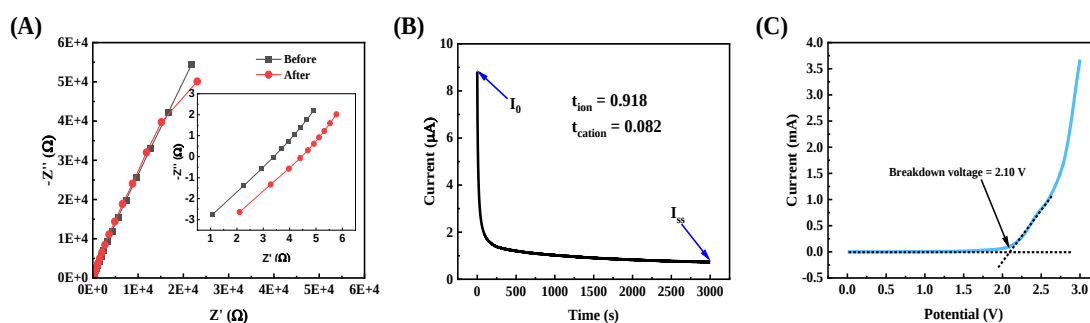


Fig.4.9 (A) Nyquist plots of OCCHME before and after the DC polarization; (B) DC polarization curve of OCCHME; (C) LSV plot of OCCHME.

Transference number measurements are instrumental in discerning the relative contributions of ionic and electronic species to the overall charge transport in quasi-SPEs. Particularly in supercapacitor systems, where charge storage is dominated by electrostatic interactions at the interface of electrode and electrolyte, high ionic transference and suppressed electronic conduction are essential to minimize self-discharge and maximize efficiency and safety [102]. As illustrated in Fig.4.9 (B) of DC polarization, the initial current (I_0) measured for the OCCHME was 8.81 μA , encompassing both ionic and electronic contributions. Over time, this current decayed to a steady-state value (I_{ss}) of 0.72 μA , indicating the suppression of ion migration due to electrode blocking and revealing the residual electronic leakage. The calculated ion transference number (t_{ion}) was 0.918, suggesting that approximately 92 % of the total charge transport is governed by mobile ions. This value is in close agreement with earlier reports on hydrogel and biopolymer-based electrolytes, where dominant ion migration pathways were observed under similar measurement protocols [103]. The predominance of ionic over electronic transport signifies efficient salt dissociation and stable ion mobility within the hydrogel network, which are prerequisites for long-term electrochemical stability in EDLC devices. A higher t_{ion} also implies minimal Faradaic side reactions and reduced internal losses, thus supporting the structural and electrochemical resilience of the membrane during prolonged cycling [103].

To further elucidate the type of ion contributing dominantly to conductivity, the cationic transference number (t_{cation}) was evaluated by coupling DC polarization with AC impedance spectroscopy. The initial and steady-state R_b , determined from Nyquist plots shown in Fig.4.9 (A), were 2.58 Ω and 4.49 Ω , respectively. The resulting t_{cation} value of 0.082 clearly indicates anion-dominated conduction. This preferential anion mobility can be attributed to the molecular structure and electrostatic environment within the oxalate cross-linked chitosan network. The oxalate dianions form strong electrostatic interactions with the protonated $-\text{NH}_3^+$ groups of chitosan, creating a semi-rigid backbone with high anion coordination capacity. Potassium cations, in

contrast, due to their monovalency and relatively large hydrated radius, experience hindered mobility, particularly within the moderately cross-linked hydrogel matrix [104]. This asymmetric mobility leads to selective anionic conduction, a feature that can enhance ion accumulation at the electrode-electrolyte interface, boosting capacitance and rate capability [103]. The OCCHME not only demonstrates superior ionic selectivity but also ensures minimal parasitic electronic conduction, which collectively enhance device longevity and operational safety. Therefore, the transference number measurements conclusively affirm that OCCHME operates as a highly ion-conducting and selectively anion-conducting electrolyte system, ideal for advanced EDLC applications requiring robust cycling performance and efficient charge-discharge characteristics.

The electrochemical stability of the OCCHME was assessed under ambient conditions using LSV, and the resulting I-V profile is presented in Fig.4.9 (C). The voltammogram shows a negligible current response from 0-2.10 V, indicating that the membrane remains electrochemically inert and stable throughout this range. This behavior implies an absence of significant faradic reactions or electrolyte degradation within the operational potential window. However, beyond 2.10 V, a sharp increase in current is observed, corresponding to the breakdown voltage of the OCCHME, which marks the onset of electrochemical decomposition likely initiated at the SS electrode-electrolyte interface. This relatively high breakdown voltage suggests that the polar functionalities present in the chitosan backbone may contribute to enhanced molecular rigidity and resistance to oxidation under elevated potentials. As noted in the previous literature, polymer-based electrolytes are generally required to exhibit a breakdown voltage of at least 1 V to be considered suitable for electrochemical energy storage applications [102]. The fact that OCCHME achieves a decomposition threshold well above this baseline, which clearly demonstrates its excellent electrochemical durability, reinforcing its potential as a reliable and high-performing solid-state electrolyte material for advanced capacitor systems.

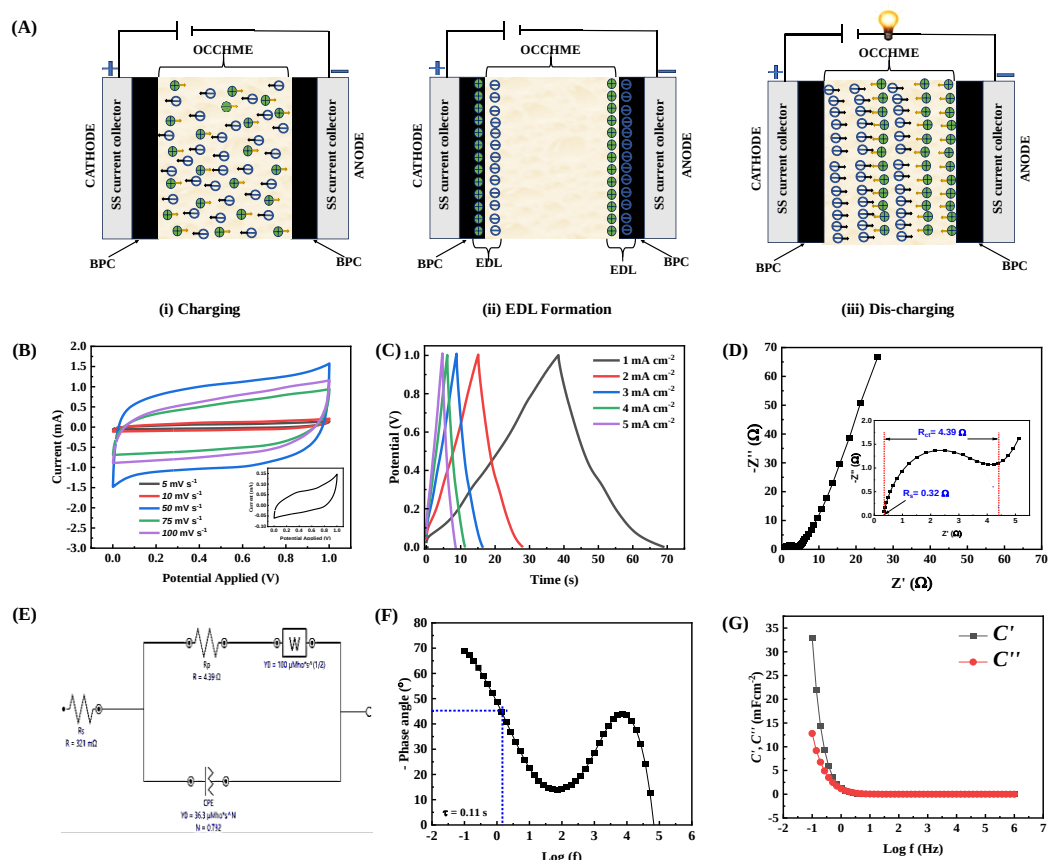


Fig.4.10 (A) Schematic illustration of the mechanism of an ideal EDLC in three stages: (i) Charging, (ii) EDL formation, and (iii) Dis-charging; (B) CVs of the EDLC at varied scan rates; (C) GCDs of the EDLC at varied current densities; (D) Nyquist plot of the EDLC obtained from EIS; (E) Electric equivalent circuit model of the EDLC; (F) Bode plot of phase angle vs frequency of the EDLC; (G) Real and imaginary components of complex capacitance as functions of frequency.

Table 4.3: Summary of the GCD performance data at varied current densities.

Current density (mA cm ⁻²)	Discharge time (s)	Areal capacitance (mF cm ⁻²)	Energy density (μWh cm ⁻²)	Power density (μW cm ⁻²)	Coulombic efficiency (%)	IR drop (mV)
1	30.7	61.4	8.60	1009	81	21
2	12.9	51.6	7.22	2016	86	40
3	7.6	45.6	6.38	3023	86	55
4	5.1	40.8	5.71	4031	84	83

5	3.8	38	5.32	5040	81	95

The operational mechanism of EDLC employing OCCHME as the dual-function electrolyte and separator is schematically represented in Fig.4.10 (A), comprising three key stages viz., (i) charging, (ii) EDL formation, and (iii) discharging. During the charging process, an external potential is applied across the electrodes, which cause the migration of ionic species within the OCCHME matrix. The OCCHME hydrogel, containing mobile ions and interconnected hydrated domains, facilitates efficient ion conduction and supports fast ionic polarization under the applied electric field. As the EDL form, oppositely charged ions accumulate at the electrode-electrolyte interfaces without undergoing any faradaic reactions. These EDLs are composed of spatially separated charges, electrons on the surface of the electrode and counter-ions in the electrolyte, which store energy electrostatically [105]. The spatial confinement of the charges across nanometer-scale distances gives rise to high capacitances. The presence of a hydrated, ionically conductive OCCHME matrix ensures uniform charge distribution, while its mechanical integrity maintains physical separation between electrodes, preventing short-circuits. Upon discharging, the stored energy is released as the ionic species diffuse back into the bulk membrane and neutralize, reversing the polarization at the interface [106]. The process is rapid and highly reversible due to the absence of faradaic transformations, allowing the EDLC to deliver energy with high power density and minimal degradation over multiple cycles [106].

The electrochemical behavior of the EDLC assembled with the optimal OCCHME was systematically evaluated using CV, GCD, and EIS, as shown in Fig.4.10 (B–G). These characterizations were performed to assess charge storage efficiency, ionic transport properties, and capacitive performance of the device. The CV curves of the EDLC recorded at varying scan rates are presented in Fig.4.10 (B). At low scan rates, the curves exhibit a nearly ideal rectangular shape, which is indicative of EDLC behavior and efficient ionic accessibility at the electrode-electrolyte interface without any faradaic redox processes [107]. With increasing scan rates, the curves begin to deviate slightly from the rectangular profile, which can be attributed to diffusion-controlled limitations in ion migration through the hydrogel matrix and electrode pores [108].

Nevertheless, the retention of capacitive features even at high scan rates reflects the excellent rate capability of the OCCHME electrolyte.

The GCD curves of the EDLC at different current densities are shown in Fig.4.10 (C), and corresponding results obtained from GCD are summarized in Table 4.3. All GCD plots display nearly symmetric triangular shapes with minimal IR drops, highlighting high Coulombic efficiency and low IR drop within the system. At the lowest current density of 0.5 mA cm^{-2} , the device delivers an areal capacitance of 66.8 mF cm^{-2} with a Coulombic efficiency of 92%. As the current density increases from 0.8 to 5.0 mA cm^{-2} , the capacitance gradually decreases to 23.4 mF cm^{-2} , which is attributed to limited ion diffusion at higher charging rates, restricting ion access to deeper electrode pores [109]. Nonetheless, the device maintains moderate Coulombic efficiency even at the highest tested current density, suggesting excellent charge recovery and stable cycling performance.

The Nyquist plot for the EDLC is displayed in Fig.4.10 (D), consisting of a semicircle in the high-frequency region and a linear segment in the low-frequency domain. The intercept of the semicircle on the real axis corresponds to the R_s , while the diameter of the semicircle represents the charge-transfer resistance. From the inset of Fig.4.10 (D), the fitted values of R_s and R_{ct} were determined to be 0.32Ω and 4.39Ω , respectively. In a study on the principles and applications of electrochemical capacitors, the ESR was reported to be a combination of R_s and R_{ct} [110,111]. Accordingly, the EDLC being reported here exhibited a low ESR value of 4.71Ω . These low resistance values highlight the efficient ion mobility and reduced interfacial polarization resistance in the device, attributed to the hydrated and porous nature of the OCCHME hydrogel matrix.

While many hydrogel electrolytes indeed exhibit R_{ct} values below 1Ω , literature reports also show significantly higher values under certain conditions. For example, Fakhruddin et al. [112] observed R_{ct} values as high as 28Ω for hydrogel-based systems, which were attributed to redox interactions between electrolyte ions and surface functional groups such as $-\text{OH}$, $-\text{C}=\text{O}$, and $-\text{COOH}$ on porous carbon

electrodes. In the case of OCCHME-based EDLCs, the initial R_{ct} is strongly influenced by the surface chemistry of the electrode and the presence of nitrogen and oxygen containing functionalities, which promote such interfacial interactions [113,114]. The gradual increase in R_{ct} during long-term cycling can be rationalized by interface degradation mechanisms. Specifically, partial loss of adhesion between the electrode coating and the current collector, as evidenced by the post-mortem analysis in Fig.4.16 (C), and progressive weakening of electrode-electrolyte interactions due to side reactions at functional groups.

EEC used to fit the impedance data is shown in Fig.4.10 (E). It comprises R_s , R_{ct} , a CPE, and a Warburg element to account for non-ideal capacitive and diffusive behaviors. The close agreement between the experimental and simulated data indicates the suitability of the model in describing the electrochemical dynamics of the system. The low R_s reflects favorable ion conduction within the OCCHME membrane, while the moderate R_{ct} value confirms efficient charge transfer at the electrode–electrolyte interface [17].

Table 4.4: The EEC fitted parameters and their corresponding error values.

Parameters with unit		Circuit values	Errors
R_s (Ω)		0.321	± 0.13
R_p or R_{ct} (Ω)		4.39	± 0.91
CPE	Y_0 ($\mu\Omega^{-1}\times s^N$)	36.3	± 18.71
	N	0.73	± 0.13

The fitted circuit parameters with their corresponding statistical errors are summarized in Table 4.4. The R_s value of $0.321 \Omega (\pm 0.13)$ confirms the intrinsically low resistance of the electrolyte, while the R_{ct} of $4.39 \Omega (\pm 0.91)$ reflects moderate interfacial charge transfer resistance, in line with the efficient ion transport discussed above. The CPE parameter ($Y_0 = 36.3 \text{ M}\omega^{-1}\cdot s^N$, ± 18.71) together with an exponent N of $0.73 (\pm 0.13)$ indicates non-ideal capacitive behavior, which can be attributed to surface heterogeneity and distributed relaxation at the electrode-electrolyte interface.

Importantly, the relatively narrow error margins, particularly for R_s and R_{ct} , demonstrate the robustness and reliability of the EIS fitting.

The Bode phase plot, shown in Fig.4.10 (F), reveals a maximum phase angle close to -60° , which further validates the capacitive behavior of the device. The relaxation time constant (τ) was found to be 0.11 s, indicating the ability of the EDLC to deliver stored energy rapidly, a crucial attribute for high-power applications [115]. The real (C') and imaginary (C'') components of complex capacitance as functions of frequency are depicted in Fig.4.10 (G). In the low-frequency region, both C' and C'' increase sharply, a sign of ion accumulation and dipolar relaxation processes. The higher magnitude of C' at low frequencies signifies a greater ability to store energy, whereas the peak in C'' represents the optimal energy dissipation frequency. These features are characteristic of porous carbon-based EDLC systems and are directly related to the ion-accessible surface area and dielectric response of the electrolyte medium [49]. The value of C' calculated at minimum frequency is closely match the capacitance value derived from GCD.

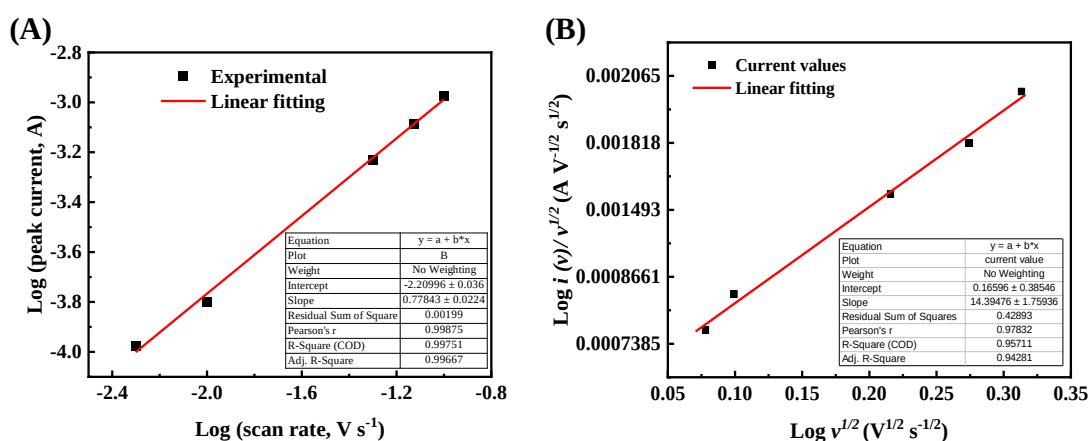


Fig.4.11 (A) b-value analysis ($\log i$ vs. $\log v$) of the EDLC; (B) Capacitive-diffusive current separation at 5 mV s^{-1} .

The b-value was determined by plotting $\log(i)$ versus $\log(v)$, as shown in Fig.4.11 (A). The slope yielded a b-value of 0.78, which lies between the theoretical limits of 0.5 for diffusion-controlled and 1.0 for ideal capacitive behavior [50]. This clearly

indicates a hybrid charge storage mechanism, dominated by surface-controlled processes but supplemented by diffusion-limited contributions. Similar intermediate b-values have been reported in other carbon-based systems; for example, RGO–Na₂SO₄ supercapacitors exhibited a b-value of 0.74, also attributed to hybrid kinetics [50]. Comparable ranges have likewise been associated with high capacitive contributions in porous carbon electrodes [51]. To further quantify these contributions, the current was deconvoluted into capacitive and diffusion-controlled terms at a representative scan rate of 5 mV s⁻¹, as shown in Fig.4.11 (B). The linear fit provided a capacitive coefficient (k_2) of 14.39 and a diffusion-controlled coefficient (k_2) of 0.17, confirming that the majority of charge arises from capacitive ion adsorption with a measurable but smaller diffusion-controlled fraction. This synergistic mechanism is consistent with findings in MXene-WO₃ composites, where b-value analysis likewise revealed mixed capacitive–diffusive kinetics [52]. The combined b-value analysis and current separation confirm that the OCCHME-based EDLC is predominantly capacitive in nature, with a secondary diffusion-controlled contribution. This nuanced characterization strengthens the mechanistic understanding of our device and aligns well with established literature reports [53,116].

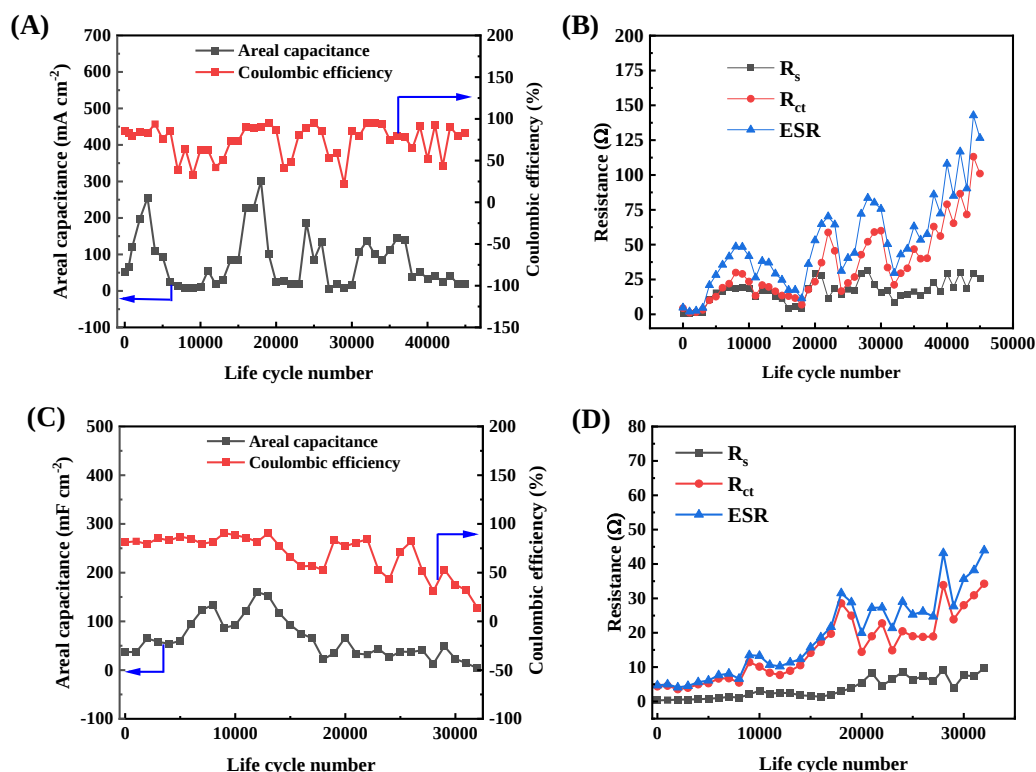


Fig.4.12 (A) Graphs depicting areal capacitance and Coulombic efficiency as functions of cycle number at a current density of 2 mA cm⁻²; (B) Graphs showing variations in R_s , R_{ct} , and ESR across cycle numbers at 2 mA cm⁻²; (C) Plots illustrating areal capacitance and Coulombic efficiency versus cycle number at 5 mA cm⁻²; (D) Graphs representing R_s , R_{ct} , and ESR trends with life cycle number at 5 mA cm⁻².

The long-term electrochemical stability of the EDLC assembled with OCCHME was investigated through extended GCD cycling at constant current densities of 2 and 5 mA cm⁻². The EDLC exhibited remarkable cycle life of 46,000 charge-discharge cycles at 2 mA cm⁻² and 32,000 charge-discharge cycles at 5 mA cm⁻². Fig.4.12 (A) and Fig.4.12 (C) illustrate the changes of areal capacitance and Coulombic efficiency as a function of cycle number under both current densities. At a moderate current density of 2 mA cm⁻², the areal capacitance initially increased over the first few thousand cycles, eventually stabilizing and exhibiting a peak value of 300.8 mA cm⁻² at 18,000 cycle, with corresponds energy and power densities of 42.11 μWh cm⁻² and 2016 μW cm⁻². Remarkably, the device sustained capacitive behavior up to

approximately 46,000 cycles, confirming the mechanical and electrochemical robustness of the OCCHME matrix under continuous operation.

Similarly, under a higher current density of 5 mA cm^{-2} , the EDLC maintained stable performance for nearly 32,000 cycles, although with a slightly earlier onset of capacitive decline compared to the lower current density. This performance is consistent with known limitations of higher current densities, where rapid charge/discharge reduces the interaction time between ions and the porous carbon electrode, resulting in diminished utilization of electrochemically active surface area. Nevertheless, the observed cycle life far exceeds typical polymer gel electrolyte-based EDLCs, reaffirming the durability of the OCCHME.

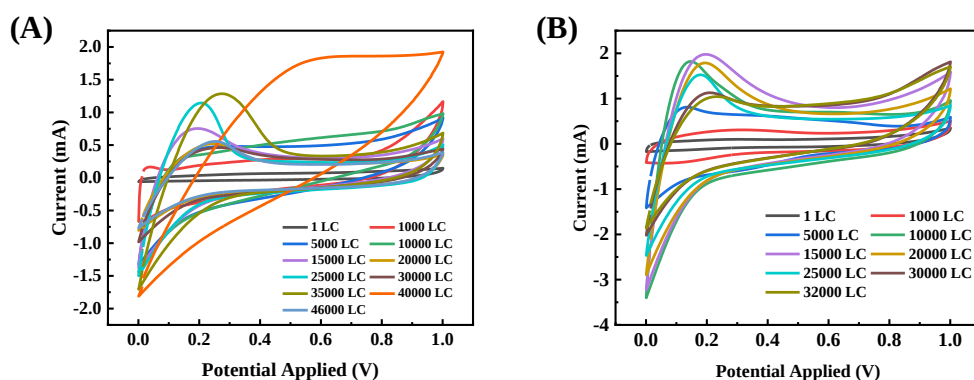


Fig.4.13 (A) Plot of CVs during life cycle studies of the EDLC tested at 2 mA cm^{-2} ; (B) Plot of CVs during life cycle studies of the EDLC tested at 5 mA cm^{-2} .

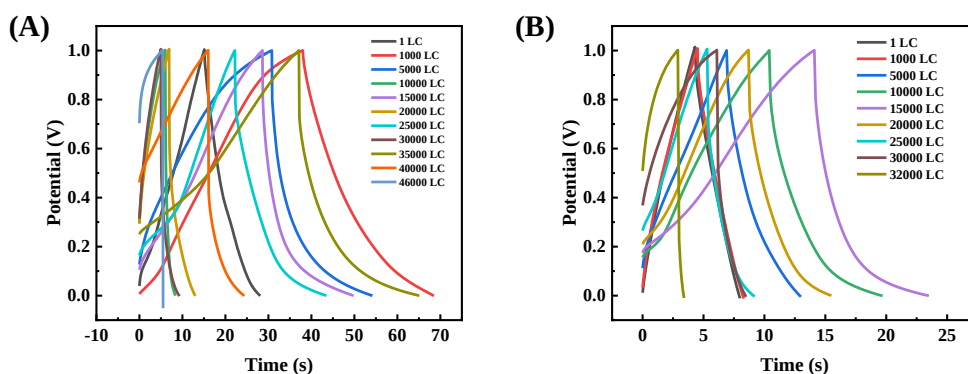


Fig.4.14 (A) Plot of GCDs during life cycle studies of the EDLC tested at 2 mA cm^{-2} ; (B) Plot of GCDs during life cycle studies of the EDLC tested at 5 mA cm^{-2} .

The progressive increase in areal capacitance during the initial cycling phases, observed in both cases, can be attributed to the gradual and deeper infiltration of hydrated ionic domains from the OCCHME into the porous structure of the carbon electrodes. This wetting effect enhances the interfacial area for double-layer formation and, in some instances, exposes additional redox-active sites capable of contributing pseudocapacitance. Supporting this interpretation, CV and GCD plots from selected cycles as given in Fig.4.13 (A-B) and 4.14 (A-B), reveal the development of broad, redox-like humps within the 0-0.3 V potential range as the cycle number increases, suggesting time-dependent electrochemical activation of surface-bound functional groups [117,118].

Such redox signatures are typically attributed to oxygen or nitrogen-containing functionalities either present on the carbon surface or interacting with the membrane–electrolyte interface. These groups undergo quasi-reversible redox reactions under repeated polarization, which complements the dominant non-faradaic double-layer charge storage and leads to cumulative capacitance enhancement. The excellent ionic conductivity and high WU of the OCCHME matrix likely facilitate this electrochemical activation by promoting fast ion transport and enhanced electrode–electrolyte interpenetration.

Coulombic efficiency for both current densities remained relatively stable at around 90–92% during the initial cycles, especially at 5 mA cm^{-2} , the coulombic efficiency values were around constant till 14000 cycle, indicating high charge retention and minimal parasitic reactions. Beyond this point, a gradual decline in Coulombic efficiency was noted, eventually decreasing to approximately 48% at 2 mA cm^{-2} and 45% at 5 mA cm^{-2} near the end of the respective cycling tests. This decline may stem from electrolyte degradation, loss of electroactive sites, or irreversible changes in the electrode–membrane interface due to extended cycling. However, the fact that the EDLC continued functioning over tens of thousands of cycles underscores the long-term resilience and structural integrity of the OCCHME electrolyte system.

Table 4.5: Summary of capacitive performance data for EDLC employing OCCHME in GCD current density of 2 mA cm^{-2} , that performed 46,000 charge-discharge cycles.

Cycle number	R_s (Ω)	R_{ct} (Ω)	ESR (Ω)	Areal capacitance (mF cm^{-2})	Coulombic efficiency (%)	Capacitance retention (%)	Energy density ($\mu\text{Wh cm}^{-2}$)
1	0.32	4.39	4.71	51.6	85.43	100	7.224
1000	0.79	1.12	1.91	121.6	80	235.7	17.02
2000	1.08	1.46	2.54	197.6	84.3	382.9	27.66
3000	1.47	3.17	4.64	255.2	83.51	494.6	35.72
4000	10.87	10.03	20.9	108.8	93.79	210.9	15.23
5000	15.54	12.65	28.19	93.2	75.65	180.6	13.04
6000	16.43	19.06	35.49	24.4	85.92	47.29	3.41
7000	19.52	21.95	41.47	13.6	38.2	26.36	1.90
8000	18.66	29.91	48.57	7.2	64.29	13.95	1.00
9000	19.37	29	48.37	9.2	32.86	17.83	1.28
10000	18.25	23.51	41.76	9.6	63.16	18.6	1.34
11000	13	13.35	26.35	55.6	62.33	107.8	7.78
12000	17.22	20.95	38.17	18.4	41.82	35.66	2.57
13000	17.38	19.68	37.06	31.2	50.98	60.47	4.36
14000	12.68	16.5	29.18	85.6	73.79	165.9	11.98
15000	11.22	13.5	24.72	84.4	73.78	163.6	11.81
16000	4.37	13.05	17.42	227.6	90.03	441.1	31.86
17000	5.81	11.65	17.46	226.4	88.99	438.8	31.69
18000	4.51	6.86	11.37	300.8	90.28	582.9	42.11
19000	18.39	17.72	36.11	101.2	95.11	196.1	14.16
20000	29.63	23.4	53.03	24	86.96	46.51	3.36
21000	27.64	37.09	64.73	28	40.94	54.26	3.92
22000	11.51	58.74	70.25	20	48.54	38.76	2.8
23000	18.83	45.54	64.37	18.8	81.03	36.43	2.63
24000	14.48	16.64	31.12	186.8	88.95	362	26.15
25000	17.87	22.48	40.35	84.8	95.5	164.3	11.87
26000	17.29	26.76	44.05	133.6	84.99	258.9	18.70

27000	29.33	42.79	72.12	4	52.63	7.752	0.56
28000	31.39	52.1	83.49	18	59.21	34.88	2.52
29000	21.13	59.03	80.16	9.2	21.9	17.83	1.28
30000	15.63	60.02	75.65	17.2	86	33.33	2.40
31000	16.81	33.57	50.38	107.6	79.59	208.5	15.04
32000	8.44	21.13	29.57	137.2	95.28	265.9	19.20
33000	13.47	29.48	42.95	100.8	95.45	195.3	14.11
34000	13.98	33	46.98	84.4	94.2	163.6	11.81
35000	16.31	46.72	63.03	111.6	75.2	216.3	15.62
36000	13.54	39.92	53.46	144.4	80.04	279.8	20.21
37000	17.34	40.19	57.53	140.4	78.17	272.1	19.65
38000	22.99	62.99	85.98	37.2	64.58	72.09	5.20
39000	16.16	56.15	72.31	52	90.91	100.8	7.28
40000	29.05	78.94	108	33.2	51.88	64.34	4.64
41000	19.59	65.36	84.95	40.8	92.73	79.07	5.71
42000	30.23	86.54	116.8	25.2	43.15	48.84	3.52
43000	18.67	71.62	90.29	42	90.52	81.4	5.88
44000	29.66	113.1	142.8	18.4	79.31	35.66	2.57
45000	25.5	101	126.5	18	83.33	34.88	2.52
46000	28.54	113.5	142.1	16.4	80.39	31.78	2.29

Table 4.6: Summary of capacitive performance data for EDLC employing OCCHME in GCD current density of 5 mA cm^{-2} , that performed 32,000 charge-discharge cycles.

Cycle number	R_s (Ω)	R_{ct} (Ω)	ESR (Ω)	Areal capacitance (mF cm^{-2})	Coulombic efficiency (%)	Capacitance retention (%)	Energy density ($\mu\text{Wh cm}^{-2}$)
1	0.32	4.4	4.7	37	81	100	5.18
1000	0.42	4.6	4.99	37	82.22	100	5.18
2000	0.53	3.6	4.1	65	79.27	175.67	9.1
3000	0.57	4	4.53	58	85.29	156.75	8.12
4000	0.62	5	5.6	54	83.08	145.94	7.56
5000	0.83	5.3	6.12	60	86.96	162.16	8.4
6000	1	6.7	7.66	95	84.82	256.75	13.3

7000	1.36	6.7	8.1	124	79.49	335.13	17.36
8000	1.13	5.5	6.61	134	81.71	362.16	18.76
9000	2.05	11	13.47	87	90.63	235.13	12.18
10000	3.16	10	13.29	92	88.46	248.64	12.88
11000	2.31	8.4	10.66	122	85.92	329.73	17.08
12000	2.51	7.7	10.22	160	81.63	432.43	22.4
13000	2.43	8.9	11.36	153	90.53	413.51	21.42
14000	1.81	11	12.34	117	77.48	316.21	16.38
15000	1.61	14	15.74	93	65.96	251.35	13.02
16000	1.38	17	18.68	75	56.39	202.70	10.5
17000	1.98	20	21.69	65	57.02	175.67	9.1
18000	2.95	29	31.51	22	52.38	59.45	3.08
19000	3.88	25	28.86	35	83.33	94.59	4.9
20000	5.51	14	19.93	67	77.01	181.01	9.38
21000	8.28	19	27.23	34	80.95	91.89	4.76
22000	4.62	23	27.36	32	84.21	86.48	4.48
23000	6.49	15	21.36	44	53.01	118.9	6.16
24000	8.59	20	29.01	26	43.33	70.27	3.64
25000	6.28	19	25.27	38	71.7	102.70	5.32
26000	7.36	19	26.14	37	82.22	100	5.18
27000	5.84	19	24.74	41	51.9	110.8	5.74
28000	9.3	34	43.18	13	30.95	35.13	1.82
29000	3.82	24	27.69	49	53.26	132.4	6.86
30000	7.65	28	35.66	23	37.7	62.16	3.22
31000	7.31	31	38.19	14	31.82	37.83	1.96
32000	9.71	34	43.96	4	13.79	10.81	0.56

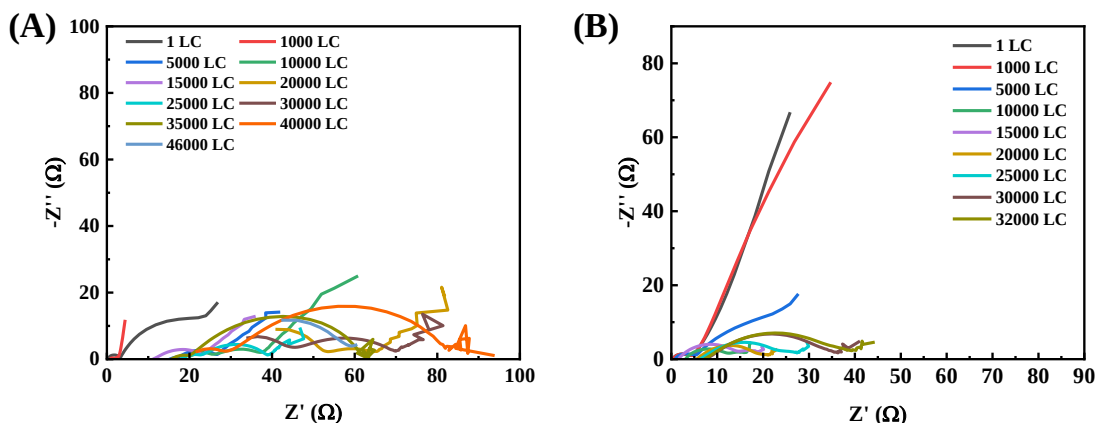


Fig.4.15 (A) Plot of Nyquist plots obtained from EIS during life cycle studies of the EDLC tested at 2 mA cm^{-2} ; (B) Plot of Nyquist plots obtained from EIS during life cycle studies of the EDLC tested at 5 mA cm^{-2} .

Fig.4.12 (B) and 4.12 (D) illustrate the variations in R_s , R_{ct} , and ESR of the EDLC assembled with OCCHME, as a function of life cycle number at 2 and 5 mA cm^{-2} , respectively. These resistive parameters were extracted from periodic EIS measurements carried out throughout the cycling tests to assess the electrochemical aging and interfacial stability of the device. At 2 mA cm^{-2} , the R_s value exhibited a moderate increase from its initial value of 0.32Ω to approximately 25.50Ω by the end of 46,000 cycles. This increase, though measurable, remained relatively constrained across the extended test period, indicating sustained ionic conduction within the OCCHME matrix. A similar trend is observed at 5 mA cm^{-2} , where R_s progressed from 0.32Ω to 9.71Ω over the span of 32,000 cycles as shown in Fig.4.12 (D). The low and slowly varying nature of R_s across both current densities suggests that the internal ionic mobility within the hydrogel membrane remained largely unaffected during the operational lifetime of the EDLCs. This behavior is indicative of robust electrolyte retention, which may be attributed to the intrinsic hydrophilicity of the chitosan backbone, as well as the ionic gelation-mediated structural integrity provided by oxalate crosslinking. Contrastingly, the R_{ct} values experienced a more pronounced increase with cycling. For the EDLC tested at 2 mA cm^{-2} , R_{ct} rose gradually from 4.39Ω to 100.98Ω , while the corresponding increase at 5 mA cm^{-2} spanned from 4.9Ω to 34.25Ω . This progressive growth in R_{ct} reflects a cumulative rise in interfacial

resistance at the electrode-electrolyte boundary. Such increases are commonly attributed to changes in the local microstructure of the carbon electrodes, possibly arising from partial pore blockage, limited ion accessibility, or chemical degradation of active surface groups during prolonged cycling [136]. The ESR displayed a composite trend largely effected by the rise in R_{ct} . At 2 mA cm^{-2} , ESR increased significantly from an initial value of $4.71 \text{ } \Omega$ to $126.48 \text{ } \Omega$ over 46,000 cycles. At 5 mA cm^{-2} , ESR followed a similar but comparatively moderated trajectory, rising from $4.7 \text{ } \Omega$ to $43.96 \text{ } \Omega$ by the end of 32,000 cycles. These observations reinforce the understanding that while the electrolyte bulk conductivity remained relatively stable, the key contributor to overall resistive aging was the gradual deterioration at the electrode–electrolyte interface [119]. Table 4.5 and 4.6 provide the complete R_s , R_{ct} , and ESR values at intervals of 1000 cycles, serving as a comprehensive record of electrochemical aging. Additionally, Nyquist plots obtained during life cycle tests are given in Fig.4.15 (A-B), corroborate the above analysis. Initially, the impedance spectra featured a singular semicircle in the high-frequency region, characteristic of ideal capacitive behavior. With increasing cycle number, a secondary semicircle began emerging at lower frequencies, indicating the development of additional resistive processes. Over extended cycling, this feature merged with the primary semicircle, forming a broadened arc that signifies increased R_{ct} due to aging effects such as pore collapse, electrolyte depletion at the interface, or ion-trapping within the porous carbon structure [120]. Overall, the evolution of resistive parameters over prolonged cycling suggests that although minor increases in R_s occurred, the OCCHME retained its essential electrolyte function. The primary aging mechanism was localized at the electrode interface, evidenced by R_{ct} escalation, while the stable low R_s confirmed sustained hydration and ion conduction through the membrane matrix. These insights validate the structural and electrochemical stability of OCCHME and underline its potential for long-term EDLC operation. Taken together, these findings highlight that the OCCHME-based EDLC not only delivers promising electrochemical performance initially, but also exhibits sustained durability under prolonged mechanical and electrical stress, which is a critical requirement for practical deployment in next-generation, flexible, solid-state energy storage platforms.

The observed capacity fading in the EDLCs employing the OCCHME is closely linked to the applied current density for cycle life name. At 2 mA cm^{-2} , the gradual decline in capacitance after extended cycling is primarily associated with interfacial polarization, as evidenced by the progressive increase in R_{ct} and ESR, which limits ion accessibility at the electrode-electrolyte interface. In contrast, at higher current density of 5 mA cm^{-2} , the earlier onset of capacitance fading can be attributed to incomplete utilization of the electroactive surface and partial detachment of electrode material. Similar current density dependent fading mechanisms have been reported in literature, where low current densities lead to polarization driven decay, while higher current densities accelerate active material loss and electrode degradation [121,122].

The excellent electrochemical performance and long cycle life stability of the OCCHME-based EDLC prompted the development of a working prototype to demonstrate its practical utility. As shown in Fig.4.16 (A), a prototype was fabricated by connecting five individual EDLC cells in series, each assembled with the optimized OCCHME as the electrolyte and charged at a current density of 2 mA cm^{-2} . The resulting device successfully powered a red LED, exhibiting a combined output voltage of approximately 1.74 V. The illumination remained stable for a duration of 1.76 minutes, thereby validating the real-world applicability of the OCCHME-based solid-state EDLC system. This proof-of-concept device underscores the ability of the chitosan–potassium oxalate membrane to function as an efficient solid electrolyte capable of supporting reliable energy delivery in practical configurations.

Following the long-term cycling test, a postmortem analysis of the EDLC was conducted to assess structural and interfacial integrity. The disassembled electrode–membrane assemblies are presented in Fig.4.16 (B) and 4.16 (C). Fig.4.16 (B)(i–ii) shows the original BPC-coated SS electrodes and the pristine OCCHME membrane prior to EDLC assembly. The post-cycling images in Fig.4.16 (C)(i–ii) reveal that while the BPC partially delaminates from the SS current collectors and adheres to the membrane surface, the OCCHME itself remains physically intact, free of cracks, delamination, or discoloration. This confirms that the OCCHME retains excellent structural integrity and mechanical resilience, even after prolonged electrochemical

cycling. These observations support the conclusion that the OCCHME not only facilitates high-performance ionic conduction but also maintains mechanical and interfacial stability essential for commercial-scale, durable solid-state supercapacitor applications.

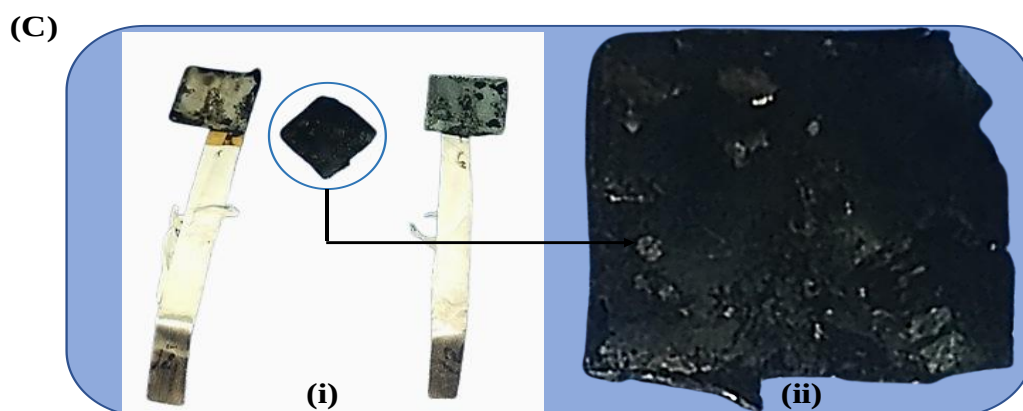
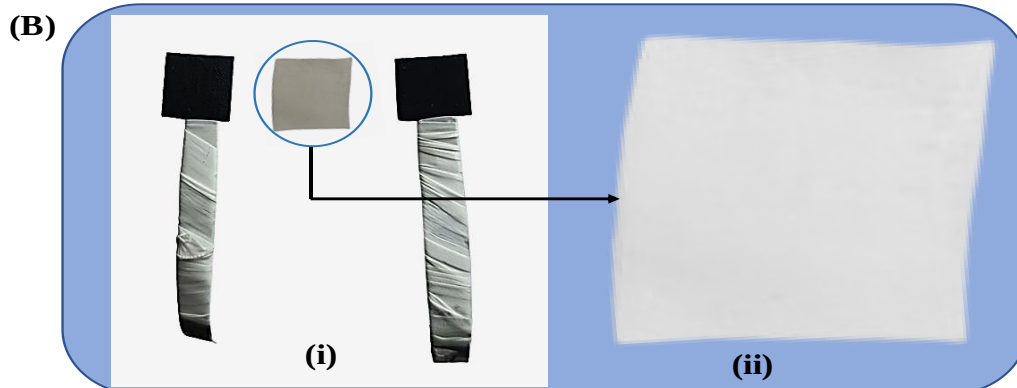
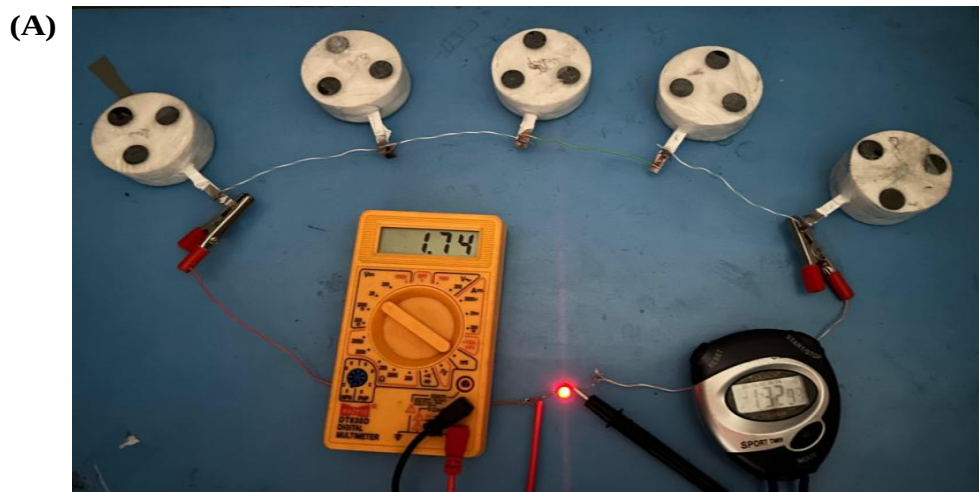


Fig.4.16 (A) A photograph displaying an LED bulb powered by the prototype energy device; (B) (i) Image showing the OCCHME and two BPC-coated SS electrodes prior to their assembly into the HMEA, (ii) A close-up of the OCCHME, highlighting its consistent, white appearance before assembly; (C) (i) Postmortem image of the disassembled HMEA, revealing the OCCHME and the BPC-coated SS electrodes after the cycle life test, (ii) A close-up view of the OCCHME following completion of the cycle life test.

The fluctuation in areal capacitance of the EDLCs during extended cycling can be attributed to multiple interconnected factors. The R_s value remained nearly constant throughout the cycle life test, confirming a stable electrolyte resistance. In contrast, the R_{ct} exhibited a gradual rise, followed by a sharp increase in both R_{ct} and ESR. Since R_{ct} reflects the interfacial resistance between the electrode and electrolyte, this trend indicates progressive interface degradation, which reduces charge-transfer efficiency and contributes directly to capacitance fading. Similar impedance growth associated with cycling-induced aging has been reported in long-term studies of electrochemical capacitors, where increased interfacial resistance correlates with declining capacitance retention [123,124]. The fluctuation could also arise from partial loss of electrode material or reduced adhesion between the electrode and current collector, which can be seen from the postmortem images in Fig.4.16 (C). From this image it is evident that after the cycle life test, the membrane retained its structure similar to the initial state, whereas the electrode layer detached from the membrane surface. During repeated cycling, such electrode delamination becomes more pronounced, which increases the interfacial resistance and decreases the effective electrochemically active surface area, thereby reducing capacitance over time [125,126].

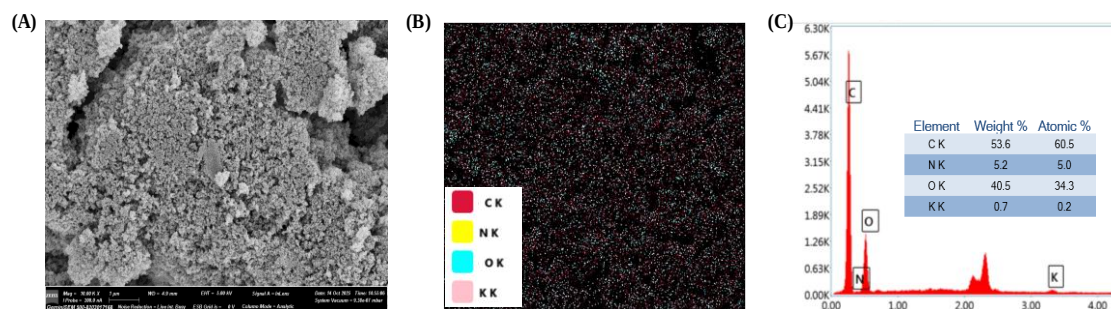


Fig.4.17 (A) Post-cycling FE-SEM image of OCCHME; (B) EDX mapping of OCCHME; (C) EDX spectrum and elemental data of OCCHME.

Post-cycling FE-SEM and EDX analyses on the OCCHME has been carried out after the cycle life test to examine possible morphological and interfacial changes. Fig.4.17. shows the FE-SEM image and EDX elemental mapping of the post-cycling OCCHME. As shown in Fig.4.17 (A), the post-cycled membrane surface retained its macroscopic structural integrity, indicating that the oxalate cross-linked chitosan matrix maintained mechanical stability even after extensive charge–discharge cycling. However, compared with the OCCHME before the cycle life test, as shown in Fig.4.8 (D), the post-cycled FE-SEM micrographs show denser clusters and the presence of carbon-rich agglomerates embedded on the membrane surface. This morphological evolution arises from the partial adherence of the carbon electrode materials during long-term cycling, as also evidenced in the post-mortem photograph of Fig.4.16 (C). The elemental mapping and EDX spectra as shown in the Fig.4.17 (B) confirm the increased carbon content (≈ 53.6 wt %) and the presence of K, O, and N elements, consistent with the residual electrolyte species and carbonaceous deposits on the surface. The detection of potassium and oxygen signals further supports that the oxalate and K^+ ions remain coordinated within the hydrogel network even after prolonged cycling, reflecting its strong ionic retention and structural stability. The small increase in oxygen content and minor reduction in nitrogen content suggest limited surface oxidation and mild interface reorganization rather than degradation of the cross-linked structure. Overall, the post-cycled FE-SEM and EDX results verify that the OCCHME hydrogel preserved its continuous network structure and that the

observed changes mainly stem from surface deposition of conductive carbon species and interfacial charge accumulation, rather than intrinsic membrane damage.

Table 4.7: Comparison of physicochemical and electrochemical properties of chitosan-based hydrogels cross-linked with different crosslinking agents.

Crosslinker agents	Polymers	Mechanical strength	Ionic conductivity	Power density	Energy density	Ref.
Citric acid	Chitosan	5.1 MPa	7.7×10^{-3} S cm ⁻¹	4999.75 Wkg ⁻¹	55.83 Wh kg ⁻¹	[127]
Sodium sulfate and sodium hydrogen phosphate	Chitosan	4.2 MPa	1.9×10^{-4} S cm ⁻¹	810 mW cm ⁻²	810 mW cm ⁻²	[128]
Sodium triphosphate and sodium phosphate tribasic dodecahydrate	Chitosan	3.2 MPa	0.114 S cm ⁻¹	685 mW cm ⁻²	---	[81]
Polyacrylamide-lithium sulfate	Chitosan	2.25 MPa	1.74×10^{-2} S cm ⁻¹	350.3 W kg ⁻¹	8.7 Wh kg ⁻¹	[129]
HCl	Carboxylated chitosan	---	8.69×10^{-2} S cm ⁻¹	226.6 W kg ⁻¹	5.2 Wh kg ⁻¹	[130]
Sodium hydroxide and glutaraldehyde	Chitosan	40.4 ± 10.7 MPa	39.7 mS cm ⁻¹	---	---	[101]

Dibenzaldehyde-terminated poly(ethylene glycol)	Chitosan	---	2.75×10^{-2} S cm ⁻¹	7.1 Wh kg ⁻¹	500.2 W kg ⁻¹	[131]
1-ethyl-3-methylimidazolium tetrafluoroborate	Chitosan	---	16.3 ± 0.2 mS cm ⁻¹	---	---	[132]
NaOH and H ₂ SO ₄	Chitosan	---	---	900 W kg ⁻¹	32.6 Wh Kg ⁻¹	[133]
Choline chloride & lactic acid	Chitosan	---	2.5 mS cm ⁻¹	0.45 mW cm ⁻²	11.1 l W h cm ⁻²	[134]
KOH	Chitosan	---	0.45×10^{-2} S cm ⁻¹	5.1 W h kg ⁻¹	32.5 W kg ⁻¹	[135]
Na ₂ MoO ₄	Chitosan and PVA	580 KPa	6.5 mS cm ⁻¹	10.03 Wh kg ⁻¹	2560 W kg ⁻¹	[136]
Sodium Carbonate	Chitosan	52.29 MPa	7.89 mS cm ⁻¹	36.16 μWh cm ⁻²	2000 μW cm ⁻²	[17]
Potassium oxalate	Chitosan	55.04 MPa	4.84 mS cm ⁻¹	42.11 μWh cm ⁻²	2016 μW cm ⁻²	This work

The comparative data in Table 4.7 illustrate clear trends in how the type of crosslinking agent governs the structural integrity and electrochemical efficiency of chitosan-based polymer electrolytes. Citrate-, sulfate-, and phosphate-based crosslinkers [81,127–129] typically show moderate ionic conductivities and limited mechanical strength. These type of anionic crosslinkers often form weak ionic bridges within the chitosan network, leading to irregular ion transport pathways and higher interfacial resistance

during charge-discharge operation. Aldehyde-type crosslinkers such as glutaraldehyde [101,131] enhance mechanical strength through covalent bonding, but their rigid and densely crosslinked structures restrict polymer chain mobility and hinder ion diffusion. Consequently, these membranes exhibit high strength but lower energy and power densities. Ionic-liquid- and polymer-salt-based system [132–136] generally achieve higher ionic conductivity due to improved ion dissociation and plasticization effects. However, the presence of mobile ionic species and weaker polymer-ion coordination often leads to reduced mechanical stability and faster performance decay. In contrast, the potassium-oxalate-crosslinked chitosan membrane demonstrates an optimal balance between mechanical integrity and electrochemical performance. This synergy yields the highest mechanical strength among all crosslinkers, moderate ionic conductivity, and excellent energy storage capacity, surpassing most systems. Compared with the sodium-carbonate-crosslinked chitosan membrane [17], the potassium-oxalate crosslinked chitosan membrane maintains comparable strength and conductivity while delivering higher energy and power densities when applied in EDLCs. Overall, the comparative analysis confirms that potassium oxalate offers the most favourable compromise between ionic mobility and network rigidity, ensuring higher electrochemical performance with enhanced energy storage capability.

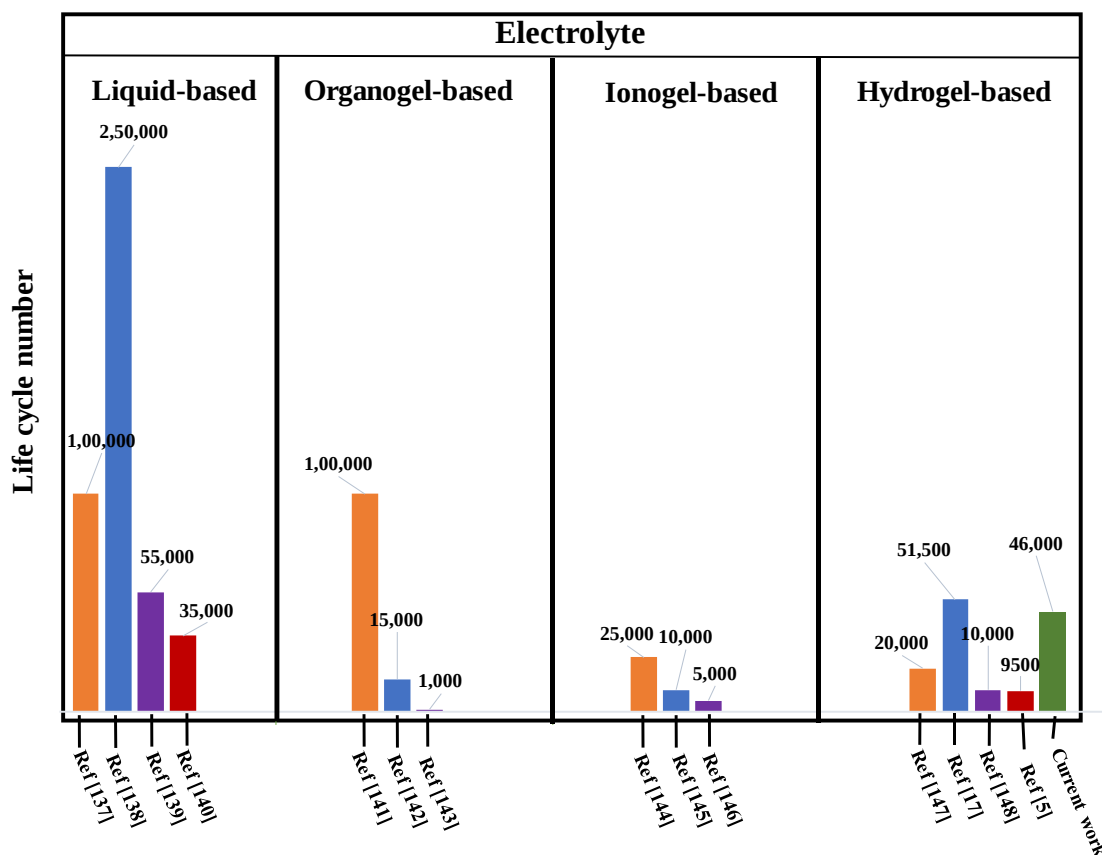


Fig.4.18 Cycle life comparison of various electrolyte systems reported for EDLC applications, presented in bar diagram format.

A concise comparative evaluation of EDLC cycle life across various electrolyte systems including liquid [137–140], organogel [141–143], ionogel [144–146], and hydrogel-based configurations [5,17,147,148] is illustrated in Fig.4.18. While liquid and organogel electrolytes have achieved impressive stabilities of up to 2,50,000 and 1,00,000 cycles respectively, hydrogel systems typically demonstrate shorter lifespans. Against this backdrop, the OCCHME-based EDLC developed in the present study delivers outstanding cycle live of 46,000 cycles at 2 mA cm^{-2} . This value is among the highest reported for solid-state hydrogel electrolytes. The results highlight the promise of OCCHME as a durable, scalable, and environmentally benign alternative to conventional electrolyte technologies for long-life supercapacitor applications.

Table 4.8: Comparison of results obtained from the previously reported ICCHME [17] of Chapter 2 and OCCHME (current work).

Properties	ICCHME [17]	OCCHME (Current work)
Crosslinker used	Na ₂ CO ₃	K ₂ C ₂ O ₄
Optimal concentration (M)	0.5	0.5
Optimal crosslinker volume (mL)	2	2
Thickness (μm)	60	60
WU (%)	226	208
DR (%)	18.24	17.80
Ionic conductivity (mScm ⁻¹)	7.89	4.84
Ion transference number	0.96	0.92
Cationic transference number	0.04	0.08
Breakdown Voltage (V)	2.32	2.10
Tensile strength (MPa)	53.23	55.04
Elongation (%)	11.13	5.60
Youngs modulus (MPa)	478.80	982.85
Maximum areal capacitance (mF cm ⁻²) at 2 mA cm ⁻²	260.40	300.80
R _s (Ω)	0.23	0.32
R _{ct} (Ω)	0.71	4.39
Life cycle number	51,500 (at 2 mA cm ⁻²) 33,000 (at 5 mA cm ⁻²)	46,000 (at 2 mA cm ⁻²) 32,000 (at 5 mA cm ⁻²)

A comprehensive comparison between our previously reported ICCHME, using Na₂CO₃ in Chapter 2 and the presently developed OCCHME highlights several critical differences in electrolyte performance, mechanical behavior, and electrochemical properties, which are summarized in the Table 4.8. Despite both systems employing the same chitosan matrix, optimal crosslinker concentration, and volume, the nature of

the crosslinking ions viz., carbonate (CO_3^{2-}) versus oxalate ($\text{C}_2\text{O}_4^{2-}$) introduces notable disparities. The WU ability, although relatively high in both cases, is slightly reduced in OCCHME compared to ICCHME, which could be attributed to differences in anion-polymer interactions. The larger oxalate ion, containing four oxygen atoms and forming bidentate coordination with the chitosan- NH_3^+ groups, may introduce stronger ionic crosslinking, thus restricting water penetration more than the planar carbonate ion. Correspondingly, OCCHME also displays a slightly lower DR than ICCHME, suggesting a more stable cross-linked network that is less susceptible to water-induced degradation. Electrochemically, the ionic conductivity of OCCHME is lower than that of ICCHME. This is attributed to the enhanced free volume and internal porosity in ICCHME caused by CO_2 bubble evolution during carbonate crosslinking, which facilitates ion mobility. Conversely, the tighter oxalate network reduces ion diffusivity despite maintaining adequate hydration. However, both systems exhibit high ion transference numbers, indicating dominant ionic conduction over electronic leakage. Notably, the cationic transference number of OCCHME is higher than ICCHME, implying that the OCCHME matrix permits slightly greater mobility of K^+ compared to Na^+ in the ICCHME. This difference could be related to the hydration radii and electrostatic affinity of the cations with the polymer matrix, where K^+ , being less strongly hydrated than Na^+ , may have enhanced diffusivity in hydrogel systems. In terms of breakdown voltage, ICCHME demonstrates a higher value compared to OCCHME, which again may stem from differences in structural integrity and internal ion aggregation. However, OCCHME compensates with marginally better mechanical performance, as evidenced by a tensile strength of 55.04 MPa and a Young's modulus of 982.85 MPa, both superior to those of ICCHME. These improvements may be linked to the dual-oxygen bridging nature of oxalate ions that form stiffer coordination crosslinks with chitosan, reinforcing the hydrogel network. The OCCHME-based EDLCs also exhibited superior areal capacitance of $300.80 \text{ mF cm}^{-2}$ at 2 mA cm^{-2} , exceeding that of ICCHME. This enhancement, despite lower ionic conductivity, may be attributed to better electrolyte-electrode interfacial interaction due to favorable wetting characteristics or improved electrode infiltration. However, R_s and R_{ct} values are higher in OCCHME than ICCHME, suggesting relatively hindered ion transport across the electrode-electrolyte interface, likely a result of denser ionic crosslinking in

OCCHME. In cyclic stability, both membranes demonstrate robust performance. The ICCHME retains capacitance for up to 51,500 cycles at 2 mA cm^{-2} , while OCCHME sustains 46,000 cycles under identical conditions. Though slightly lower in comparison, the OCCHME's performance remains commendable, especially when considering its mechanical robustness and higher capacitance output. This trade-off highlights how varying crosslinker chemistry influences not only ionic transport but also mechanical-electrochemical synergy. In summary, while ICCHME presents superior ionic conductivity and lower interfacial resistance owing to its more porous, loosely bound network, the OCCHME offers higher mechanical stiffness, more selective cationic mobility, and enhanced electrochemical capacitance. The choice of oxalate as the crosslinker introduces tunable transport behavior and improved mechanical strength, thereby offering a strategic advantage in designing structurally robust hydrogel electrolytes tailored for high-performance ESSs.

4.4 Conclusions

In this study, quasi-solid OCCHME was developed by ionic crosslinking chitosan with potassium oxalate. The synthesized OCCHME demonstrated excellent hydration properties, with WU and DR of 208% and 17.80%, respectively, supporting mechanical stability under prolonged operation. FTIR spectral shifts confirmed electrostatic complexation between chitosan and oxalate ions, while XRD analysis revealed a reduced crystallinity of 10.19%, confirming enhanced amorphous domain formation post-crosslinking. Dielectric analysis indicated strong interfacial polarization, and a high dielectric constant was observed at low frequencies, particularly at 0.5 M oxalate concentration, correlating with the highest ionic conductivity of 4.84 mS cm^{-1} and an ionic transference number of 0.92. The membrane exhibited an electrochemical stability window of 2.10 V, suitable for energy storage operation. Morphological examination via SEM revealed a continuous, wrinkle-free, and porous structure, while POM analysis highlighted the transformation from weakly birefringent, amorphous chitosan morphology to localized birefringent domains and spherulitic structures in OCCHME. Mechanical testing showed a tensile strength of 55.04 MPa and a Young's modulus of 982.85 MPa, indicating suitability for device assembly without risk of rupture or deformation. When implemented in EDLC assemblies, OCCHME enabled an areal capacitance of $300.80 \text{ mF cm}^{-2}$ at 2 mA cm^{-2} , alongside energy and power densities of $42.11 \text{ μWh cm}^{-2}$ and 2016 μW cm^{-2} , respectively. Long-term cycling performance was outstanding, with the EDLC maintained stable operation over 46,000 and 32,000 charge-discharge cycles at 2 and 5 mA cm^{-2} . The charge storage and relaxation behaviors were validated by Bode and Nyquist analysis, showed minimal resistance increase and a fast relaxation time constant of 0.11 s. A prototype device was constructed by connecting five OCCHME-based EDLCs in series successfully powered a red LED for 1.76 minutes, showcasing practical viability. Postmortem analysis after cycling confirmed the intact structural integrity of the membrane, with negligible delamination or material degradation. This work positions potassium oxalate cross-linked chitosan membranes as scalable, eco-friendly, and high-performance electrolytes for next-generation solid-state energy storage devices. Although the OCCHME-based EDLCs demonstrated excellent cycling stability and promising electrochemical performance, certain limitations were

observed. Specifically, minor fluctuations in Coulombic efficiency and a sharp rise in R_{ct} during prolonged cycling suggest progressive interfacial degradation, likely due to partial detachment of electrode material and reduced adhesion between the electrode layer and stainless-steel current collectors. These issues may be mitigated through optimization of the electrode formulation, use of more conductive and flexible current collectors (e.g., nickel foam, carbon cloth, or aluminium foil), and improved binder-electrode interactions. Future work will focus on addressing these aspects in parallel with further optimization of the electrolyte composition to enhance overall device performance.

4.5 References

- [1] Q. Hassan, P. Viktor, T. J. Al-Musawi, B. Mahmood Ali, S. Algburi, H.M. Alzoubi, A. Khudhair Al-Jiboory, A. Zuhair Sameen, H.M. Salman, M. Jaszczur, The renewable energy role in the global energy Transformations, *Renewable Energy Focus* 48 (2024) 100545. <https://doi.org/10.1016/j.ref.2024.100545>.
- [2] T.M. Gür, Review of electrical energy storage technologies, materials and systems: challenges and prospects for large-scale grid storage, *Energy Environ Sci* 11 (2018) 2696–2767. <https://doi.org/10.1039/C8EE01419A>.
- [3] P. Phogat, S. Sharma, R. Jha, S. Singh, Electrochemical Capacitors: EDLCs and Pseudocapacitors, in: 2024: pp. 225–255. https://doi.org/10.1007/978-981-96-0527-9_6.
- [4] S.B. Aziz, T.J. Woo, M.F.Z. Kadir, H.M. Ahmed, A conceptual review on polymer electrolytes and ion transport models, *Journal of Science: Advanced Materials and Devices* 3 (2018) 1–17. <https://doi.org/10.1016/j.jsamd.2018.01.002>.
- [5] D. Kamei, N.A. Choudhury, KI-doped redox-active gelatin chemical hydrogel membrane electrolytes for solid-state electrical double layer capacitors, *Mater Today Chem* 37 (2024) 101891. <https://doi.org/10.1016/j.mtchem.2023.101891>.
- [6] H. Kaur, A. Thakur, R.C. Thakur, A. Kumar, A Review on Multifaceted Role of Ionic Liquids in Modern Energy Storage Systems: From Electrochemical Performance to Environmental Sustainability, *Energy & Fuels* 39 (2025) 3703–3734. <https://doi.org/10.1021/acs.energyfuels.4c05274>.
- [7] M. Najafloo, L. Naji, Binary solvent-reinforced poly (vinyl alcohol)/sodium alginate double network hydrogel as a highly ion-conducting, resilient, and self-healing gel polymer electrolyte for flexible supercapacitors, *Int J Biol Macromol* 279 (2024) 135008. <https://doi.org/10.1016/j.ijbiomac.2024.135008>.
- [8] J. Yang, X. Hu, X. Fang, L. Fan, G. Qin, Z. Zhang, J. Xu, Y. Liang, Q. Chen, Tough and redox-mediated alkaline gel polymer electrolyte membrane for flexible supercapacitor with high energy density and low temperature resistance, *J Memb Sci* 650 (2022) 120386. <https://doi.org/10.1016/j.memsci.2022.120386>.

-
- [9] S.-A. Safavi-Mirmahalleh, A. Dadkhah-Janqor, M. Salami-Kalajahi, Chitosan-based gel polymer electrolytes for high performance Li-ion battery, *Int J Biol Macromol* 282 (2024) 137304. <https://doi.org/10.1016/j.ijbiomac.2024.137304>.
- [10] J. Huang, C. Li, D. Jiang, J. Gao, L. Cheng, G. Li, H. Luo, Z. Xu, D. Shin, Y. Wang, Y. Lu, Y. Kim, Solid-State Electrolytes for Lithium Metal Batteries: State-of-the-Art and Perspectives, *Adv Funct Mater* 35 (2025). <https://doi.org/10.1002/adfm.202411171>.
- [11] K.A. Uyanga, H. Zhao, X. Bo, W.A. Daoud, Advances and opportunities of hydrogels for metal-ion batteries, *Energy Storage Mater* 72 (2024) 103707. <https://doi.org/10.1016/j.ensm.2024.103707>.
- [12] T. Zhao, Q. Xin, G. Yang, S. Liang, J. Lin, Utilizing carboxymethyl cellulose sodium/sodium lignosulfonate hydrogel to build efficient electrolyte/electrode interfaces for multifunctional high-performance supercapacitors, *Int J Biol Macromol* 314 (2025) 144273. <https://doi.org/10.1016/j.ijbiomac.2025.144273>.
- [13] Z. Liu, L. Chen, X. Zhang, X. Lu, M. Peng, C. Wang, Y. Liu, X. Zhang, Carboxymethyl chitosan modified double-skeleton hydrogel electrolyte enables high performance for flexible zinc-air batteries, *Int J Biol Macromol* 303 (2025) 140678. <https://doi.org/10.1016/j.ijbiomac.2025.140678>.
- [14] Z. Zhang, N. Zhu, Q. Teng, J. Wang, X. Wan, Fire-resistant and low-temperature self-healing bio-based hydrogel electrolytes based on peach gum polysaccharide/sisal nanofibers for flexible supercapacitors, *Int J Biol Macromol* 276 (2024) 133759. <https://doi.org/10.1016/j.ijbiomac.2024.133759>.
- [15] N.A. Choudhury, S. Sampath, A.K. Shukla, Gelatin Hydrogel Electrolytes and Their Application to Electrochemical Supercapacitors, *J Electrochem Soc* 155 (2008) A74. <https://doi.org/10.1149/1.2803501>.
- [16] M. Wang, L. Fan, G. Qin, X. Hu, Y. Wang, C. Wang, J. Yang, Q. Chen, Flexible and low temperature resistant semi-IPN network gel polymer electrolyte membrane and its application in supercapacitor, *J Memb Sci* 597 (2020) 117740. <https://doi.org/10.1016/j.memsci.2019.117740>.

-
- [17] D. Hazarika, D. Kamei, N. Shijoh, N.A. Choudhury, An ionically cross-linked chitosan hydrogel membrane electrolyte for long-lived electrical double layer capacitors, *J Power Sources* 629 (2025) 236037. <https://doi.org/10.1016/j.jpowsour.2024.236037>.
- [18] T. Khandaker, T. Islam, A. Nandi, M.A.A.M. Anik, Md.S. Hossain, Md.K. Hasan, M.S. Hossain, Biomass-derived carbon materials for sustainable energy applications: a comprehensive review, *Sustain Energy Fuels* 9 (2025) 693–723. <https://doi.org/10.1039/D4SE01393J>.
- [19] M. Stoica, C.I. Bichescu, C.-M. Crețu, M. Dragomir, A.S. Ivan, G.M. Podaru, D. Stoica, M. Stuparu-Crețu, Review of Bio-Based Biodegradable Polymers: Smart Solutions for Sustainable Food Packaging, *Foods* 13 (2024) 3027. <https://doi.org/10.3390/foods13193027>.
- [20] N.A. Rahman, S.A. Hanifah, N.N. Mobarak, A. Ahmad, N.A. Ludin, F. Bella, M.S. Su'ait, Chitosan as a paradigm for biopolymer electrolytes in solid-state dye-sensitised solar cells, *Polymer (Guildf)* 230 (2021) 124092. <https://doi.org/10.1016/j.polymer.2021.124092>.
- [21] N.M. Sadiq, R.T. Abdulwahid, S.B. Aziz, H.J. Woo, M.F.Z. Kadir, Chitosan as a suitable host for sustainable plasticized nanocomposite sodium ion conducting polymer electrolyte in EDLC applications: Structural, ion transport and electrochemical studies, *Int J Biol Macromol* 265 (2024) 130751. <https://doi.org/10.1016/j.ijbiomac.2024.130751>.
- [22] J. Ding, Y. Yang, J. Poisson, Y. He, H. Zhang, Y. Zhang, Y. Bao, S. Chen, Y.M. Chen, K. Zhang, Recent Advances in Biopolymer-Based Hydrogel Electrolytes for Flexible Supercapacitors, *ACS Energy Lett* 9 (2024) 1803–1825. <https://doi.org/10.1021/acsenergylett.3c02567>.
- [23] L. Lan, J. Ping, J. Xiong, Y. Ying, Sustainable Natural Bio-Origin Materials for Future Flexible Devices, *Advanced Science* 9 (2022). <https://doi.org/10.1002/advs.202200560>.

-
- [24] N.-M. Blebea, C. Pușcașu, R.-A. Vlad, G. Hancu, Chitosan-Based Gel Development: Extraction, Gelation Mechanisms, and Biomedical Applications, *Gels* 11 (2025) 275. <https://doi.org/10.3390/gels11040275>.
- [25] T.M.T. Vo, T. Kobayashi, Chitosan-Based Hydrogels, in: 2024: pp. 203–240. <https://doi.org/10.4018/979-8-3693-0003-9.ch008>.
- [26] N.A. Choudhury, P.W.C. Northrop, A.C. Crothers, S. Jain, V.R. Subramanian, Chitosan hydrogel-based electrode binder and electrolyte membrane for EDLCs: experimental studies and model validation, *J Appl Electrochem* 42 (2012) 935–943. <https://doi.org/10.1007/s10800-012-0469-2>.
- [27] S. Jiang, C. Qiao, R. Liu, Q. Liu, J. Xu, J. Yao, Structure and properties of citric acid cross-linked chitosan/poly(vinyl alcohol) composite films for food packaging applications, *Carbohydr Polym* 312 (2023) 120842. <https://doi.org/10.1016/j.carbpol.2023.120842>.
- [28] J. Qian, X. Wang, J. Shu, C. Su, J. Gong, Z. Xu, J. Jin, J. Shi, A Novel Complex of Chitosan–Sodium Carbonate and Its Properties, *Mar Drugs* 16 (2018) 416. <https://doi.org/10.3390/md16110416>.
- [29] T.E. Benavidez, A.M. Baruzzi, Comparative behavior of glucose oxidase and oxalate oxidase immobilized in mucin/chitosan hydrogels for biosensors applications, *Polymer (Guildf)* 53 (2012) 438–444. <https://doi.org/10.1016/j.polymer.2011.12.014>.
- [30] T.E. Benavidez, C.I. Alvarez, A.M. Baruzzi, Physicochemical properties of a mucin/chitosan matrix used for the development of an oxalate biosensor, *Sens Actuators B Chem* 143 (2010) 660–665. <https://doi.org/10.1016/j.snb.2009.10.031>.
- [31] C. Chen, A. Dong, J. Yang, L. Deng, Preparation and properties of an injectable thermo-sensitive double crosslinking hydrogel based on thiolated chitosan/beta-glycerophosphate, *J Mater Sci* 47 (2012) 2509–2517. <https://doi.org/10.1007/s10853-011-6075-6>.
- [32] A. Shahab Marf, R. M. Abdullah, S. B. Aziz, Structural, Morphological, Electrical and Electrochemical Properties of PVA: CS-Based Proton-Conducting

Polymer Blend Electrolytes, Membranes (Basel) 10 (2020) 71. <https://doi.org/10.3390/membranes10040071>.

[33] D. Kamei, D. Hazarika, N.A. Choudhury, Pure and KI-doped glyoxal-crosslinked gelatin hydrogel membrane electrolytes for solid-state EDLCs, *Mater Today Chem* 43 (2025) 102470. <https://doi.org/10.1016/j.mtchem.2024.102470>.

[34] S.B. Aziz, S. Al-Zangana, M.A. Brza, S.R. Saeed, R.T. Abdulwahid, M.F.Z. Kadir, Study of Dielectric Properties and Ion Transport Parameters in Chitosan-Barium Nitrate Based Solid Polymer Electrolytes, *Int J Electrochem Sci* 14 (2019) 10580–10595. <https://doi.org/10.20964/2019.12.39>.

[35] S.B. Aziz, M.F.Z. Kadir, M.H. Hamsan, H.J. Woo, M.A. Brza, Development of Polymer Blends Based on PVA:POZ with Low Dielectric Constant for Microelectronic Applications, *Sci Rep* 9 (2019) 13163. <https://doi.org/10.1038/s41598-019-49715-8>.

[36] A.K. Arof, S. Amirudin, S.Z. Yusof, I.M. Noor, A method based on impedance spectroscopy to determine transport properties of polymer electrolytes, *Phys. Chem. Chem. Phys.* 16 (2014) 1856–1867. <https://doi.org/10.1039/C3CP53830C>.

[37] R.T. Abdulwahid, S.B. Aziz, M.F.Z. Kadir, N.M. Sadiq, N.A. Halim, M.H. Hamsan, S.R. Saeed, H.J. Woo, Biodegradable polymer membrane K⁺ ion conductor for electrochemical device application, *J Mater Sci* 57 (2022) 19902–19923. <https://doi.org/10.1007/s10853-022-07825-1>.

[38] H. Nagahama, H. Maeda, T. Kashiki, R. Jayakumar, T. Furuike, H. Tamura, Preparation and characterization of novel chitosan/gelatin membranes using chitosan hydrogel, *Carbohydr Polym* 76 (2009) 255–260. <https://doi.org/10.1016/j.carbpol.2008.10.015>.

[39] Y. Hu, V. Topolkaraev, A. Hiltner, E. Baer, Measurement of water vapor transmission rate in highly permeable films, *J Appl Polym Sci* 81 (2001) 1624–1633. <https://doi.org/10.1002/app.1593>.

-
- [40] M.A. Jahid, J. Hu, Water vapor transmission and water resistant: opposite but may coexist, *Mater Today Proc* 16 (2019) 1485–1490. <https://doi.org/10.1016/j.matpr.2019.05.328>.
- [41] S. Iizuka, K. Murata, M. Sekine, C. Sato, A novel cup with a pressure-adjusting mechanism for high-temperature water vapor transmission rate measurements, *Polym Test* 50 (2016) 73–78. <https://doi.org/10.1016/j.polymertesting.2015.11.018>.
- [42] A.S.F.M. Asnawi, S.B. Aziz, I. Brevik, M.A. Brza, Y.M. Yusof, S.M. Alshehri, T. Ahamad, M.F.Z. Kadir, The Study of Plasticized Sodium Ion Conducting Polymer Blend Electrolyte Membranes Based on Chitosan/Dextran Biopolymers: Ion Transport, Structural, Morphological and Potential Stability, *Polymers (Basel)* 13 (2021) 383. <https://doi.org/10.3390/polym13030383>.
- [43] R. Deivanayagam, R. Shahbazian-Yassar, *Electrochemical Methods and Protocols for Characterization of Ceramic and Polymer Electrolytes for Rechargeable Batteries, Batter Supercaps* 4 (2021) 596–606. <https://doi.org/10.1002/batt.202000221>.
- [44] A.K. Arof, N.E.A. Shuhaimi, S. Amirudin, M.Z. Kufian, H.J. Woo, M.A. Careem, Polyacrylonitrile-lithium bis(oxalato) borate polymer electrolyte for electrical double layer capacitors, *Polym Adv Technol* 25 (2014) 265–272. <https://doi.org/10.1002/pat.3231>.
- [45] R. Na, Y. Liu, N. Lu, S. Zhang, F. Liu, G. Wang, Mechanically robust hydrophobic association hydrogel electrolyte with efficient ionic transport for flexible supercapacitors, *Chemical Engineering Journal* 374 (2019) 738–747. <https://doi.org/10.1016/j.cej.2019.06.004>.
- [46] Metrohm, *Electrochemical Impedance Spectroscopy (EIS) on battery electrodes using NOVA*, Application Note AN-EIS-005 (2014).
- [47] A.Ch. Lazanas, M.I. Prodromidis, *Electrochemical Impedance Spectroscopy—A Tutorial*, *ACS Measurement Science Au* 3 (2023) 162–193. <https://doi.org/10.1021/acsmeasuresciau.2c00070>.

- [48] S. Mahmoudi-Qashqay, M.-R. Zamani-Meymian, A. Maleki, A simple method of fabrication hybrid electrodes for supercapacitors, *Sci Rep* 14 (2024) 29105. <https://doi.org/10.1038/s41598-024-80243-2>.
- [49] N. Yadav, N. Yadav, S.A. Hashmi, Ionic liquid incorporated, redox-active blend polymer electrolyte for high energy density quasi-solid-state carbon supercapacitor, *J Power Sources* 451 (2020) 227771. <https://doi.org/10.1016/j.jpowsour.2020.227771>.
- [50] P. Krishnan, V. Biju, Effect of electrolyte concentration on the electrochemical performance of RGO-Na₂SO₄ supercapacitor, *Mater Today Proc* 54 (2022) 958–962. <https://doi.org/10.1016/j.matpr.2021.10.512>.
- [51] S. Pervez, M.Z. Iqbal, Capacitive and Diffusive Contributions in Supercapacitors and Batteries: A Critique of *b* -Value and the $v-v^{1/2}$ Model, *Small* 19 (2023). <https://doi.org/10.1002/sml.202305059>.
- [52] T.J. Jenila, W.T. Infancy, R. Rathikha, P.A. Vinosha, M. Ayyar, S. Ramasamy, S. Maruthasalamoorthy, R. Navamathavan, B. Xavier, A.M.S. Alhuthali, H.M. Abo-Dief, M.H. Abdellattif, R. Balachandran, M.K. Hossain, Unraveling the role of MXene (Ti₃C₂T_x) integrated Cu-doped WO₃ nanocomposites via co-precipitation technique for enhanced supercapacitor performance, *Sci Rep* 15 (2025) 25007. <https://doi.org/10.1038/s41598-025-10174-z>.
- [53] A. Laheäär, P. Przygocki, Q. Abbas, F. Béguin, Appropriate methods for evaluating the efficiency and capacitive behavior of different types of supercapacitors, *Electrochem Commun* 60 (2015) 21–25. <https://doi.org/10.1016/j.elecom.2015.07.022>.
- [54] S. Yeasmin, M. Bora, B.K. Saikia, D. Mahanta, Binder mediated enhanced electrochemical capacitance in sodium silicate-graphite paint coated filter paper electrodes for all-solid-state symmetric electrochemical capacitors, *J Energy Storage* 73 (2023) 108945. <https://doi.org/10.1016/j.est.2023.108945>.
- [55] X. He, T. Zhuang, S. Ruan, X. Xia, Y. Xia, J. Zhang, H. Huang, Y. Gan, W. Zhang, An innovative poly(ionic liquid) hydrogel-based anti-freezing electrolyte with

high conductivity for supercapacitor, *Chemical Engineering Journal* 466 (2023) 143209. <https://doi.org/10.1016/j.cej.2023.143209>.

[56] D. Alemu, E. Getachew, A.K. Mondal, Study on the Physicochemical Properties of Chitosan and their Applications in the Biomedical Sector, *Int J Polym Sci* 2023 (2023) 1–13. <https://doi.org/10.1155/2023/5025341>.

[57] S. Bashir, M. Hina, J. Iqbal, A.H. Rajpar, M.A. Mujtaba, N.A. Alghamdi, S. Wageh, K. Ramesh, S. Ramesh, Fundamental Concepts of Hydrogels: Synthesis, Properties, and Their Applications, *Polymers (Basel)* 12 (2020) 2702. <https://doi.org/10.3390/polym12112702>.

[58] A. Shekhawat, V. Gomase, A. Bambal, M. Khapre, P. Waghe, D. Saravanan, R. Jugade, Chemical functionalization of Chitosan biopolymer with diacetyl monoxime for enhanced Cr(VI) removal from aqueous media, *Int J Biol Macromol* 282 (2024) 137038. <https://doi.org/10.1016/j.ijbiomac.2024.137038>.

[59] P. Doondani, V. Gomase, D. Saravanan, R.M. Jugade, Chitosan coated cotton-straw-biochar as an admirable adsorbent for reactive red dye, *Results in Engineering* 15 (2022) 100515. <https://doi.org/10.1016/j.rineng.2022.100515>.

[60] K. Mohan, A.R. Ganesan, P.N. Ezhilarasi, K.K. Kondamareddy, D.K. Rajan, P. Sathishkumar, J. Rajarajeswaran, L. Conterno, Green and eco-friendly approaches for the extraction of chitin and chitosan: A review, *Carbohydr Polym* 287 (2022) 119349. <https://doi.org/10.1016/j.carbpol.2022.119349>.

[61] E.Yu. Pisarevskaya, A. L. Klyuev, O. N. Efimov, Comparison of electrochemical behavior of composites based on graphene oxide, poly-o-phenylenediamine, and heteropolyacids, *Polym Adv Technol* 33 (2022) 1137–1145. <https://doi.org/10.1002/pat.5587>.

[62] J. Pérez-Calderón, M.V. Santos, N. Zaritzky, Synthesis, characterization and application of cross-linked chitosan/oxalic acid hydrogels to improve azo dye (Reactive Red 195) adsorption, *React Funct Polym* 155 (2020) 104699. <https://doi.org/10.1016/j.reactfunctpolym.2020.104699>.

- [63] A.H. Khan, S. Imran, J. Talati, L. Jafri, Fourier transform infrared spectroscopy for analysis of kidney stones, *Investig Clin Urol* 59 (2018) 32. <https://doi.org/10.4111/icu.2018.59.1.32>.
- [64] X. Wang, W. Li, Z. Li, T. Han, J. Rong, J. Fan, L. Huang, Y. Lu, Z. Wang, Human milk whey glycoprotein N-glycans varied greatly among different maternal secretor status, *Carbohydr Polym* 310 (2023) 120728. <https://doi.org/10.1016/j.carbpol.2023.120728>.
- [65] K. Tamilarasan, A. Annapoorani, R. Manikandan, S. Janarthanan, Isolation, characterization of galactose-specific lectin from *Odoiporus longicollis* and its antibacterial and anticancer activities, *Int J Biol Macromol* 183 (2021) 1119–1135. <https://doi.org/10.1016/j.ijbiomac.2021.05.054>.
- [66] N. Kumar, K.S. Rao, U.P. Deshpande, V. Sathe, A.K. Sahu, S.N. Achary, S.K. Deshpande, Enhanced oxygen ion conductivity in $\text{Ba}_3\text{W}_{1+x}\text{V}_{1-x}\text{O}_{8.5+x/2}$ ($-0.2 \leq x \leq 0.2$) hexagonal perovskite derivative compounds, *Ionics (Kiel)* 31 (2025) 2593–2610. <https://doi.org/10.1007/s11581-025-06112-8>.
- [67] S. Aziz, R. Abdullah, M. Rasheed, H. Ahmed, Role of Ion Dissociation on DC Conductivity and Silver Nanoparticle Formation in PVA:AgNt Based Polymer Electrolytes: Deep Insights to Ion Transport Mechanism, *Polymers (Basel)* 9 (2017) 338. <https://doi.org/10.3390/polym9080338>.
- [68] S.B. Aziz, Occurrence of electrical percolation threshold and observation of phase transition in chitosan(1-x):AgI x ($0.05 \leq x \leq 0.2$)-based ion-conducting solid polymer composites, *Applied Physics A* 122 (2016) 706. <https://doi.org/10.1007/s00339-016-0235-0>.
- [69] S.B. Aziz, Z.H.Z. Abidin, Electrical and morphological analysis of chitosan:AgTf solid electrolyte, *Mater Chem Phys* 144 (2014) 280–286. <https://doi.org/10.1016/j.matchemphys.2013.12.029>.
- [70] S.B. Aziz, M.A. Brza, M.F.Z. Kadir, M.H. Hamsan, Z.H.Z. Abidin, D.A. Tahir, O.Gh. Abdullah, Ion in Chitosan Based Solid Electrolyte, *Int J Electrochem Sci* 14 (2019) 5521–5534. <https://doi.org/10.20964/2019.06.13>.

-
- [71] S. Ramesh, Dielectric behaviour of PVC-based polymer electrolytes, *Solid State Ion* 152–153 (2002) 291–294. [https://doi.org/10.1016/S0167-2738\(02\)00311-9](https://doi.org/10.1016/S0167-2738(02)00311-9).
- [72] J. M. Hadi, S. B. Aziz, M. M. Nofal, S.A. Hussein, M.H. Hafiz, M.A. Brza, R.T. Abdulwahid, M.F.Z. Kadir, H.J. Woo, Electrical, Dielectric Property and Electrochemical Performances of Plasticized Silver Ion-Conducting Chitosan-Based Polymer Nanocomposites, *Membranes (Basel)* 10 (2020) 151. <https://doi.org/10.3390/membranes10070151>.
- [73] S.B. Aziz, S.M. Mamand, The Study of Dielectric Properties and Conductivity Relaxation of Ion Conducting Chitosan:NaTf Based Solid Electrolyte, *Int J Electrochem Sci* 13 (2018) 10274–10288. <https://doi.org/10.20964/2018.11.05>.
- [74] S.B. Aziz, S.M. Mamand, The Study of Dielectric Properties and Conductivity Relaxation of Ion Conducting Chitosan:NaTf Based Solid Electrolyte, *Int J Electrochem Sci* 13 (2018) 10274–10288. <https://doi.org/10.20964/2018.11.05>.
- [75] S. Majumdar, R. Ray, Ionic conduction and charge carrier relaxation in chitosan acetate based solid biopolymer electrolyte embedded with LiClO₄, *Journal of Polymer Research* 28 (2021) 157. <https://doi.org/10.1007/s10965-021-02509-x>.
- [76] Y.M. Yusof, M.F. Shukur, M.H. Hamsan, K. Jumbri, M.F.Z. Kadir, Plasticized solid polymer electrolyte based on natural polymer blend incorporated with lithium perchlorate for electrical double-layer capacitor fabrication, *Ionics (Kiel)* 25 (2019) 5473–5484. <https://doi.org/10.1007/s11581-019-03096-0>.
- [77] J.M. Hadi, S.B. Aziz, M.A. Brza, M.F.Z. Kadir, R.T. Abdulwahid, B. Ali Al-Asbahi, A. Ahmed Ali Ahmed, Structural and energy storage behavior of ion conducting biopolymer blend electrolytes based on methylcellulose: Dextran polymers, *Alexandria Engineering Journal* 61 (2022) 9273–9285. <https://doi.org/10.1016/j.aej.2022.03.042>.
- [78] Y. Xiao, Y. Xiang, R. Xiu, S. Lu, Development of cesium phosphotungstate salt and chitosan composite membrane for direct methanol fuel cells, *Carbohydr Polym* 98 (2013) 233–240. <https://doi.org/10.1016/j.carbpol.2013.06.017>.

-
- [79] D.M. Correia, M.A. Gámiz-González, G. Botelho, A. Vidaurre, J.L. Gomez Ribelles, S. Lanceros-Mendez, V. Sencadas, Effect of neutralization and cross-linking on the thermal degradation of chitosan electrospun membranes, *J Therm Anal Calorim* 117 (2014) 123–130. <https://doi.org/10.1007/s10973-014-3707-5>.
- [80] T. Mitra, G. Sailakshmi, A. Gnanamani, A.B. Mandal, Studies on Cross-linking of succinic acid with chitosan/collagen, *Materials Research* 16 (2013) 755–765. <https://doi.org/10.1590/S1516-14392013005000059>.
- [81] J. Ma, Y. Sahai, R.G. Buchheit, Evaluation of multivalent phosphate cross-linked chitosan biopolymer membrane for direct borohydride fuel cells, *J Power Sources* 202 (2012) 18–27. <https://doi.org/10.1016/j.jpowsour.2011.11.003>.
- [82] J.W. Lawson, D. Srivastava, Formation and structure of amorphous carbon char from polymer materials, *Phys Rev B* 77 (2008) 144209. <https://doi.org/10.1103/PhysRevB.77.144209>.
- [83] J.W. Lawson, D. Srivastava, Formation and structure of amorphous carbon char from polymer materials, *Phys Rev B* 77 (2008) 144209. <https://doi.org/10.1103/PhysRevB.77.144209>.
- [84] J. Ratto, T. Hatakeyama, R.B. Blumstein, Differential scanning calorimetry investigation of phase transitions in water/ chitosan systems, *Polymer (Guildf)* 36 (1995) 2915–2919. [https://doi.org/10.1016/0032-3861\(95\)94340-Y](https://doi.org/10.1016/0032-3861(95)94340-Y).
- [85] K. Sakurai, Glass transition temperature of chitosan and miscibility of chitosan/poly(N-vinyl pyrrolidone) blends, *Polymer (Guildf)* 41 (2000) 7051–7056. [https://doi.org/10.1016/S0032-3861\(00\)00067-7](https://doi.org/10.1016/S0032-3861(00)00067-7).
- [86] V. Rao, J. Johns, Thermal behavior of chitosan/natural rubber latex blends TG and DSC analysis, *J Therm Anal Calorim* 92 (2008) 801–806. <https://doi.org/10.1007/s10973-007-8854-5>.
- [87] F.S. Kittur, K.V. Harish Prashanth, K. Udaya Sankar, R.N. Tharanathan, Characterization of chitin, chitosan and their carboxymethyl derivatives by differential scanning calorimetry, *Carbohydr Polym* 49 (2002) 185–193. [https://doi.org/10.1016/S0144-8617\(01\)00320-4](https://doi.org/10.1016/S0144-8617(01)00320-4).

-
- [88] M. Mucha, A. Pawlak, Thermal analysis of chitosan and its blends, *Thermochim Acta* 427 (2005) 69–76. <https://doi.org/10.1016/j.tca.2004.08.014>.
- [89] E.Y. Wardhono, M.P. Pinem, S. Susilo, B.J. Siom, A. Sudrajad, A. Pramono, Y. Meliana, E. Guénin, Modification of Physio-Mechanical Properties of Chitosan-Based Films via Physical Treatment Approach, *Polymers (Basel)* 14 (2022) 5216. <https://doi.org/10.3390/polym14235216>.
- [90] P. Kesharwani, M. Fatima, V. Singh, A. Sheikh, W.H. Almalki, V. Gajbhiye, A. Sahebkar, Itraconazole and Difluorinated-Curcumin Containing Chitosan Nanoparticle Loaded Hydrogel for Amelioration of Onychomycosis, *Biomimetics* 7 (2022) 206. <https://doi.org/10.3390/biomimetics7040206>.
- [91] S. Valizadeh, M. Naseri, S. Babaei, S.M.H. Hosseini, A. Imani, Development of bioactive composite films from chitosan and carboxymethyl cellulose using glutaraldehyde, cinnamon essential oil and oleic acid, *Int J Biol Macromol* 134 (2019) 604–612. <https://doi.org/10.1016/j.ijbiomac.2019.05.071>.
- [92] F. Jahan, R.D. Mathad, S. Farheen, Effect of mechanical strength on chitosan-pva blend through ionic crosslinking for food packaging application, *Mater Today Proc* 3 (2016) 3689–3696. <https://doi.org/10.1016/j.matpr.2016.11.014>.
- [93] M. Wang, C. Yang, H. Deng, Y. Du, L. Xiao, X. Shi, Electrically induced anisotropic assembly of chitosan with different molecular weights, *Carbohydr Polym* 304 (2023) 120494. <https://doi.org/10.1016/j.carbpol.2022.120494>.
- [94] K. Li, S.O. Correa, P. Pham, C.B. Raub, X. Luo, Birefringence of flow-assembled chitosan membranes in microfluidics, *Biofabrication* 9 (2017) 034101. <https://doi.org/10.1088/1758-5090/aa786e>.
- [95] K. Guo, W. Zhu, J. Wang, W. Sun, S. Zhou, M. He, Fabrication of gradient anisotropic cellulose hydrogels for applications in micro-strain sensing, *Carbohydr Polym* 258 (2021) 117694. <https://doi.org/10.1016/j.carbpol.2021.117694>.
- [96] A. Haji, R.S. Rahbar, B. Kalantari, The effect of hot multistage drawing on molecular structure and optical properties of polyethylene terephthalate fibers,

Materials Research 15 (2012) 554–560. <https://doi.org/10.1590/S1516-14392012005000076>.

[97] P.G. Gan, S.T. Sam, A.M. Faiq, Tensile Properties and Crystallinity of Crosslinked Nanocrystalline Cellulose/Chitosan Composite, IOP Conf Ser Mater Sci Eng 429 (2018) 012042. <https://doi.org/10.1088/1757-899X/429/1/012042>.

[98] S.N.S. Begum, R. Pandian, V.K. Aswal, R.P. Ramasamy, Chitosan–Gold–Lithium Nanocomposites as Solid Polymer Electrolyte, J Nanosci Nanotechnol 14 (2014) 5761–5773. <https://doi.org/10.1166/jnn.2014.8994>.

[99] S.U. Rahman, S. Bilal, A. ul Haq Ali Shah, Synthesis and Characterization of Polyaniline-Chitosan Patches with Enhanced Stability in Physiological Conditions, Polymers (Basel) 12 (2020) 2870. <https://doi.org/10.3390/polym12122870>.

[100] D. Baskar, R. Balu, T.S.S. Kumar, Mineralization of pristine chitosan film through biomimetic process, Int J Biol Macromol 49 (2011) 385–389. <https://doi.org/10.1016/j.ijbiomac.2011.05.021>.

[101] K. Nowacki, M. Galiński, I. Stępnia, Synthesis and characterization of modified chitosan membranes for applications in electrochemical capacitor, Electrochim Acta 320 (2019) 134632. <https://doi.org/10.1016/j.electacta.2019.134632>.

[102] S.B. Aziz, A.S.F.M. Asnawi, P.A. Mohammed, R.T. Abdulwahid, Y.M. Yusof, R.M. Abdullah, M.F.Z. Kadir, Impedance, circuit simulation, transport properties and energy storage behavior of plasticized lithium ion conducting chitosan based polymer electrolytes, Polym Test 101 (2021) 107286. <https://doi.org/10.1016/j.polymertesting.2021.107286>.

[103] C. Tang, M.L. Bruening, Ion separations with membranes, Journal of Polymer Science 58 (2020) 2831–2856. <https://doi.org/10.1002/pol.20200500>.

[104] Y. Guo, J. Bae, Z. Fang, P. Li, F. Zhao, G. Yu, Hydrogels and Hydrogel-Derived Materials for Energy and Water Sustainability, Chem Rev 120 (2020) 7642–7707. <https://doi.org/10.1021/acs.chemrev.0c00345>.

- [105] G. Feng, R. Qiao, J. Huang, S. Dai, B.G. Sumpter, V. Meunier, The importance of ion size and electrode curvature on electrical double layers in ionic liquids, *Phys. Chem. Chem. Phys.* 13 (2011) 1152–1161. <https://doi.org/10.1039/C0CP02077J>.
- [106] S.B. Aziz, P.O. Hama, P.A. Mohammed, M.B. Ahmed, R.M. Abdullah, N.M. Sadiq, M.F.Z. Kadir, H.J. Woo, Electrochemical properties of plasticized PVA-based electrolyte inserted with alumina nanoparticles for EDLC application with enhanced dielectric constant, *J Energy Storage* 103 (2024) 114264. <https://doi.org/10.1016/j.est.2024.114264>.
- [107] R. Kant, M.B. Singh, Theory of the Electrochemical Impedance of Mesoporous Electrodes Embedded with Heterogeneous Micropores, *The Journal of Physical Chemistry C* 121 (2017) 7164–7174. <https://doi.org/10.1021/acs.jpcc.7b01287>.
- [108] X. Zhang, M. Kar, T.C. Mendes, Y. Wu, D.R. MacFarlane, Supported Ionic Liquid Gel Membrane Electrolytes for Flexible Supercapacitors, *Adv Energy Mater* 8 (2018). <https://doi.org/10.1002/aenm.201702702>.
- [109] C.-C. Hu, E. Chen, J.-Y. Lin, Capacitive and textural characteristics of polyaniline-platinum composite films, *Electrochim Acta* 47 (2002) 2741–2749. [https://doi.org/10.1016/S0013-4686\(02\)00139-1](https://doi.org/10.1016/S0013-4686(02)00139-1).
- [110] U. Mahanta, D. Kundu, R.P. Venkatesh, S. Sujatha, S.A. Ilangovan, T. Banerjee, Electrochemical Performance and Molecular Structure of Diluted 1-Alkyl-3-methylimidazolium Tetrafluoroborate Ionic Liquids and Their Mixture as Electrolytes for Double-Layer Capacitors: An Integrated Approach by Electrochemical Characterization and Molecular Dynamics Simulation, *Ind Eng Chem Res* 58 (2019) 22741–22753. <https://doi.org/10.1021/acs.iecr.9b04350>.
- [111] R. Kötz, M. Carlen, Principles and applications of electrochemical capacitors, *Electrochim Acta* 45 (2000) 2483–2498. [https://doi.org/10.1016/S0013-4686\(00\)00354-6](https://doi.org/10.1016/S0013-4686(00)00354-6).
- [112] F. A., F. Kamarulazam, N.K. Farhana, M. Pershaanaa, S. Bashir, S. Ramesh, K. Ramesh, Studies of ionic conduction properties of polyacrylamide hydrogel

polymer electrolytes at different medium (alkaline, acid, and salt) via impedance approach, *Ionics* (Kiel) 31 (2025) 5663–5675. <https://doi.org/10.1007/s11581-025-06325-x>.

[113] P. Forouzandeh, V. Kumaravel, S.C. Pillai, Electrode Materials for Supercapacitors: A Review of Recent Advances, *Catalysts* 10 (2020) 969. <https://doi.org/10.3390/catal10090969>.

[114] S. Balasubramaniam, A. Mohanty, S.K. Balasingam, S.J. Kim, A. Ramadoss, Comprehensive Insight into the Mechanism, Material Selection and Performance Evaluation of Supercapatteries, *Nanomicro Lett* 12 (2020) 85. <https://doi.org/10.1007/s40820-020-0413-7>.

[115] I. Stepniak, A. Ciszewski, Electric double layer capacitors with polymer hydrogel electrolyte based on poly(acrylamide) and modified electrode and separator materials, *Electrochim Acta* 54 (2009) 7396–7400. <https://doi.org/10.1016/j.electacta.2009.07.072>.

[116] S. Yu, N. Yang, H. Zhuang, J. Meyer, S. Mandal, O.A. Williams, I. Lilge, H. Schönherr, X. Jiang, Electrochemical Supercapacitors from Diamond, *The Journal of Physical Chemistry C* 119 (2015) 18918–18926. <https://doi.org/10.1021/acs.jpcc.5b04719>.

[117] C. Jiang, M. Gao, S. Zhang, L. Huang, S. Yu, Z. Song, Q. Wu, Chitosan/graphene oxide hybrid hydrogel electrode with porous network boosting ultrahigh energy density flexible supercapacitor, *Int J Biol Macromol* 225 (2023) 1437–1448. <https://doi.org/10.1016/j.ijbiomac.2022.11.201>.

[118] S. Balasubramaniam, A. Mohanty, S.K. Balasingam, S.J. Kim, A. Ramadoss, Comprehensive Insight into the Mechanism, Material Selection and Performance Evaluation of Supercapatteries, *Nanomicro Lett* 12 (2020) 85. <https://doi.org/10.1007/s40820-020-0413-7>.

[119] N.A. Choudhury, J. Ma, Y. Sahai, R.G. Buchheit, High performance polymer chemical hydrogel-based electrode binder materials for direct borohydride fuel cells,

J Power Sources 196 (2011) 5817–5822.
<https://doi.org/10.1016/j.jpowsour.2011.03.004>.

[120] B.-A. Mei, J. Lau, T. Lin, S.H. Tolbert, B.S. Dunn, L. Pilon, Physical Interpretations of Electrochemical Impedance Spectroscopy of Redox Active Electrodes for Electrical Energy Storage, *The Journal of Physical Chemistry C* 122 (2018) 24499–24511. <https://doi.org/10.1021/acs.jpcc.8b05241>.

[121] M. Suleman, M. Deraman, S.A. Hashmi, M.A.R. Othman, Y. Kumar, S.K. Rajouria, M.R.M. Jasni, Accommodating succinonitrile rotators in micro-pores of 3D nano-structured cactus carbon for assisting micro-crystallite organization, ion transport and surplus pseudo-capacitance: An extreme temperature supercapacitor behavior, *Electrochim Acta* 333 (2020) 135547.
<https://doi.org/10.1016/j.electacta.2019.135547>.

[122] A. Khazaeli, G. Godbille-Cardona, D.P.J. Barz, A Novel Flexible Hybrid Battery–Supercapacitor Based on a Self-Assembled Vanadium-Graphene Hydrogel, *Adv Funct Mater* 30 (2020). <https://doi.org/10.1002/adfm.201910738>.

[123] E. Pameté, L. Köps, F.A. Kreth, S. Pohlmann, A. Varzi, T. Brousse, A. Balducci, V. Presser, The Many Deaths of Supercapacitors: Degradation, Aging, and Performance Fading, *Adv Energy Mater* 13 (2023).
<https://doi.org/10.1002/aenm.202301008>.

[124] E.-H. El Brouji, O. Briat, J.-M. Vinassa, N. Bertrand, E. Woirgard, Impact of Calendar Life and Cycling Ageing on Supercapacitor Performance, *IEEE Trans Veh Technol* 58 (2009) 3917–3929. <https://doi.org/10.1109/TVT.2009.2028431>.

[125] X. Chen, Y. Wu, R. Holze, Ag(e)ing and Degradation of Supercapacitors: Causes, Mechanisms, Models and Countermeasures, *Molecules* 28 (2023) 5028.
<https://doi.org/10.3390/molecules28135028>.

[126] Z. Fu, M. Hannula, A. Jauho, K.-L. Väisänen, M. Välimäki, J. Keskinen, M. Mäntysalo, Cyclic Bending Reliability and Failure Mechanism of Printed Biodegradable Flexible Supercapacitor on Polymer Substrate, *ACS Appl Mater Interfaces* 14 (2022) 40145–40157. <https://doi.org/10.1021/acsami.2c08502>.

-
- [127] H.-H. Xu, L. Yue, Y. Tang, F. Liu, H.-J. Zhu, S.-J. Bao, Preparation of chitosan and citric acid crosslinked membrane and its application in quasi-solid supercapacitors, *Rare Metals* 42 (2023) 430–437. <https://doi.org/10.1007/s12598-022-02115-w>.
- [128] N.A. Choudhury, J. Ma, Y. Sahai, High performance and eco-friendly chitosan hydrogel membrane electrolytes for direct borohydride fuel cells, *J Power Sources* 210 (2012) 358–365. <https://doi.org/10.1016/j.jpowsour.2012.03.013>.
- [129] H. Yang, X. Ji, Y. Tan, Y. Liu, F. Ran, Modified supramolecular carboxylated chitosan as hydrogel electrolyte for quasi-solid-state supercapacitors, *J Power Sources* 441 (2019) 227174. <https://doi.org/10.1016/j.jpowsour.2019.227174>.
- [130] H. Yang, Y. Liu, L. Kong, L. Kang, F. Ran, Biopolymer-based carboxylated chitosan hydrogel film crosslinked by HCl as gel polymer electrolyte for all-solid-state supercapacitors, *J Power Sources* 426 (2019) 47–54. <https://doi.org/10.1016/j.jpowsour.2019.04.023>.
- [131] X. Xue, L. Wan, W. Li, X. Tan, X. Du, Y. Tong, A Self-Healing Gel Polymer Electrolyte, Based on a Macromolecule Cross-Linked Chitosan for Flexible Supercapacitors, *Gels* 9 (2022) 8. <https://doi.org/10.3390/gels9010008>.
- [132] M. Yamagata, K. Soeda, S. Ikebe, S. Yamazaki, M. Ishikawa, Chitosan-based gel electrolyte containing an ionic liquid for high-performance nonaqueous supercapacitors, *Electrochim Acta* 100 (2013) 275–280. <https://doi.org/10.1016/j.electacta.2012.05.073>.
- [133] C.-H. Lin, P.-H. Wang, W.-N. Lee, W.-C. Li, T.-C. Wen, Chitosan with various degrees of carboxylation as hydrogel electrolyte for pseudo solid-state supercapacitors, *J Power Sources* 494 (2021) 229736. <https://doi.org/10.1016/j.jpowsour.2021.229736>.
- [134] V.K. Vorobiov, M.A. Smirnov, N. V. Bobrova, M.P. Sokolova, Chitosan-supported deep eutectic solvent as bio-based electrolyte for flexible supercapacitor, *Mater Lett* 283 (2021) 128889. <https://doi.org/10.1016/j.matlet.2020.128889>.

- [135] S. Zallouz, J.-M. Le Meins, C. Matei Ghimbeu, Alkaline hydrogel electrolyte from biosourced chitosan to enhance the rate capability and energy density of carbon-based supercapacitors, *Energy Advances* 1 (2022) 1051–1064. <https://doi.org/10.1039/D2YA00250G>.
- [136] C. Li, G. Liu, S. Wang, D. Wang, F. Liu, Y. Cui, D. Liang, X. Wang, Z. Yong, Y. Chi, Polyvinyl alcohol/quaternary ammonium chitosan hydrogel electrolyte for sensing supercapacitors with excellent performance, *J Energy Storage* 46 (2022) 103918. <https://doi.org/10.1016/j.est.2021.103918>.
- [137] S. Wu, B. Su, M. Sun, S. Gu, Z. Lu, K. Zhang, D.Y.W. Yu, B. Huang, P. Wang, C. Lee, W. Zhang, Dilute Aqueous-Aprotic Hybrid Electrolyte Enabling a Wide Electrochemical Window through Solvation Structure Engineering, *Advanced Materials* 33 (2021). <https://doi.org/10.1002/adma.202102390>.
- [138] J. Liu, C. Wu, I.D. Gates, B. Jia, Z. Huang, T. Ma, Integrated <scp>Electrode-Electrolyte</scp> Optimization to Manufacture a <scp>Real-Life</scp> Applicable Aqueous Supercapacitor with <scp>Record-Breaking</scp> Lifespan, *ENERGY & ENVIRONMENTAL MATERIALS* 6 (2023). <https://doi.org/10.1002/eem2.12520>.
- [139] S. Pohlmann, T. Olyschläger, P. Goodrich, J.A. Vicente, J. Jacquemin, A. Balducci, Mixtures of Azepanium Based Ionic Liquids and Propylene Carbonate as High Voltage Electrolytes for Supercapacitors, *Electrochim Acta* 153 (2015) 426–432. <https://doi.org/10.1016/j.electacta.2014.11.189>.
- [140] S. Pohlmann, T. Olyschläger, P. Goodrich, J. Alvarez Vicente, J. Jacquemin, A. Balducci, Azepanium-based ionic liquids as green electrolytes for high voltage supercapacitors, *J Power Sources* 273 (2015) 931–936. <https://doi.org/10.1016/j.jpowsour.2014.09.167>.
- [141] X. Jin, L. Song, H. Yang, C. Dai, Y. Xiao, X. Zhang, Y. Han, C. Bai, B. Lu, Q. Liu, Y. Zhao, J. Zhang, Z. Zhang, L. Qu, Stretchable supercapacitor at $-30\text{ }^{\circ}\text{C}$, *Energy Environ Sci* 14 (2021) 3075–3085. <https://doi.org/10.1039/D0EE04066E>.
- [142] C. Yang, M. Sun, X. Wang, G. Wang, A Novel Flexible Supercapacitor Based on Cross-Linked PVDF-HFP Porous Organogel Electrolyte and Carbon Nanotube

Paper@ π -Conjugated Polymer Film Electrodes, *ACS Sustain Chem Eng* 3 (2015) 2067–2076. <https://doi.org/10.1021/acssuschemeng.5b00334>.

[143] Y. Liang, Q. Song, Y. Chen, C. Hu, S. Zhang, Stretch-Induced Robust Intrinsic Antibacterial Thermoplastic Gelatin Organohydrogel for a Thermoenhanced Supercapacitor and Mono-gauge-factor Sensor, *ACS Appl Mater Interfaces* 15 (2023) 20278–20293. <https://doi.org/10.1021/acsami.3c02255>.

[144] B. Asbani, C. Douard, T. Brousse, J. Le Bideau, High temperature solid-state supercapacitor designed with ionogel electrolyte, *Energy Storage Mater* 21 (2019) 439–445. <https://doi.org/10.1016/j.ensm.2019.06.004>.

[145] M. Brachet, T. Brousse, J. Le Bideau, All Solid-State Symmetrical Activated Carbon Electrochemical Double Layer Capacitors Designed with Ionogel Electrolyte, *ECS Electrochemistry Letters* 3 (2014) A112–A115. <https://doi.org/10.1149/2.0051411eel>.

[146] Q. Zheng, X. Li, Q. Yang, C. Li, G. Liu, Y. Wang, P. Sun, H. Tian, C. Wang, X. Chen, J. Shao, High performance solid-state supercapacitors based on highly conductive organogel electrolyte at low temperature, *J Power Sources* 524 (2022) 231102. <https://doi.org/10.1016/j.jpowsour.2022.231102>.

[147] Q. Liu, D. Wu, T. Wang, Y. Guo, Polysaccharide of agar based ultra-high specific surface area porous carbon for superior supercapacitor, *Int J Biol Macromol* 228 (2023) 40–47. <https://doi.org/10.1016/j.ijbiomac.2022.12.126>.

[148] C. Lu, X. Chen, All-Temperature Flexible Supercapacitors Enabled by Antifreezing and Thermally Stable Hydrogel Electrolyte, *Nano Lett* 20 (2020) 1907–1914. <https://doi.org/10.1021/acs.nanolett.9b05148>.

CHAPTER 5

High-performance EDLCs from Borax Cross-linked Chitosan Hydrogel Electrolytes and BPC Electrodes: A Biodegradable Route to Sustainable Energy Storage

This chapter presents the synthesis, characterizations of BCCHMEs for application as electrolyte cum separator in EDLCs. BCCHMEs were fabricated by both ionic and covalent crosslinking of chitosan with borax, and their physicochemical properties such as WU, dissolution stability, crystallinity, and mechanical strength were examined. Structural and morphological features of the membranes were analyzed using FTIR, XRD, FE-SEM, and EDX. Electrochemical techniques, including transference number measurement, LSV, CV, EIS, and GCD were employed to evaluate conductivity, transport parameters, electrochemical stability window, capacitance, resistance, and energy storage behavior of the EDLCs utilizing BCCHMEs.

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5.1 Introduction

The escalating global demand for sustainable energy solutions has intensified the search for environmentally friendly alternatives to conventional electrochemical ESSs [1,2]. As the world transitions toward renewable energy sources and carbon-neutral technologies, the development of biodegradable and non-toxic materials for energy storage applications has become increasingly critical. Traditional Li-ion batteries, while effective, pose significant environmental challenges due to their toxic components, complex recycling processes, and potential safety hazards. This growing environmental consciousness has catalysed research efforts toward developing green energy storage devices that can deliver comparable performance while minimizing ecological impact [3]. EDLCs, a type of supercapacitors, represent a promising class of energy storage devices that bridge the gap between conventional capacitors and batteries. These devices offer several advantages over traditional batteries, including rapid charge-discharge capabilities, exceptional cycling stability, high power density, and extended operational lifetimes [4–6]. The energy storage mechanism in EDLCs relies on the electrostatic adsorption of ions at the electrode-electrolyte interface, forming an electric double layer without involving faradaic reactions, which contributes to their remarkable cycle stability and fast response times [6]. However, the widespread adoption of EDLCs has been limited by their relatively lower energy density compared to batteries and the environmental concerns associated with conventional liquid electrolytes.

The electrolyte component plays a pivotal role in determining the overall performance, safety, and environmental impact of EDLC systems. Conventional liquid electrolytes, despite their high ionic conductivity, suffer from several drawbacks including potential leakage, flammability, volatility, and limited thermal stability [7]. The limitations of conventional electrolytes have driven the development of GPEs. First introduced by Feuillade and Perche in 1975 [8], GPEs can be prepared through various methods, including polymer matrix polymerization and chemical or physical crosslinking [9]. Due to their electrode compatibility, broad electrochemical stability window, and relatively high ionic conductivity, they are regarded as a promising alternative to liquid electrolytes [10]. Semi-solid structure of GPEs provides greater flexibility and

adaptability [11], while their high ionic conductivity is essential for enhancing the performance of electrochemical systems. Among various polymer matrices investigated for GPE applications, biodegradable polymers have emerged as particularly attractive candidates due to their inherent environmental friendliness, biocompatibility, and potential for sustainable manufacturing processes.

Chitosan, a biopolymer derived from chitin, exhibits remarkable properties such as biocompatibility, film-forming capability, and intrinsic ion-transport functionality through its amino and hydroxyl groups [12]. However, its application in membrane-based electrochemical devices has historically been constrained by its limited mechanical stability and low conductivity under dry or quasi-solid conditions. To address these shortcomings, various crosslinking strategies ranging from carbonate [13,14], citrate [15], sulphate [16], glutaraldehyde [17], tripolyphosphate [18], and genipin [19] have been adopted for different applications, often with additional fillers or dopants to improve electrochemical performance when used in energy storage devices. Yet, these types of multi-component systems introduce processing complexity, reduced environmental compatibility, and long-term instability due to phase separation or migration of low-molecular-weight additives. In this context, borax (disodium tetraborate decahydrate, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), a naturally occurring and environmentally benign salt, serves as an effective crosslinking agent by facilitating both ionic and covalent interactions with polysaccharides. In aqueous environments, the protonated amino groups ($-\text{NH}_3^+$) of chitosan engage in electrostatic interactions with anionic borate species such as $\text{B}(\text{OH})_4^-$, forming a network of ionic crosslinks that enhance ionic conductivity and structural cohesion. Simultaneously, borate ions form dynamic covalent borate ester bonds with the cis-diol groups present on the chitosan backbone, further stabilizing the hydrogel matrix through reversible chemical crosslinking [20]. Without the need for synthetic additives, surfactants, or plasticizers, this dual crosslinking mechanism results in a robust hydrogel structure. This study presents a borax cross-linked chitosan hydrogel membrane synthesized via a single-step green process, functioning as a dual-purpose membrane electrolyte cum separator for EDLCs. Comprising only two components chitosan and borax, the resulting

membrane exhibits both excellent mechanical integrity and enhanced ion transport properties.

Previous studies have utilized borax in conjunction with chitosan [20–22] as well as other polymers, such as PVA [23,24], starch [25,26], PAAm [27], cellulose [28], to form gels. For instance, borax-PAM hydrogels have been shown to enhance mechanical strength and ion diffusivity in aqueous energy devices [27]. Likewise, recent studies on functionalized chitosan hydrogels incorporated various inorganic salts or co-polymerized backbones to reinforce membrane functionality [29]. However, these approaches often compromise structural homogeneity, increase the possibility of electrochemical side reactions, or degrade long-term material performance under bias. Although, the direct formation of a hydrogel membrane composed exclusively of chitosan and borax, without any secondary doping or plasticizing components and its successful deployment as a quasi-solid electrolyte cum separator for EDLCs has not been previously reported. Herein, single-component hydrogel membrane, however, achieves comparable or superior performance without such complex formulations, indicating that a simplified, green chemistry route can deliver materials suitable for integration into practical electrochemical devices. The novelty of the current work lies not only in the chemical simplicity of the hydrogel membrane but also in the demonstration of its electrochemical performance in an EDLC platform. The membrane bridges the gap between material sustainability and device-level efficiency, setting a precedent for future work on additive-free hydrogel electrolytes. This study, therefore, contributes fundamentally to the design of next-generation functional membranes by proposing a chemically minimalistic yet performance-optimized system. Its relevance extends beyond supercapacitors to potential applications in green batteries, wearable energy modules, and bio-interfacing electronics.

5.2 Materials and methods

5.2.1 Experimental materials

Chitosan (CAS No.: 9012-76-4; 75 % deacetylation, Loba Chemie Pvt. Ltd.), borax or disodium tetraborate decahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, Loba Chemie Pvt. Ltd.), Marck Milli-Q deionised water, glacial acetic acid (CH_3COOH , 90-100 %, Merck), Cabot BPC, PVA (Loba Chemie Pvt. Ltd.), ethanol (99.9 %), and glutaraldehyde solution (25 %).

5.2.2 Preparation of aqueous chitosan stock solution

A 2 % (w/v) chitosan stock solution (100 mL) was prepared by dissolving 2 g of chitosan flakes in 100 mL of 2 % (v/v) aqueous acetic acid. The mixture was stirred continuously at ambient temperature for approximately 24 hours to achieve complete dissolution. It was then subjected to heating in a water bath at 93 °C for an additional 2 hours to improve homogeneity and further enhance solubility.

5.2.3 Preparation of Borax Cross-linked Chitosan Hydrogels and Hydrogel Membrane Electrolytes

Borax cross-linked chitosan hydrogels (BCCH) were produced by combining 10 mL of the prepared chitosan stock solution with a predetermined volume of borax crosslinker solution of known concentration in a 25 mL glass beaker. The mixture was magnetically stirred at room temperature until it thickened and transformed into a viscous hydrogel.

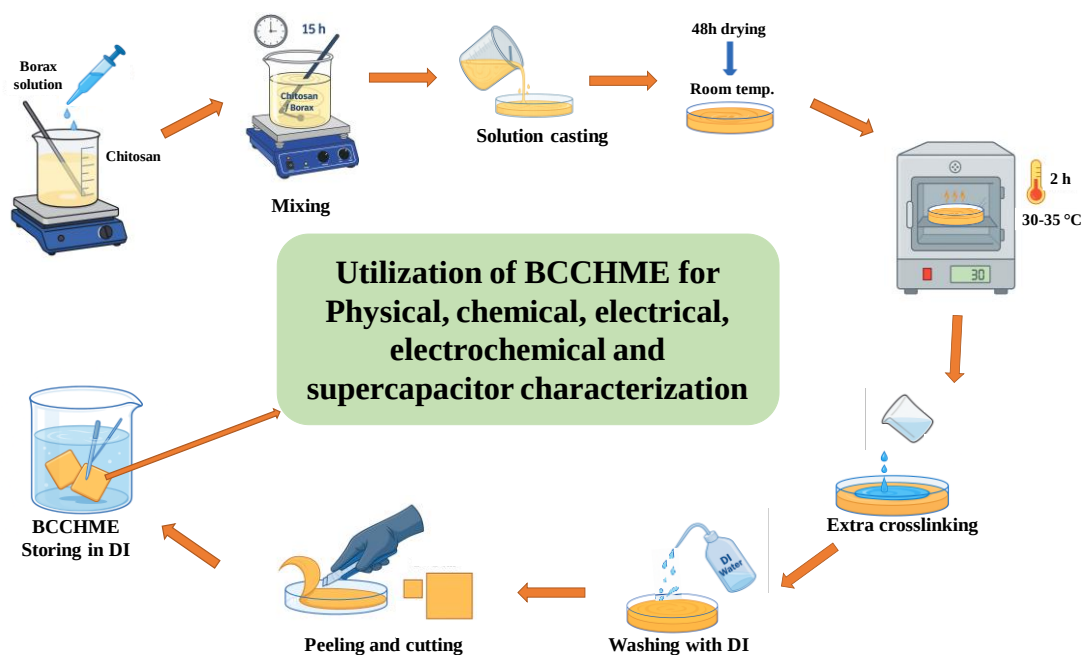


Fig.5.1 Schematic representation of the synthesis process for BCCHMEs.

The fabrication steps for BCCHMEs is shown in Fig.5.1. Briefly, 10 mL of chitosan stock solution was blended with 2 mL of borax solution of specified molarity and mixed vigorously to obtain a uniform, viscous mixture. This was poured into sterile plastic Petri dishes and left to stand at room temperature for 15 h to enable ionic crosslinking and solvent evaporation, resulting in membrane formation. The membranes were then dried in an oven at 30-35 °C for 2 h, followed by immersion in fresh borax solution for an additional 30 min to promote further ionic crosslinking. After decanting the excess solution, the membranes were rinsed thoroughly with DI water to remove any residual, unbound ions. The final BCCHMEs were peeled, cut into the desired dimensions, and stored in DI water until further use.

5.2.4 FT-IR spectroscopic studies

FTIR spectra of borax powder, chitosan flakes, and BCCHME were obtained using a PerkinElmer Spectrum Two spectrometer over a wavenumber range of 4000-500 cm^{-1} . For powder samples, pellets were prepared by homogenizing the material with spectroscopic-grade KBr, followed by compression using a hydraulic press.

5.2.5 DC and AC ionic conductivity studies

The DC and AC ionic conductivities of BCCHMEs with borax concentrations from 0.1 to 0.5 M, were evaluated using a HMEA, as shown in Fig.5.2. The HMEA was assembled by placing the BCCHME sample of area 1 cm² in between two SS blocking electrodes of the same dimensions and covered using Teflon tape. EIS was performed with a 5 mV_{rms} potential amplitude.

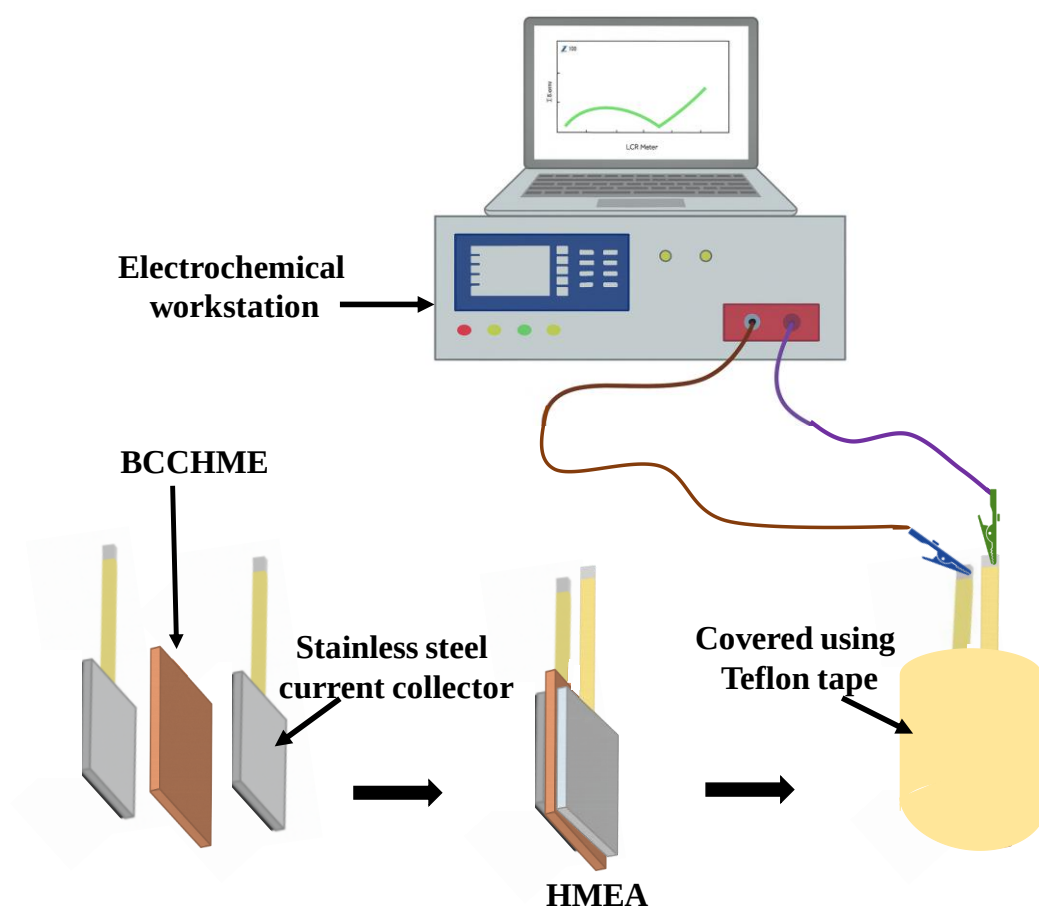


Fig.5.2 Schematic representation of the HMEA setup and electrochemical setup.

For DC conductivity (σ_{DC}), the R_b was determined from the Nyquist plot, and conductivity was calculated using Equation (1) [30]

$$\sigma_{DC} = \frac{L}{A \times R_b} \quad (1)$$

where L and A represent the sample thickness and area, respectively.

The AC conductivity (σ_{AC}) of BCCHMEs was obtained from Equation (2) [30].

$$\sigma_{AC} = \left[\frac{z'}{z'^2 + z''^2} \right] \times \left(\frac{L}{A} \right) \quad (2)$$

Where, z' and z'' are the real and imaginary components of the impedance, respectively.

5.2.6 Dielectric properties

Dielectric parameters, including the dielectric constant (ϵ'), dielectric loss (ϵ''), loss tangent ($\tan \delta$), and the real (M') and imaginary (M'') components of the dielectric modulus, serve as critical indicators for assessing ion transport dynamics in polymer-based electrolytes. In this study the dielectric parameters were determined using the following equations [31].

$$\epsilon' = \frac{z''}{\omega C_0 (z'^2 + z''^2)} \quad (3)$$

$$\epsilon'' = \frac{z'}{\omega C_0 (z'^2 + z''^2)} \quad (4)$$

$$\tan(\delta) = \frac{\epsilon''}{\epsilon'} \quad (5)$$

$$M' = \frac{\epsilon'}{\epsilon'^2 + \epsilon''^2} \quad (6)$$

$$M'' = \frac{\epsilon''}{\epsilon'^2 + \epsilon''^2} \quad (7)$$

Here, $\omega = 2\pi f$, where f is frequency; $C_0 = \frac{\epsilon_0 A}{L}$ is vacuum capacitance, where $\epsilon_0 = 8.85 \times 10^{-14} \text{ F cm}^{-1}$ is the permittivity of free space, L is the membrane thickness, A is blocking electrode area.

5.2.7 Determination of ion transport parameters

EIS method was utilized to determine key ion transport parameters, including the diffusion coefficient (D), ionic mobility (μ), and ion number density (n). These quantities were calculated using established relationships that form the theoretical basis for impedance data interpretation [32]. The diffusion coefficient (D) was obtained using the following equation [33].

$$D = \left(\frac{(k\varepsilon_0\varepsilon' A)^2}{\tau} \right) \quad (8)$$

In equation (8), k denotes the reciprocal of the CPE, while τ represents the reciprocal of the angular frequency (ω), which is related to frequency (f) by $\omega = 2\pi f$. A is the geometric area of the BCCHME, and ε_0 is the vacuum permittivity (8.85×10^{-12} F). The dielectric constant (ε') is calculated using $\varepsilon' = \frac{z''}{\omega C_0(z'^2 + z''^2)}$; where the vacuum capacitance (C_0) is given by $C_0 = \frac{\varepsilon_0 A}{L}$, with L representing the BCCHME thickness. Ionic mobility (μ) was subsequently determined using equation (9) below [33].

$$\mu = \left(\frac{eD}{k_B T} \right) \quad (9)$$

Here, T denotes the absolute temperature, k_B is the Boltzmann constant (1.38×10^{-23} J K^{-1}), and e represents the elementary charge (1.602×10^{-19} C). The ion number density (n) of the BCCHME was determined using the following equation (10) [33].

$$n = \left(\frac{\sigma_{DC} k_B T \tau}{(e k \varepsilon_0 \varepsilon' A)^2} \right) \quad (10)$$

5.2.8 WU studies

WU measurement was performed on BCCHME sample cut into 4×4 cm² sections. Each sample was immersed in DI water to allow complete absorption into the polymeric matrix. Excess surface water was gently removed using filter paper, and the hydrated weight (W_h) was recorded. The membranes were then dried in an oven at 45

°C for 48 h to remove absorbed moisture, with weights measured every 12 h until a constant dry weight (W_d) was obtained. The percentage WU was calculated using the following relation [34].

$$WU (\%) = \left(\frac{W_h - W_d}{W_d} \right) \times 100 \quad (11)$$

5.2.9 DR study

The DR (%) of BCCHME was assessed using 2 cm² samples. The initial wet weight (W_1) of each sample was recorded prior to testing. To study dissolution behaviour under accelerated conditions, the samples were immersed in boiling DI water for continuous 6 h. They were then oven-dried at 35 °C for 48 h to obtain the final dry weight (W_2). Finally, the DR was calculated according to Equation (12) [34].

$$DR (\%) = \left(\frac{W_1 - W_2}{W_1} \right) \times 100 \quad (12)$$

5.2.10 WVTR study

WVTR of BCCHME was measured using the wet cup method, following ASTM E-96-95 [35]. A plastic Petri dish containing 30 mL of DI water was sealed with the membrane sample, providing an exposed surface area of $4.29 \times 10^{-3} \text{ m}^2$. The mass was measured at 12 h intervals. WVTR ($\text{g m}^{-2} \text{ h}^{-1}$) was calculated using the following equation [34,35].

$$WVTR = \frac{G}{t \times A} \quad (13)$$

Where, G is the change in weight (g), A is the exposed membrane area (m^2), and t is the time (h).

5.2.11 TGA studies

TGA of the UCM and BCCHME was carried out using a PerkinElmer TGA 4000 instrument under a controlled N₂ atmosphere. Samples were heated from room temperature to 800 °C at a constant rate of 10 °C min to 110 °C min⁻¹.

5.2.12 DSC studies

The thermal properties of the UCM and BCCHME were examined using a NETZSCH DSC 204 F1 Phoenix differential scanning calorimeter under a nitrogen atmosphere.

5.2.13 XRD studies

XRD was employed to investigate the structural features of borax powder, UCM, and BCCHME. Measurements were performed using a Bruker D8 Advance diffractometer (Germany) equipped with a Cu radiation source and Ni filter, operated at 30 mA and 30 kV. Diffraction patterns were collected over a 2θ range of 5° – 65° . Deconvolution of the UCM and BCCHME diffraction profiles was carried out using OriginPro 2022 software, applying Gaussian fitting functions to differentiate and quantify crystalline (A_c) and amorphous (A_a) domains. The degree of crystallinity (X_c) was then calculated using the following Equation (14) [13].

$$X_c = \left[\frac{A_c}{A_c + A_a} \right] \times 100 \% \quad (14)$$

5.2.14 FE-SEM and EDX studies

The surface morphology of the UCM and BCCHME was examined using a ZEISS FE-SEM. Elemental composition analysis was performed on the same samples using EDX spectroscopy.

5.2.15 Mechanical strength studies

The mechanical properties of the UCM and BCCHME were evaluated using a universal testing machine (Instron E-3000) operated at a constant crosshead speed of 1 mm min^{-1} .

5.2.16 Transference number measurements

The ion transference number (t_{ion}) was determined using the DC polarization method. In this approach, the HMEA, as prepared using the steps shown in Fig. 5.2, was polarized under a constant voltage of 1 V, and the resulting current–time profile was recorded. The initial current (I_0) represents contributions from both ionic and electronic charge carriers, while the steady-state current (I_{ss}), obtained after

polarization stabilization, reflects only the electronic contribution. The ion transference number was calculated using Equation (15) [13].

$$t_{\text{ion}} = \frac{I_0 - I_{\text{ss}}}{I_0} \quad (15)$$

The cationic and anionic transference numbers are important parameters for assessing electrolyte performance. To determine the cationic transference number (t_{cation}), the Bruce-Vincent method was employed, which combines DC polarization with AC impedance measurements. Impedance spectra were collected before and after polarization to account for variations in interfacial resistance. The cationic transference number was calculated according to equation (16) [36].

$$t_{\text{cation}} = \frac{I_{\text{ss}} (\Delta V - I_0 R_0)}{I_0 (\Delta V - I_{\text{ss}} R_{\text{ss}})} \quad (16)$$

where R_0 and R_{ss} denote the initial and steady-state resistances, respectively.

5.2.17 LSV study

LSV was conducted to determine the decomposition voltage of the BCCHME. The HMEA was subjected to a potential sweep from 1 to 3 V, and the current response was recorded. The onset of decomposition was identified by a sharp increase in current during the voltage sweep.

5.2.18 Electrode material preparation and EDLC assembly

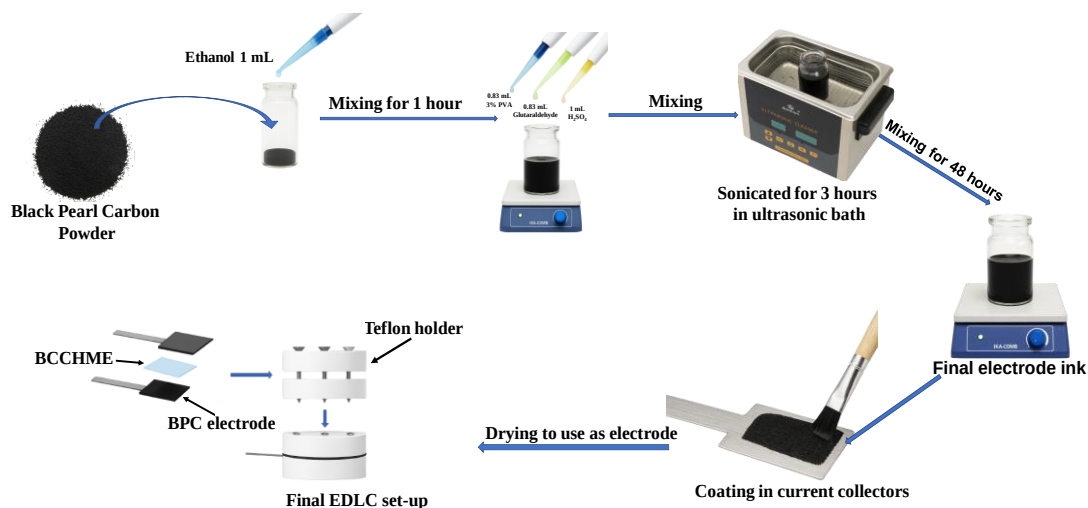


Fig.5.3 Schematic representation of the preparation process for BPC-based electrode material and assembly of solid-state EDLCs using BCCHME as electrolyte and separator.

The electrode material was prepared using BPC, following the schematic procedure shown in Fig.5.3. Firstly, 0.10 g of BPC was dispersed in 1 mL of ethanol and magnetically stirred for 1 h to obtain a uniform suspension. Subsequently, 0.83 mL of 3% (w/v) aqueous PVA solution was added dropwise, followed by the gradual addition of 0.83 mL of glutaraldehyde solution. Concentrated sulfuric acid was then introduced dropwise as a catalyst. The resulting mixture was sonicated in a water bath for 3 h and further stirred for 48 h to yield a homogeneous electrode ink [34,37]. The prepared ink was applied to SS current collectors using a paintbrush, ensuring a consistent active material loading of approximately 1 mg cm^{-2} . Solid-state EDLCs were assembled using these electrodes in conjunction with BCCHMEs, which served as both the electrolyte and separator. The devices were sealed with Teflon tape, secured with Teflon holders, and wrapped with Parafilm to prevent water loss and leakage.

5.2.19 Electrochemical characterizations of BCCHME

All electrochemical characterizations, except for cycle life analysis, were performed using a Metrohm M204 Multi Autolab system. Cycle life analysis was carried out

separately using a battery analyser (MTI Corporation, USA). The electrochemical performance of the assembled EDLCs was assessed using CV, GCD, and EIS. CV measurements were conducted over a potential range of 0-1 V at scan rates between 5 and 100 mV s⁻¹. GCD tests were performed within the same voltage window at current densities from 0.5 to 5 mA cm⁻². EIS analysis was carried out over a frequency range of 1 MHz to 0.1 Hz with an applied AC amplitude of 5 mV_{rms}.

Areal capacitance C_A (mF cm⁻²), energy density E (μWh cm⁻²), as well as power density P (mW cm⁻²) of EDLCs were mathematically calculated from GCD plots employing equations (17), (18), and (19), respectively [38,39].

$$C_A = 2 \times \frac{I \times t_d}{A \times \Delta V} \quad (17)$$

$$E = \frac{1}{2} \times \frac{1000}{3600} C_A \times (\Delta V)^2 \quad (18)$$

$$P = \frac{E}{t_d} \times 3600 \quad (19)$$

Where, I (mA) represents the current density, t_d represents discharge time, A denotes area (cm²) of electrodes, and ΔV denotes potential window (V). The EEC was developed by analysing the EIS data using the “Fit and Simulation” module in Nova 2.1.5 software. Non-linear least squares fitting was applied to optimize the correlation between the experimental impedance spectra and the theoretical model. The goodness of fit was assessed using the chi-squared (χ^2) statistic, where lower χ^2 values indicate a closer agreement between measured and simulated data, thereby reflecting the accuracy of the circuit model in representing the electrochemical behaviour of the hydrogel electrolyte [13,40].

From the Bode plot of phase angle versus frequency, obtained from EIS measurements, the relaxation time constant (τ) was calculated using equation (20) [41].

$$\tau = \frac{1}{2\pi f^*} \quad (20)$$

where f^* (in Hz) is the frequency corresponding to a phase angle of 45° .

The real (C') and imaginary (C'') components of capacitance were determined from the Bode plot using the following expressions [42].

$$C'(\omega) = \frac{-z''(\omega)}{\omega|z(\omega)|^2} \quad (21)$$

$$C''(\omega) = \frac{z'(\omega)}{\omega|z(\omega)|^2} \quad (22)$$

The cycle life stability of the EDLCs was evaluated through GCD testing at constant current densities of 2 and 5 mA cm⁻², with performance monitored until the completion of their charge-discharge cycles.

5.3 Results and discussion

The formation mechanism of the BCCHME is schematically illustrated in Fig.5.4 (A), while Fig.5.4 (B) shows the prepared BCCH held in an inverted beaker, confirming its robust three-dimensional network structure. Fig.5.4 (C) shows the flexible, free-standing BCCHME film with a uniform thickness of 60 μm and a whitish hue, indicative of homogeneous borax dispersion and consistent crosslinking throughout the membrane.

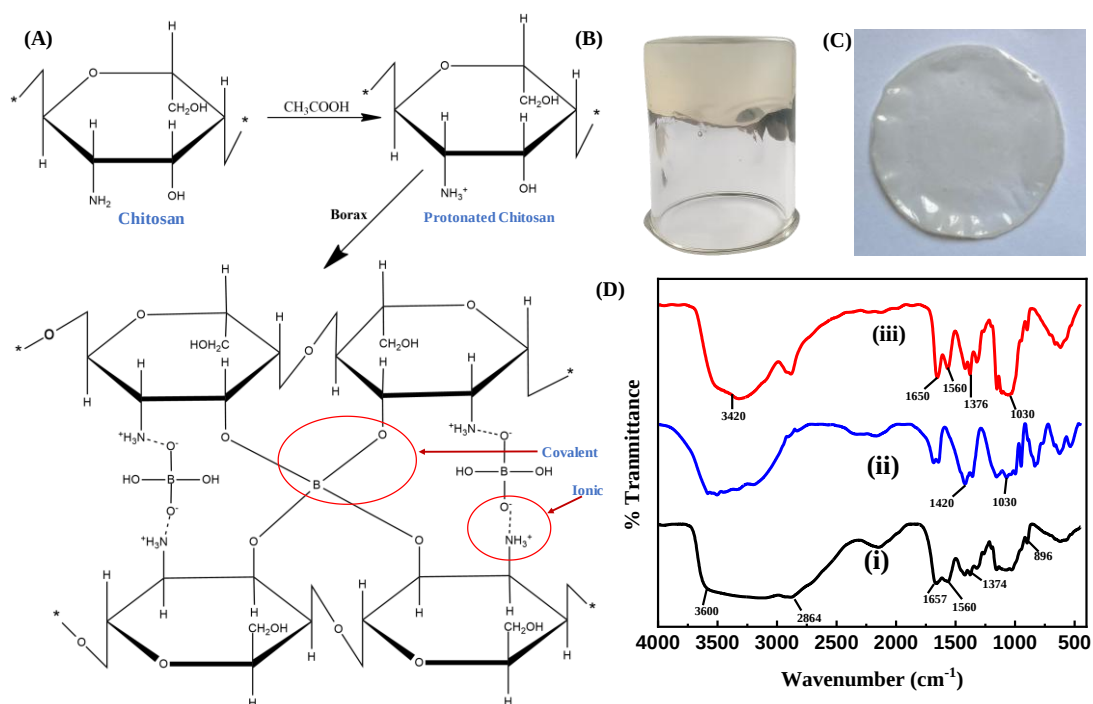
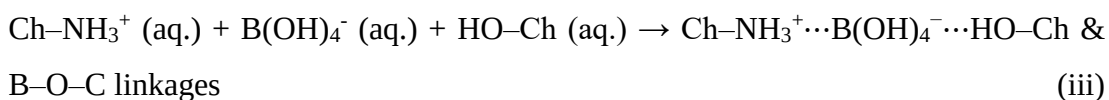
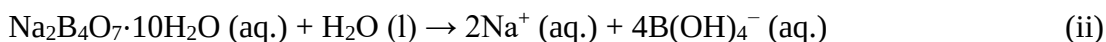
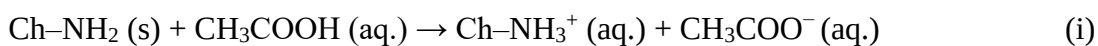


Fig.5.4 (A) Schematic diagram of the cross-linking reaction between protonated chitosan and borax; (B) Image shows the BCCH in an inverted beaker; (C) Image shows free standing BCCHME; (D) FTIR profiles of chitosan flakes (i), borax powder (ii), and BCCHME (iii).

Chitosan, a naturally occurring cationic polysaccharide, consists of β -(1 $\rightarrow$ 4)-linked D-glucosamine units bearing primary amino groups ($-\text{NH}_2$) at the C-2 position [43]. In its native form, chitosan exhibits poor solubility in water due to strong inter and intramolecular hydrogen bonding [44]. Upon the addition of dilute acetic acid, the amino functionalities are protonated to form ammonium groups ($-\text{NH}_3^+$), thereby enhancing solubility through increased electrostatic repulsion between polymer

chains, as shown in the reaction (i). Borax, when dissolved in aqueous medium, undergoes hydrolysis to generate tetrahydroxyborate anions (B(OH)_4^-) and sodium cations, as described in reaction (ii). These borate species engage in two simultaneous crosslinking pathways within the chitosan matrix, *Viz.*, ionic and covalent crosslinking. In the ionic crosslinking the B(OH)_4^- anions electrostatically interact with protonated NH_3^+ groups and form hydrogen bonds with hydroxyl (OH) groups on the chitosan backbone. In the covalent crosslinking the B(OH)_4^- anions condense with vicinal OH groups to form borate ester linkages (B-O-C). These interactions, as represented in Eq. (iii).



Altogether, the synthesis reactions generate multiple mobile charge carriers within the BCCHME matrix, namely H^+ , CH_3COO^- , Na^+ , and B(OH)_4^- . The synergy between ionic and covalent crosslinking enhances the mechanical robustness of BCCHME, enabling it to withstand the stresses during electrochemical use.

The FTIR spectroscopy was utilized to confirm the chemical interactions and structural modifications occurring in the chitosan matrix upon borax crosslinking. Fig.5.4 (D) shows the comparative FTIR spectra of chitosan flakes, borax powder, and the BCCHME. The FTIR spectrum of chitosan flakes displays a broad absorption band in the $3100\text{--}3600 \text{ cm}^{-1}$ range, which corresponds to overlapping O-H and N-H stretching vibrations arising from intra- and intermolecular hydrogen bonding [45]. A distinct aliphatic C-H stretching band is observed at 2864 cm^{-1} , confirming the presence of methylene groups. Absorption peaks at 1657 cm^{-1} and 1560 cm^{-1} are assigned to amide I (C=O stretching) and amide II (N-H bending) vibrations, respectively, reflecting the residual *N*-acetyl groups due to incomplete deacetylation of chitin [46]. Furthermore, the band at 896 cm^{-1} is characteristic of β -glycosidic ($\beta\text{-1}\rightarrow\text{4}$) linkages in the polysaccharide backbone. A weaker but distinguishable band at 1374 cm^{-1} can be

attributed to -NH_2 scissoring vibrations, indicating interactions involving amino groups [47]. The pure borax powder showed distinct vibrational bands near 1330 cm^{-1} and 1030 cm^{-1} , which are assigned to B–O asymmetric and symmetric stretching modes of B(OH)_4^- ions, confirming the tetrahedral coordination environment of borate species [23]. Upon incorporation of borax into the chitosan matrix, the hydrogel spectrum showed significant spectral modifications. The broad -OH stretching band was reduced in intensity and slightly shifted to 3420 cm^{-1} , suggesting extensive hydrogen bonding [48] and possible ionic interactions between protonated amine groups (-NH_3^+) and borate ions (B(OH)_4^-). A clear change in intensity and shift in the amide I (1650 cm^{-1}) and amide II (1560 cm^{-1}) bands were observed in the BCCHME. This change strongly supports ionic crosslinking between chitosan's protonated amine groups and the anionic borate species. Additionally, the enhanced absorption around 1376 cm^{-1} and a sharpened band near 1025 cm^{-1} in the BCCHME indicates the formation of borate ester linkages, i.e., covalent B–O–C bonds between borate ions and chitosan hydroxyl groups [22,28]. These dual interactions, ionic crosslinking via $\text{NH}_3^+\cdots\text{B(OH)}_4^-$ electrostatic attraction and covalent borate esterification, are key to enhancing the mechanical and electrochemical properties of the BCCHME. Hence, the FTIR spectra confirm the successful crosslinking of chitosan by borax through a synergistic mechanism involving both ionic and covalent interactions, leading to the formation of a stable, mechanically robust, and ionically conductive membrane.

Table 5.1: Conductivity related data of BCCHMEs with varying borax concentrations.

Concentration of borax (M)	Thickness (mm)	R_b (Ω)	DC Ionic conductivity (S cm^{-1})	AC ionic conductivity (S cm^{-1})
0.1	0.05	24.06	2.07×10^{-4}	1.80×10^{-4}
0.2	0.05	43.31	1.15×10^{-4}	1.09×10^{-4}
0.3	0.05	28.06	1.78×10^{-4}	1.65×10^{-4}
0.4	0.06	10.98	5.46×10^{-4}	3.65×10^{-4}
0.5	0.06	8.54	7.03×10^{-4}	5.83×10^{-4}

The Nyquist plots of BCCHME samples containing 0.1 to 0.5 M borax, as shown in Fig.5.5 (A), reveal the anticipated combination of a high-frequency capacitive arc and a low-frequency diffusion tail. The point at which the arc intercepts the real axis corresponds to the R_b of each membrane; these values (Table 5.1) decrease progressively as borax concentration increases from 0.1 M to 0.5 M. Concurrently, the calculated DC ionic conductivity (σ_{DC}) rises from $2.07 \times 10^{-4} \text{ S cm}^{-1}$ at 0.1 M to $7.03 \times 10^{-4} \text{ S cm}^{-1}$ at 0.5 M. This trend is showed in the Fig.5.5 (B). At low borax concentration, the number of mobile borate species is insufficient to form continuous ionic pathways, resulting in relatively high R_b and modest σ_{DC} . As the borax concentration is increased, more $B(OH)_4^-$ and Na^+ become available to carry charge through the chitosan network, thereby lowering R_b and promoting ion transport. The optimal conductivity at 0.5 M arises from a balance between abundant charge carriers and a still-open hydrogel microstructure that does not yet hinder ion mobility.

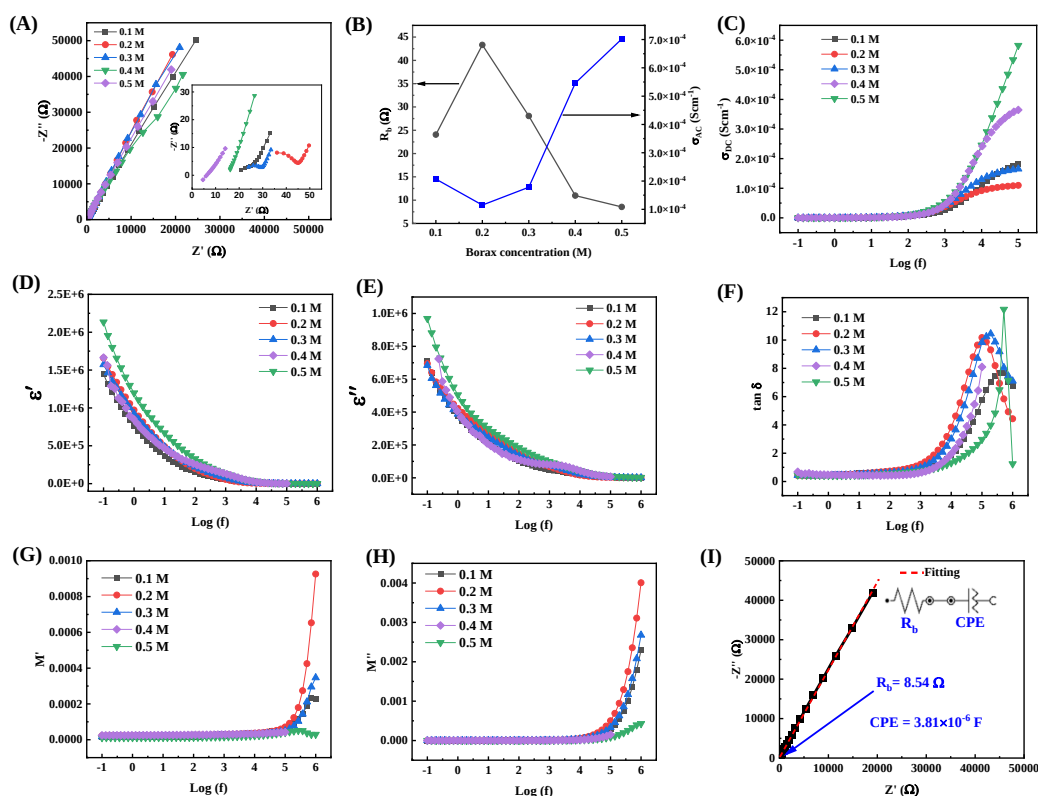


Fig.5.5 (A) Nyquist plots obtained during conductivity measurement for BCCHMEs with varying borax concentrations (inserts provide enlarged views of the regions with higher frequencies); (B) Plot of R_b and DC ionic conductivity as a function of borax concentrations; (C) Graph of AC ionic conductivity as a function of borax

concentrations; (D) Plots of dielectric constant vs. frequency; (E) Plots of dielectric loss vs. frequency; (F) Plots of dielectric loss tangent vs. frequency; (G) Plots of real dielectric modulus vs. frequency; (H) Plots of imaginary dielectric modulus vs. frequency; (I) Fitted Nyquist plot with circuit diagram of the optimum BCCHME for ion transport parameters calculations.

The frequency-dependent AC ionic conductivity analysis of BCCHME membranes provides valuable insights into the charge transport mechanisms and electrode-electrolyte interactions within the hydrogel network. Fig.5.5 (C) displays the AC conductivity spectra for all borax concentrations upto the frequency of 1 MHz, revealing characteristic frequency-dependent behaviour typical of ion-conducting polymer electrolytes. The AC conductivity plots exhibit two distinct regions that reflect different charge transport processes within the BCCHME system. At low frequencies, the conductivity shows an electrode polarization (EP) region characterized by limited ion mobility due to charge accumulation at the electrode-electrolyte interface [49]. This polarization effect occurs when the applied electric field frequency is insufficient to overcome the interfacial barriers, resulting in reduced effective ion transport. As frequency increases, the conductivity enters a DC contribution region where ion hopping becomes more prominent and space charge accumulation effects are minimized [50]. This transition reflects the ability of mobile ions viz., B(OH)_4^- and Na^+ to overcome interfacial barriers and contribute effectively to bulk conductivity through successful hopping between coordination sites within the chitosan matrix. The quantitative AC conductivity values presented in Table 5.1 demonstrate that the 0.5 M borax concentration achieves the highest AC conductivity of $5.83 \times 10^{-4} \text{ S cm}^{-1}$, which aligns well with the corresponding DC conductivity value of $7.03 \times 10^{-4} \text{ S cm}^{-1}$. This close agreement between AC and DC conductivity values indicates consistent ion transport behaviour across the frequency spectrum and confirms the reliability of the R_b measurements. The slight differences observed between AC and DC conductivity values can be attributed to frequency-dependent polarization effects and the contribution of interfacial processes at different time scales. DC conductivity primarily reflects long-range ionic motion and bulk transport properties, while AC conductivity captures both bulk ionic conduction and frequency-

dependent processes including ion hopping, dipolar relaxation, and electrode polarization effects.

Table 5.2: Comparison of ionic conductivity of BCCHME with some reported polymer electrolyte.

Electrolyte composition	Ionic conductivity (S cm^{-1})	Ref.
PVA-ionic liquid	6.21×10^{-4}	[51]
PS-PVA-Gly + NaClO_4	1.03×10^{-4}	[52]
Starch-Gly	9.56×10^{-4}	[53]
PVA-Gly	1.49×10^{-4}	[54]
Gelatin-Glutaraldehyde	8.83×10^{-4}	[34]
Cellulose acetate + NH_4BF_4	1.41×10^{-5}	[55]
Chitosan + LiOAc	7.60×10^{-6}	[56]
Chitosan-borax	7.03×10^{-4}	This work

Table 5.2 compares the room-temperature ionic conductivity of the present borax-chitosan membrane against a range of reported polymer-based electrolytes. The BCCHME, with a conductivity of $7.03 \times 10^{-4} \text{ S cm}^{-1}$, outperforms cellulose-acetate-PEG and starch-Gly membranes and approaches the performance of PVA-HFP/PMMA-IL composites, demonstrating that the simple chitosan–borax network achieves competitive ion transport without additional plasticizers or ionic liquids.

Fig.5.5 (D) and 5.5 (E) plot the dielectric constant (ϵ') and loss (ϵ'') for BCCHME membranes containing 0.1 to 0.5 M borax as a function of frequency ($\log f$). ϵ' represents the material's capacity to store electrical energy, while ϵ'' quantifies energy dissipation through ion migration and dipolar relaxation under alternating fields [57]. At low frequencies, both ϵ' and ϵ'' attain their highest values, which arise from extensive ion accumulation at the BCCHME-SS blocking electrode interface and interfacial polarization. As the frequency increases, the field reverses more rapidly than ions and dipoles can respond, causing both ϵ' and ϵ'' to decrease and approach frequency independence after $\log f$ of 4. The 0.5 M based BCCHME consistently exhibits the largest low-frequency ϵ' and ϵ'' among all formulations, reflecting its

highest density of mobile charge carriers and enhanced dipolar mobility within the hydrogel network. The enhanced dielectric response at 0.5 M can be rationalized by considering the relationships [58]

$$n_i = n_0 \exp\left(-\frac{U}{\varepsilon' k_B T}\right) \quad (23)$$

$$\sigma = \sum q n_i u_i \quad (24)$$

In equation (23), n_i , n_0 , U , K_B , and T denote the charge carrier density, pre-exponential constant, dissociation energy, Boltzmann constant, and absolute temperature, respectively. In equation (24), q represents the charge of the carriers, and u_i denotes their ionic mobility. Based on these relationships, an increase in ε' leads to improved ionic conductivity, as n_i is directly proportional to conductivity. Consequently, the higher dielectric constant observed for the BCCHME synthesized with 0.5 M borax is associated with its enhanced ionic conductivity. Coulomb's law, which defines the electrostatic interaction between ions, is essential for understanding dielectric behaviour and ion transport in polymer electrolytes. As expressed by Coulomb's equation, the electrostatic force F between two ions carrying charges q_1 and q_2 is given by $F = \frac{q_1 q_2}{4\pi \varepsilon' r^2}$ [59], where ε' is the dielectric constant and r is the separation distance. The force is inversely related to ε' , meaning that a higher dielectric constant reduces the strength of ion-ion electrostatic interactions. This weakening of attraction facilitates greater ion mobility and increases the charge carrier density, both of which contribute to improved ionic conductivity. In the present work, the BCCHME synthesized with 0.5 M borax exhibited a high ε' at low frequencies, attributed to ion accumulation at the electrode-electrolyte interface, which corresponds to its superior ionic conductivity relative to other BCCHME samples.

Fig.5.5 (F) presents the loss tangent over the same frequency range. At low frequencies, $\tan \delta$ remains modest and nearly constant, indicating minimal relaxation losses. Beyond $\log f$ of 3.5, $\tan \delta$ increases sharply as ion hopping and dipole reorientation contribute progressively to dielectric loss. The 0.5 M based membrane

reaches the highest $\tan \delta$ peak, signifying the greatest extent of ionic relaxation and correlating with its superior conductivity and reduced resistive obstacles to ion transport [60].

The dielectric modulus, provides complementary insight into relaxation dynamics by suppressing electrode polarization effects. The real (M') and imaginary (M'') modulus, are plotted and showed in the Fig.5.5 (G) and 5.5 (H) respectively, for each borax concentration. In the low-frequency regime, M' remains close to zero, reflecting dominant interfacial polarization [61]. Above $\log f$ of approximately 4, M' rises steeply as bulk dielectric relaxation emerges. The 0.5 M membrane exhibits the lowest M' values across the frequency spectrum, indicating the least impediment to ionic displacement and the most open polymer network. M'' spectra display relaxation peaks at high frequencies, marking the characteristic frequency where charge carriers overcome local binding constraints [62]. With increasing borax concentration, the M'' peak shifts slightly toward lower frequencies and decreases in intensity, reflecting longer relaxation times but more facile long-range ion transport. The smallest M'' peak for the 0.5 M membrane corroborates its highest DC and AC conductivities, confirming that an optimal borax content both enhances carrier density and maintains sufficient polymer free volume for efficient ion migration. Together, the ϵ' , ϵ'' , $\tan \delta$, M' , and M'' analyses demonstrate that borax concentration critically dictates the dielectric storage, loss, and relaxation behaviour of BCCHME membranes. A 0.5 M borax loading delivers the most favourable combination of high dielectric constant, controlled losses, and rapid dielectric relaxation, underscoring its suitability as a high-performance quasi-solid electrolyte for EDLC applications.

The ion transport characteristics of the optimized BCCHME membrane prepared with 0.5 M borax concentration, which demonstrated the highest ionic conductivity, were analysed using EIS and modelled through equivalent circuit fitting. The Nyquist plot, as shown in the Fig.5.5 (I) exhibits a characteristic spike in the low-frequency region, indicating dominant capacitive behaviour. Accordingly, the equivalent electrical circuit was configured as a R_b in parallel with a CPE to accurately represent the membrane's electrochemical response. The extracted CPE value of 3.8×10^{-6} F

confirms the capacitive nature of the BCCHME and demonstrates effective interfacial charge storage at the electrode-electrolyte interface. From the fitted parameters, the diffusion coefficient (D) was calculated as $4.19 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, which reflects the moderate ionic diffusion typical of cross-linked chitosan hydrogel networks where polymer chain interactions influence ion mobility pathways. The ionic mobility (μ) was determined to be $1.6 \times 10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$, indicating the ability of mobile charge carriers to respond efficiently under applied electric fields, a crucial parameter for rapid ion transport during charging and discharging cycles. Furthermore, the ion number density (n) was calculated as $1.05 \times 10^{31} \text{ m}^{-3}$, revealing an exceptionally high population of free charge carriers available for conduction within the membrane matrix. This substantial carrier density correlates well with the enhanced ionic conductivity observed and validates the effectiveness of the borax-crosslinking mechanism in creating a well-hydrated, ion-conductive environment with abundant mobile $\text{B}(\text{OH})_4^-$ and Na^+ species. These comprehensive ion transport parameters collectively confirm the suitability of BCCHME as an efficient quasi-solid electrolyte for EDLC applications, where high ionic conductivity and stable charge transport dynamics are essential for optimal device performance.

The optimal BCCHME exhibited a WU of 182 %, indicating a substantial ability to absorb and retain moisture within its network. This high hydration capacity originates from the intrinsic hydrophilicity of chitosan, whose backbone contains abundant polar functional groups, namely primary amines, hydroxyls, and ether linkages [63]. These groups form strong hydrogen bonds with water molecules, driving the sorption process. Additionally, the dual crosslinking mechanism introduced by borax creates a three-dimensional network that retains structural integrity while maintaining interstitial free volume. This structural arrangement promotes water diffusion into the membrane without excessive network collapse, balancing swelling and mechanical stability. The borate-mediated crosslinking also introduces localized hydrophilic domains, which act as micro-reservoirs for water molecules, further enhancing retention. Such hydration is critical for ensuring ion conduction in electrochemical applications, as the absorbed water facilitates ion dissociation and mobility within the membrane matrix.

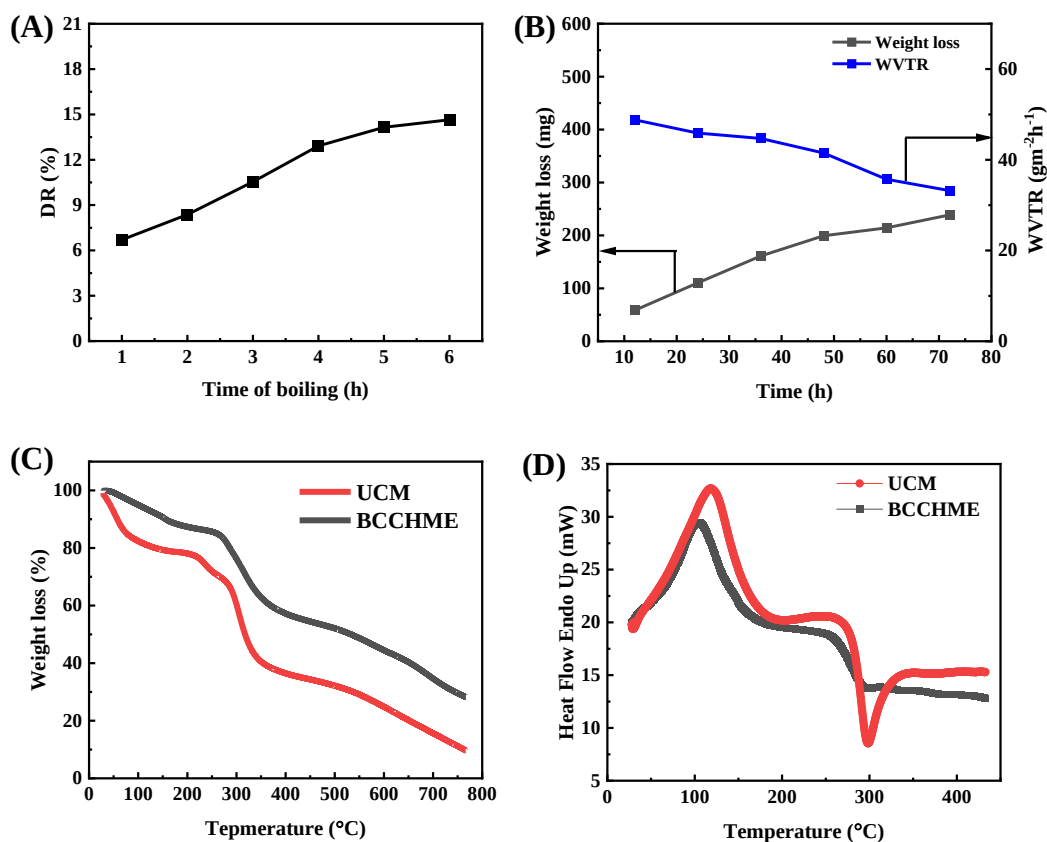


Fig.5.6 (A) Variation of DR with boiling time; (B) Variation of WVTR and weight loss with time; (C) TGA thermograph of UCM and BCCHME; (D) DSC plots of UCM and BCCHME.

The DR of the BCCHME was plotted with respect to the time of boiling time is showed in Fig.5.6 (A) and determined to be 14.65 % after immersion under accelerated hydrolytic conditions. This relatively low DR indicates a high degree of structural stability, which can be attributed to the formation of a densely interconnected network within the membrane. The presence of strong borate–polymer interactions through both electrostatic association with protonated amino groups and covalent ester linkages with hydroxyl functionalities, reduces the number of loosely bound polymer chains susceptible to leaching. Furthermore, the compact internal architecture restricts excessive water-induced polymer disentanglement, thereby limiting mass loss during prolonged aqueous exposure. Such stability is advantageous for electrochemical applications, where dimensional integrity and sustained ionic pathways are essential over extended operational lifetimes.

The WVTR serves as an essential marker for quantifying the permeability of cross-linked hydrogel membranes to moisture vapor and directly reflects both the internal porosity and the efficacy of vapor transport channels within the network [35]. As depicted in Fig.5.6 (B), the WVTR of the BCCHME demonstrates a progressive increase with time, ultimately reaching a maximum value of $20.4 \text{ g m}^{-2} \text{ h}^{-1}$ at 70 h. This upward trend signifies the presence of continuous hydrophilic pathways and interconnected microscale voids within the hydrogel, which are formed as a consequence of the precisely tuned crosslinking regime. The concurrently measured mass loss reflects a steady and controlled rate of water evaporation, indicative of ongoing, but not excessive, vapor transmission. This behaviour confirms that the BCCHME not only mitigates rapid dehydration, but also avoids trapping excess water both of which are crucial for preserving ionic conductivity, dimensional stability, and electrochemical performance over time. Critically, the moderately low WVTR observed here is attributable to the synergistic effect of ionic and covalent linkages. The borate-diol esters dramatically limit excessive moisture flux by densifying the network, while the remaining ionic crosslinks maintain local hydrophilicity and facilitate essential humidity exchange. This balance enables the hydrogel to sustain both moisture and electrolyte ion mobility, making it ideally suited for solid-state energy storage or biomedical devices requiring stable, hydrated interfaces.

The TGA curves for the UCM and BCCHME are shown in Fig.5.6 (C). An initial weight loss was observed between 25°C and 100°C for both membranes, corresponding to the evaporation of physically adsorbed and bound water molecules [64]. A major decomposition event began around 223°C in both samples, marking the onset of thermal degradation of the chitosan backbone. This stage involves the cleavage of glycosidic linkages, depolymerization of the polysaccharide chains, and breakdown of functional groups such as acetylated and deacetylated units [65]. At this point, BCCHME retained approximately 85 % of its original weight, while UCM retained only 76 %, indicating that borax crosslinking significantly enhances thermal stability. The improved stability in BCCHME is attributed to the formation of crosslinks between borate ions and the amino groups in chitosan. These interactions reduce the segmental mobility of polymer chains, thereby increasing resistance to

thermal degradation [64]. Beyond 240 °C, both membranes exhibited continuous weight loss. However, UCM degraded more extensively across the higher temperature range. At 800 °C, BCCHME exhibited a residual mass of approximately 30 %, while UCM retained only about 15 %. This substantial difference further confirms that borax crosslinking enhances the thermal integrity of the chitosan matrix, making BCCHME a more thermally robust candidate for energy storage applications such as EDLCs [64,66,67].

DSC analysis of UCM and BCCHME is presented in Fig.5.6 (D). Both membranes displayed a broad endothermic peak between 90 °C and 130 °C, associated with the loss of bound and physically adsorbed water, a common feature in hydrophilic polymers like chitosan [68]. The glass transition temperature (T_g) was identified at around 226 °C for UCM and 205 °C for BCCHME. The reduction in T_g upon borax crosslinking is consistent with literature reports suggesting that borax disrupts inter-chain hydrogen bonding within the chitosan matrix [69]. As a result, the polymer network becomes more flexible, which lowers T_g but simultaneously enhances thermal decomposition resistance due to the formation of ionic crosslinks. Beyond the T_g , an additional thermal event was observed around 280-290 °C in both samples. This exothermic transition is likely associated with further degradation or the breakdown of crystalline domains [70]. UCM exhibited a sharper, more intense peak, indicating a faster and less controlled decomposition process. In contrast, BCCHME showed a broader, less intense peak, suggesting a slower and more thermally stable degradation pathway. These DSC results align well with the TGA findings, collectively demonstrating that borax crosslinking improves both the thermal resistance and structural integrity of the chitosan membranes [68].

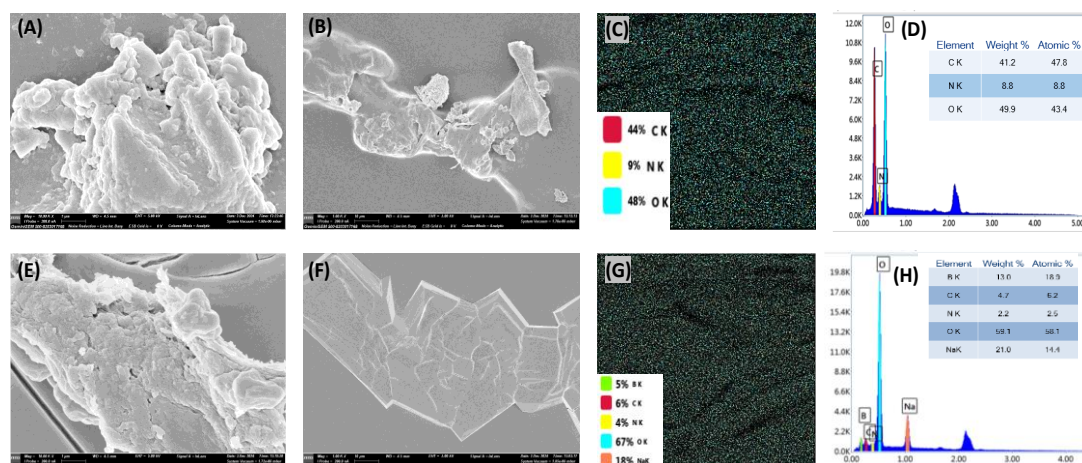


Fig.5.7 (A) FE-SEM image of UCM at 1 μm ; (B) FE-SEM image of UCM at 10 μm ; (C) EDX mapping of UCM; (D) EDX elemental spectra of UCM; (E) FE-SEM image of BCCHME at 1 μm ; (F) FE-SEM image of BCCHME at 10 μm ; (G) EDX mapping of BCCHME; (H) EDX elemental spectra of BCCHME.

The surface morphology and elemental composition of UCM and BCCHME are shown in Fig.5.7. The FESEM micrographs of UCM reveal an irregular and highly rough surface structure [71]. The morphology is characterized by loosely packed layers and amorphous aggregates, which is typical for chitosan films formed via solution casting without any crosslinking treatment [72]. This indicates a lack of internal cohesion, which could limit the mechanical integrity and barrier properties of the membrane. In contrast, the BCCHME exhibits a much denser and more compact surface [73]. The presence of well-defined layered regions and plate-like crystalline domains suggests that borax crosslinking induces significant structural reorganization within the polymer matrix. In BCCHME, both covalent linkage between borax and hydroxyl groups of chitosan, and ionic interactions between the protonated amine of chitosan and negatively charged borate ions contribute to the formation of a smooth architecture than UCM. EDX mapping and the spectral profile of UCM confirmed the presence of carbon (41.2 wt%), nitrogen (8.8 wt%), and oxygen (49.9 wt%), which is consistent with the chemical structure of chitosan [72,74,75]. In the case of BCCHME, the EDX results revealed the incorporation of boron (13.0 wt%) and sodium (21.0 wt%), along with a notable increase in oxygen content (59.1 wt%). The detection of

boron (5 wt%) and sodium (18 wt%) further confirms the successful crosslinking with borax.

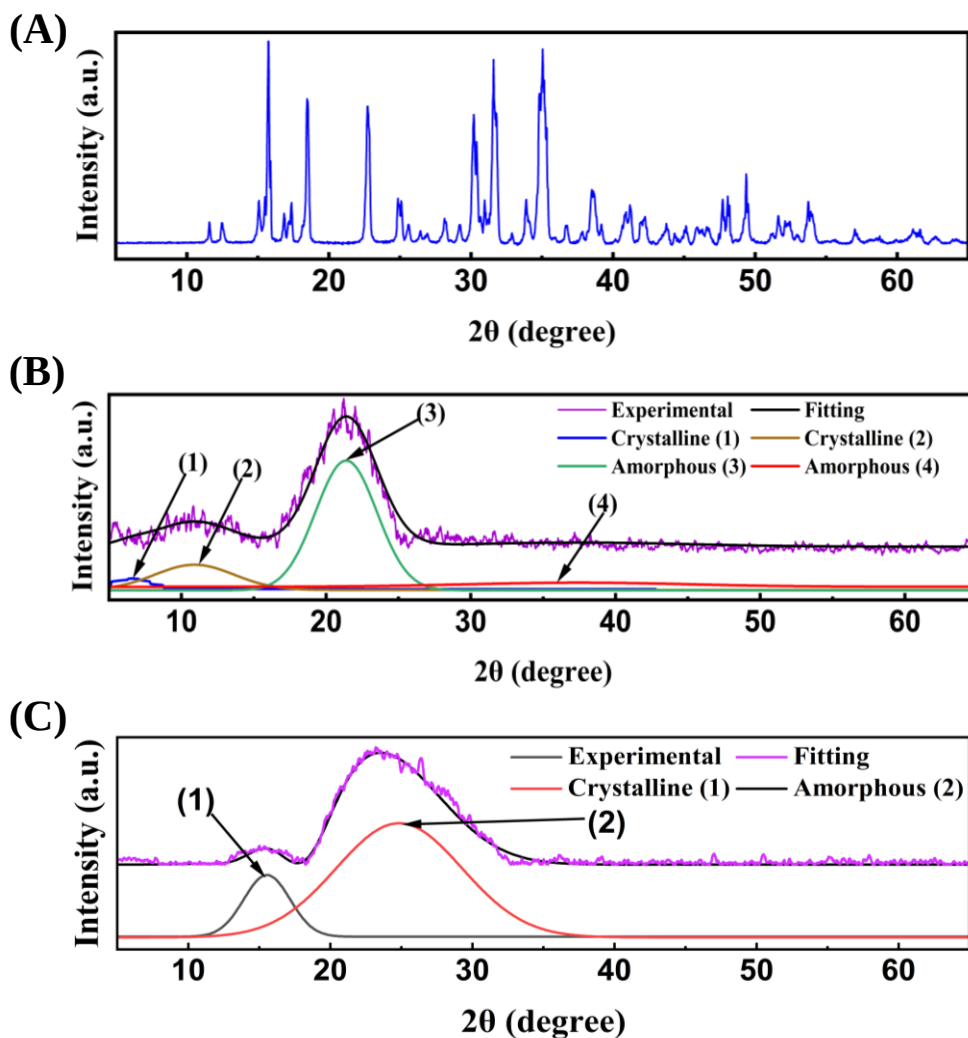


Fig.5.8 (A) XRD graph of borax powder; (B) Deconvoluted XRD graph of UCM; (C) Deconvoluted XRD graph of BCCHME

The XRD pattern of borax powder and the deconvoluted XRD patterns of the UCM and BCCHME are presented in Fig.5.8 (A), 5.8 (B), and 5.8 (C), respectively. As shown in Fig.5.8 (A), borax powder exhibits multiple sharp and well-defined diffraction peaks, indicating its highly crystalline nature. In Fig.5.8 (B), the deconvoluted XRD profile of the UCM shows two crystalline peaks (bands 1 and 2) at 2θ of 6° and 11°, along with two amorphous peaks (bands 3 and 4) at 2θ of 21° and 38°. This pattern is consistent with earlier reports for UCM [13,76]. The deconvoluted

XRD pattern of BCCHME, shown in Fig.5.8 (C), reveals one crystalline peak (bands 1) at 2θ of 15° , and one amorphous peak (bands 2) at 2θ of 24° . The degree of crystallinity for both membranes, calculated using equation (14), is 19.50% for the UCM and 16.59 % for BCCHME, indicating that both materials possess a semi-crystalline structure. The decrease in crystallinity for BCCHME is attributed to crosslinker-induced disruption of the ordered crystalline domains, thereby increasing the amorphous fraction. The sharp crystalline peaks characteristic of borax is absent in the BCCHME pattern, confirming the complete dissolution of borax within the chitosan hydrogel matrix. This crosslinking process between borax and chitosan generates new chemical bonds that disrupt the native intra and intermolecular hydrogen bonding in chitosan [77]. Such a reduction in crystallinity is favourable for improving ionic conductivity, thereby enhancing the potential of BCCHME for electrochemical energy storage applications.

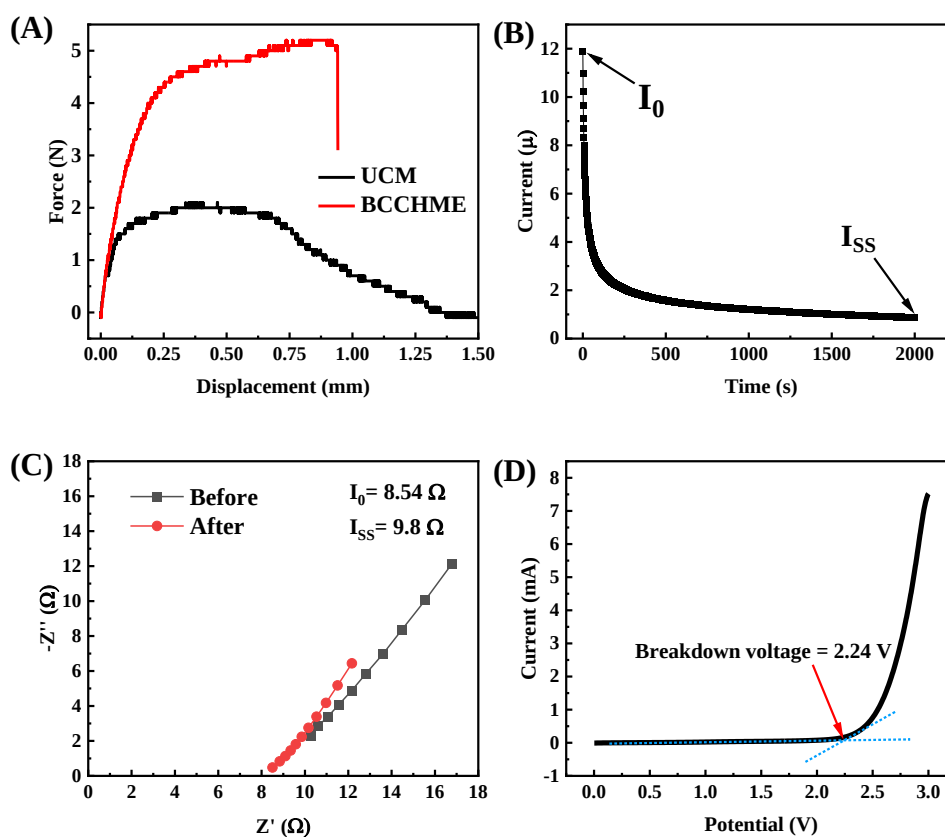


Fig.5.9 (A) Force vs. displacement curves of UCM and BCCHME for mechanical strength measurements; (B) DC polarization curve of BCCHME; (C) Plots of Nyquist plots before and after the DC polarization; (D) LSV profile of BCCHME.

The mechanical performance of both UCM and BCCHME is illustrated in Fig.5.9 (A). The UCM demonstrated a tensile strength of 30.51 MPa, an elongation at break of 6.48 %, and a Young's modulus of 470.84 MPa, characteristic of a moderately strong yet flexible biopolymer film. Crosslinking with borax led to a pronounced increase in tensile strength, reaching 45.87 MPa, indicating stronger intermolecular bonding and improved resistance to mechanical stress. However, this enhancement in strength came at the cost of flexibility. The elongation at break declined to 3.13 %, suggesting that the polymer chains in the cross-linked network experience restricted mobility. This loss in extensibility is typical of rigidified polymer systems. Furthermore, the Young's modulus increased more than threefold to 1465.50 MPa, highlighting the formation of a significantly stiffer and more rigid structure. These changes confirm that borax-induced ionic crosslinking enhances the mechanical integrity of chitosan membranes, making them more appropriate for applications demanding high mechanical durability and dimensional stability. Comparable outcomes have been reported in earlier investigations of cross-linked chitosan systems, where improved tensile strength and stiffness were consistently attributed to the formation of reinforced polymeric networks [78–80].

The DC polarization curve for BCCHME is presented in Fig.5.9 (B). Using Equation (15), the t_{ion} was calculated to be 0.93, confirming that ionic conduction is the dominant charge transport mechanism in BCCHME, with negligible contribution from electronic conduction. Fig.5.9 (C) shows the Nyquist plots obtained before and after DC polarization. From Equation (16), using the data from Fig.5.9 (B) and 5.9 (C), the t_{cation} was determined to be 0.08. This result indicates that anions serve as the primary mobile charge carriers in BCCHME, while cations contribute only minimally to the total ionic conductivity.

The electrochemical stability of the BCCHME was evaluated using LSV under ambient conditions to determine its operational voltage window [81]. The LSV curve showed in Fig.5.9 (D), reveals a stable current response with negligible increase in current up to approximately 2.24 V, indicating that the membrane exhibits excellent electrochemical inertness within this potential range. This stability signifies the

absence of significant faradaic reactions or decomposition processes [82], confirming that the BCCHME remains intact and does not undergo degradation under these conditions. Beyond this threshold voltage, a noticeable and sharp increase in current density is observed, marking the onset of electrochemical decomposition or breakdown of the membrane. This behaviour typically arises from the initiation of irreversible oxidation or reduction reactions, likely occurring at the electrode-electrolyte interface [13]. The relatively high breakdown voltage surpasses the minimum requirement of about 1 V commonly accepted for polymer electrolytes in energy storage applications [83], underscoring the robust electrochemical durability of the BCCHME. The high electrochemical stability of BCCHME can be attributed to the intrinsic molecular architecture of the chitosan backbone and the dual ionic-covalent crosslinking introduced by borax.

Although the BCCHME exhibits a relatively high breakdown voltage of 2.24 V, the electrochemical testing in this study was limited to 1.0 V to align with the standard operational window for EDLCs employing polymer-based hydrogel electrolytes. As reported by Shujahadeen B. Aziz et al. [54], prolonged cycling at elevated potentials can trigger multiple degradation pathways that impair electrolyte performance. These include mechanical weakening of the polymer matrix due to repetitive electrochemical stress, partial cleavage of polymer chains leading to reduced ionic conductivity, and gradual depletion of mobile ions within the hydrogel network, which lowers capacitance and energy storage capability. High-voltage operation may also accelerate parasitic reactions at the electrode-electrolyte interface, forming resistive interfacial layers that impede ion transport and increase internal resistance. Furthermore, in systems containing plasticizing agents, excessive potentials can induce volatilization or migration of these species, thereby reducing flexibility and ionic mobility. Additionally, elevated local temperatures during high-voltage cycling can promote thermal or oxidative degradation of the polymer-borate cross-linked framework, ultimately diminishing structural stability and electrochemical durability.

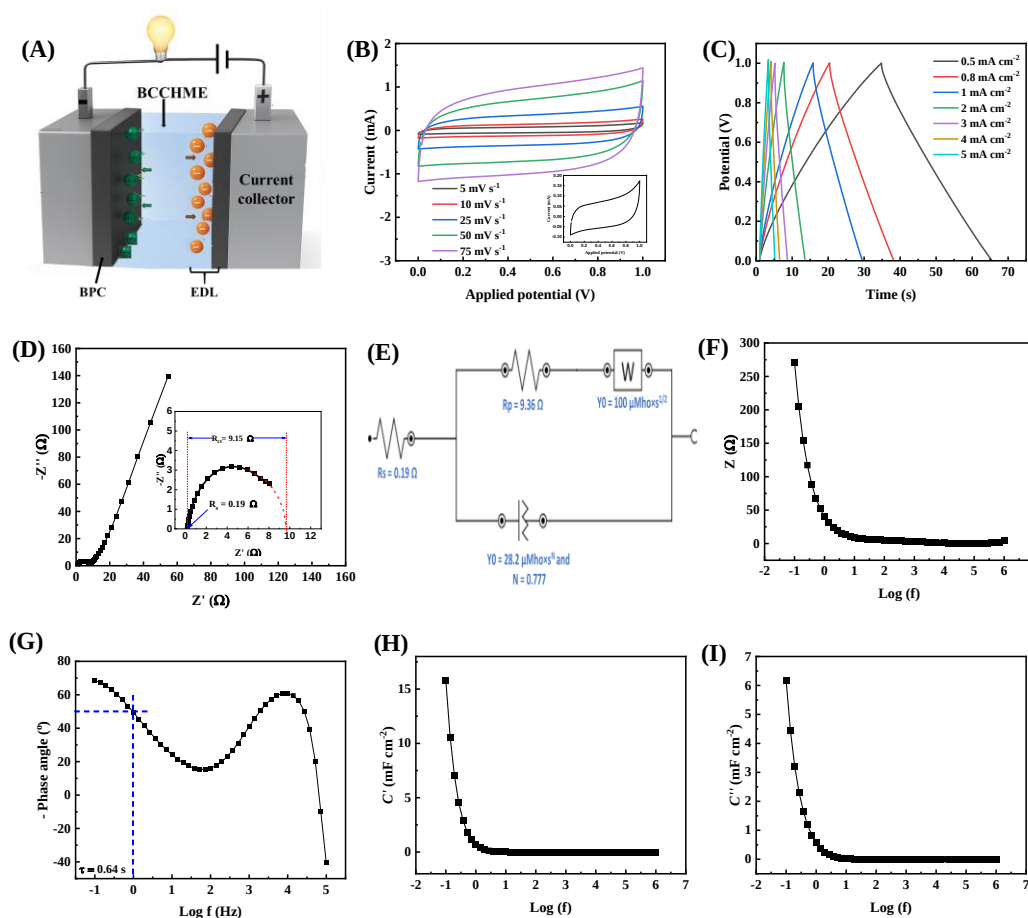


Fig.5.10 (A) Schematic of EDLC working mechanism; (B) Plots of CVs at varying scan rates for the EDLC employing BCCHME; (C) Plots of GCDs at varying current densities for the EDLC employing BCCHME; (D) Plots of Nyquist plot of the EDLC with the inset shows the enlarged view of the high-frequency region); (E) EES of the EDLC obtained from electrochemical workstation; (F) Bode plot of total impedance with respect to the frequency; (G) Bode plot of phase angle with respect to frequency; (H) Real component of capacitance vs frequency; (I) Imaginary component of capacitance vs frequency.

Fig.5.10 (A) illustrates the working principle of an EDLC incorporating BCCHME as both the electrolyte and separator. The process involves three main stages viz., charging, EDL formation, and discharging. During charging, the applied potential across the electrodes drives the migration of mobile ions within the hydrated BCCHME network. Its interconnected water-rich domains enable rapid ion transport and efficient polarization under the electric field. As the EDL forms, counter-ions

accumulate at the electrode–electrolyte interface, balancing the electronic charge on the electrode surface without any faradaic reactions [84]. This electrostatic storage mechanism, based on nanometres-scale separation of charges, yields high capacitance. The hydrated, ionically conductive BCCHME ensures uniform charge distribution, while its robust gel structure maintains electrode separation to prevent short-circuits. During discharge, the ions redistribute back into the bulk membrane, reversing interfacial polarization and releasing the stored energy. This non-faradaic, highly reversible process allows for fast power delivery and minimal performance loss over repeated cycles [84].

Fig.5.10 (B) presents the CVs of the EDLC measured at different scan rates. The inset of Fig.5.10 (B) displays the CV recorded at the lowest scan rate of 5 mV s^{-1} . The CV curves do not exhibit any redox peaks, indicating the absence of faradaic reactions within the potential range of 0–1 V. This lack of redox activity confirms that the capacitance arises from an electric double-layer mechanism. The CV profile gradually changes from an almost rectangular shape at low scan rates to a leaf-like shape at higher scan rates. The ideal rectangular shape is associated with efficient charge transport [85,86], whereas deviations observed at higher scan rates are attributed to diffusion-limited ion movement [87]. Factors such as carbon material porosity and internal resistance are known to influence the current-voltage behaviour [88].

Table 5.3: Summary of the GCD performance data at varied current densities.

Current density (mA cm^{-2})	Discharge time (s)	Areal capacitance (mF cm^{-2})	Energy density ($\mu\text{Wh cm}^{-2}$)	Power density (mW cm^{-2})	Coulombic efficiency (%)	IR drop (mV)
0.5	30.7	30.70	4.26	500	91	2
0.8	17.8	28.48	3.96	800	92	3
1.0	13.7	27.40	3.81	1000	93	4
2.0	5.9	23.60	3.27	2000	89	8
3.0	3.5	21.00	2.92	3000	84	13
4.0	2.4	19.20	2.70	4000	78	16
5.0	1.8	18.00	2.50	5000	75	20

Fig.5.10 (C) illustrates the GCD profiles of the EDLC recorded at various current densities, with the corresponding parameters summarized in Table 5.3. The GCD curves exhibit nearly symmetric triangular shapes with minimal internal resistance (IR) drops, indicating high Coulombic efficiency and low resistive losses in the system [89]. At the lowest applied current density of 0.5 mA cm^{-2} , the device achieves an areal capacitance of 30.7 mF cm^{-2} and a Coulombic efficiency of 91 %. Increasing the current density from 0.5 to 5.0 mA cm^{-2} results in a gradual reduction in capacitance to 18 mF cm^{-2} . This decline is primarily due to restricted ion diffusion at higher charging rates, which limits ion penetration into the deeper pores of the electrode material [90]. Despite this decrease, the device retains relatively high Coulombic efficiency even at the maximum tested current density, indicating efficient charge recovery and stable cycling characteristics. EIS was conducted to examine the charge transport characteristics of the EDLC. The Nyquist plot, presented in Fig.5.10 (D), consists of a semicircle in the high-frequency region followed by an almost vertical line at low frequencies, indicating capacitive behaviour. The corresponding EEC model is shown in Fig.5.10 (E), comprising R_s , R_{ct} , a CPE, and W. The R_s value is obtained from the intercept of the Nyquist plot with the real axis, while the semicircle diameter in the high-frequency region corresponds to R_{ct} of the active material [13,91]. R_s reflects the bulk electrolyte resistance, which is influenced by ion mobility and electrolyte thickness. It is composed of two components: electronic resistance, arising from the electrode material and contact points with the current collector and ionic resistance, originating from ion transport within the electrolyte and the pores of the electrode [92]. A lower R_s value corresponds to higher ionic conductivity and reduced ohmic losses. In this work, the R_s was measured to be only 0.19Ω , signifying excellent performance of the BCCHME in facilitating rapid ion transport for supercapacitor applications. R_{ct} represents the interfacial resistance at the electrode–electrolyte interface during charge–discharge cycles. The R_{ct} value of 9.36Ω indicates effective charge transfer processes, which are essential for achieving high power density and fast response times. The CPE models the non-ideal capacitive behaviour associated with the porous carbon electrode structure, while the Warburg element accounts for ion diffusion effects at low frequencies [40,93]. A CPE with parameters $Y_0 = 28.2 \mu \Omega^{-1} \times s^N$ and $N = 0.777$ reflects a capacitive response approaching ideal behaviour, which

is desirable for EDLC operation [94]. The ESR, calculated as the sum of R_s and R_{ct} , is $9.55\ \Omega$, a moderately low value that confirms efficient ion mobility and minimal polarization effects [95,96]. The presence of the Warburg component further indicates well-regulated ion diffusion within the porous electrode and electrolyte matrix, ensuring stable electrochemical performance over a wide frequency range. Overall, these results confirm that the hydrated, porous BCCHME hydrogel matrix plays a crucial role in delivering superior ionic conductivity, low interfacial resistance, and stable capacitive behaviour in the EDLC.

Fig.5.10 (F) demonstrates the characteristic bode plot of the total impedance magnitude (Z) as a function of frequency. The impedance magnitude displays a distinct decrease with increasing frequency, which is fundamentally attributed to the enhanced ionic mobility and reduced R_{ct} at higher frequencies [97]. At low frequencies, the electrolyte ions possess sufficient time to penetrate deep into the hierarchical porous network of the electrode, resulting in elevated impedance values due to the tortuous diffusion pathways within the porous matrix. This low-frequency behaviour reflects the complete utilization of the available electrode surface area, including micropores and mesopores that contribute to the overall capacitive response. Conversely, at higher frequencies, the impedance approaches a frequency-independent plateau, indicating the dominance of resistive contributions from the electrolyte and intrinsic electrode resistance. This transition signifies that at elevated frequencies, the ions primarily interact with the outer surface of the electrode, as insufficient time is available for deep penetration into the porous structure [42]. Fig.5.10 (G) illustrates the phase angle variation across the frequency spectrum, revealing exceptional capacitive performance of the EDLC. The maximum phase angle approaches the theoretical ideal of 90° , which is characteristic of pure capacitive behaviour in electrochemical double-layer capacitors [97]. This near-ideal phase response indicates minimal resistive and faradaic contributions to the overall impedance, demonstrating excellent charge storage efficiency through the formation of a well-developed electrical double layer at the electrode-electrolyte interface. The high phase angle values observed across a broad frequency range suggest uniform charge distribution and optimal ion accessibility throughout the porous electrode structure [98]. This behaviour is

indicative of efficient electrostatic charge storage mechanisms, where ions from the electrolyte form organized layers at the electrode surface, creating a capacitive interface with minimal energy dissipation. The relaxation time constant (τ) of 0.64 s, determined from the frequency at which the phase angle reaches -45° , represents the characteristic time required for the electrode to discharge approximately 50% of its stored energy [99]. This relatively short relaxation time demonstrates the excellent rate capability of the electrolyte and the electrode, highlighting its suitability for high-power applications requiring rapid charge-discharge cycles. Such fast response times are crucial for ESSs where quick energy delivery and uptake are essential.

Fig.5.10 (H) presents the real component of capacitance (C'), which exhibits a characteristic sharp increase at frequencies below 1 Hz. This behaviour indicates the transition from surface-limited to diffusion-controlled charging processes, where the electrode approaches its maximum capacitive performance [100]. The rising trend of C' at low frequencies suggests enhanced accessibility of electrolyte ions to the internal surface area of the porous electrode at slower scan rates, enabling more complete utilization of the available surface area for charge storage [101]. Fig.5.10 (I) depicts the C'' , displaying a distinct peak that corresponds to the maximum energy dissipation frequency. This peak serves as an independent validation of the calculated relaxation time constant and represents the frequency at which resistive losses are maximized during the charge-discharge process. The appearance of this peak, combined with the behaviour observed in C' , provides strong evidence of relaxation-type behaviour characteristic of well-developed porous electrodes with efficient ion diffusion pathways [42]. The sharp rise in the real capacitance component at low frequencies, coupled with the distinct peak in the imaginary component, demonstrates the presence of well-developed porosity that facilitates efficient ion transport and storage. The maximum value of C' obtained at the lowest measurable frequency shows excellent agreement with GCD measurements, confirming the consistency between frequency-domain and time-domain analyses.

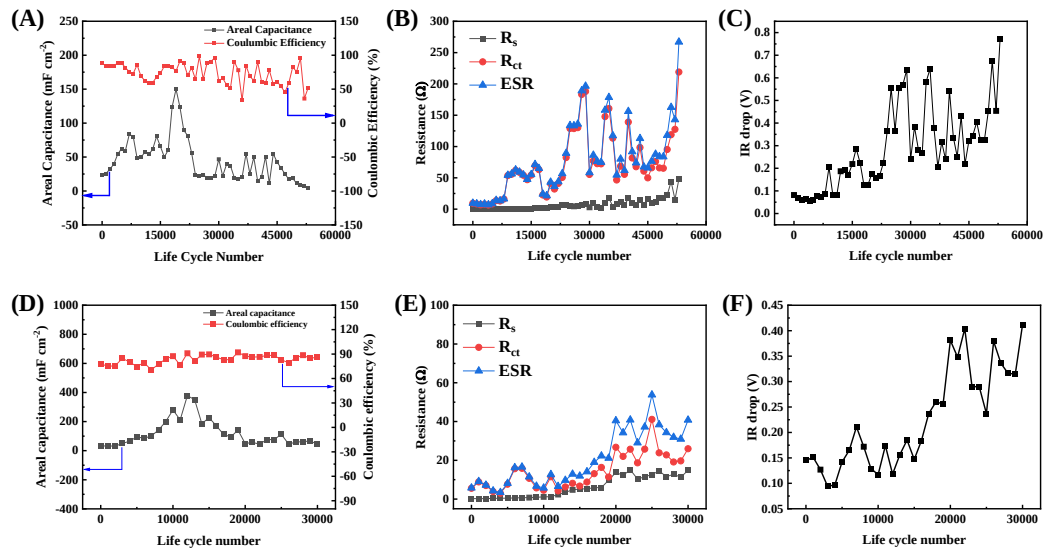


Fig.5.11 (A) Variation of areal capacitance and Coulombic efficiency with cycle number at 2 mA cm⁻²; (B) Variation of R_s , R_{ct} , and ESR with cycling at 2 mA cm⁻²; (C) Change in IR drop as a function of cycle number at 2 mA cm⁻²; (D) Variation of areal capacitance and Coulombic efficiency with cycle number at 5 mA cm⁻²; (E) Variation of R_s , R_{ct} , and ESR with cycling at 5 mA cm⁻²; (F) Change in IR drop as a function of cycle number at 5 mA cm⁻².

To assess the practical viability of the BCCHME for energy storage applications, two identical EDLCs underwent extensive GCD testing at current densities of 2 and 5 mA cm⁻². Systematic performance monitoring was conducted at 1000-cycle intervals, encompassing measurements of areal capacitance, Coulombic efficiency, equivalent circuit resistances (R_s , R_{ct} , and ESR), and voltage drop characteristics. The experimental data presented in Fig.5.11 (A) through 5.11 (F) demonstrate that the BCCHME-based EDLCs achieved remarkable operational lifespans of 53,000 cycles at 2 mA cm⁻² and 30,000 cycles at 5 mA cm⁻².

Figs.5.11 (A) and 5.11 (D) illustrate the temporal evolution of areal capacitance and Coulombic efficiency throughout the operational lifetime of EDLCs at 2 and 5 mA cm⁻², respectively. The device operated at 2 mA cm⁻² exhibited an extraordinary 635.59 % capacitance enhancement from an initial value of 23.6 mF cm⁻² to a maximum of 150 mF cm⁻² achieved after 19,000 cycles. Correspondingly, the device

cycled at 5 mA cm^{-2} displayed a substantial 1181.25 % capacitance improvement from 32 mF cm^{-2} to 378 mF cm^{-2} following 12,000 cycles. At this stage, the EDLC employed 2 mA cm^{-2} exhibited maximum energy and power densities of $17.17 \text{ } \mu\text{Wh cm}^{-2}$ and $2000 \text{ } \mu\text{W cm}^{-2}$, respectively; the EDLC cycled using 5 mA cm^{-2} exhibited maximum energy and power densities of $52.5 \text{ } \mu\text{Wh cm}^{-2}$ and $5000 \text{ } \mu\text{W cm}^{-2}$, respectively. This pronounced capacitance enhancement is fundamentally attributed to the unique electrolyte-electrode interaction mechanisms specific to the BCCHME system [102]. The borax-chitosan cross-linked network facilitates progressive electrolyte infiltration into the hierarchical porous electrode structure, enabling access to previously unutilized surface area within micropores and mesopores. This phenomenon is enhanced by the dual crosslinking mechanism of the BCCHME.

Table 5.4: Summary of capacitive performance data for EDLC employing BCCHME in GCD current density of 2 mAcm^{-2} , that performed 53,000 charge-discharge cycles.

Cycle life Number	Areal capacitance (mF cm^{-2})	Energy density ($\mu\text{Wh cm}^{-2}$)	R_s (Ω)	R_{ct} (Ω)	ESR (Ω)	IR drop (V)	Coulombic efficiency (%)
1	23.6	3.27	0.191	9.36	9.55	0.08	88.05
1000	25.6	3.55	0.28	8.31	8.59	0.06	84.21
2000	32.4	4.5	0.39	6.94	7.33	0.05	83.5
3000	39.2	5.44	0.49	7.85	8.34	0.06	83.76
4000	54	7.5	0.48	6.53	7.01	0.05	88.81
5000	62.4	8.66	0.53	8.29	8.82	0.05	88.13
6000	59.6	8.27	0.63	13.59	14.22	0.07	81.86
7000	83.6	11.61	0.48	12.98	13.46	0.07	75.17
8000	80	11.11	0.25	16.2	16.45	0.08	72.99
9000	48.4	6.72	0.63	53.6	54.23	0.2	85.81
10000	49.6	6.88	0.66	55.76	56.42	0.08	68.88
11000	57.2	7.94	0.74	62.06	62.8	0.08	62.44
12000	54	7.5	0.61	58.74	59.35	0.18	59.73
13000	61.2	8.5	0.62	54.07	54.69	0.19	59.53
14000	80.4	11.16	0.56	46.99	47.55	0.17	67.9

15000	65.6	9.11	1.01	54.25	55.26	0.21	73.21
16000	50	6.94	2.28	69.21	71.49	0.28	83.89
17000	60.4	8.38	1.97	63.11	65.08	0.22	83.88
18000	123.6	17.16	1.62	22.62	24.24	0.12	82.4
19000	150	20.83	2.07	19.36	21.43	0.12	76.53
20000	124	17.22	2.74	40.54	43.28	0.17	91.17
21000	89.2	12.38	4.08	32.147	36.22	0.15	88.14
22000	81.6	11.33	2.77	41.08	43.85	0.16	70.34
23000	56.4	7.83	6.22	50.55	56.77	0.22	81.5
24000	23.6	3.27	6.89	82.42	89.31	0.36	64.83
25000	21.6	3	4.73	128.87	133.6	0.55	98.18
26000	23.6	3.27	4.6	128.67	133.27	0.36	64.83
27000	19.6	2.72	5.8	130.12	135.92	0.55	89.09
28000	19.6	2.72	6.01	183.07	189.08	0.56	90.74
29000	22.4	3.11	8.56	187.98	196.54	0.63	96.55
30000	46.8	6.5	3.01	55.35	58.36	0.24	61.9
31000	22	3.05	9.14	77.11	86.25	0.38	66.26
32000	39.2	5.44	3.98	72.59	76.57	0.28	56.32
33000	37.2	5.16	2.53	72.32	74.85	0.26	51.66
34000	19.6	2.72	10.37	147.84	158.21	0.58	90.74
35000	18.4	2.55	17.79	160.72	178.51	0.64	77.96
36000	20	2.77	4.09	113.38	117.47	0.37	33.55
37000	54.8	7.61	7.97	46.56	54.53	0.2	84.56
38000	25.6	3.55	11.42	68.66	80.08	0.31	68.81
39000	49.6	6.88	6.31	55.53	61.84	0.23	62.62
40000	14	1.94	17.12	139.06	156.18	0.54	89.74
41000	21.2	2.94	10.16	81.64	91.8	0.33	60.91
42000	50.4	7	6.19	67.74	73.93	0.25	58.87
43000	11.2	1.55	14.55	98.39	112.94	0.43	77.77
44000	54.8	7.61	6.75	60.72	67.47	0.21	57.08
45000	42.4	5.88	15.97	49.91	65.88	0.32	60.91
46000	34	4.72	10.62	65.98	76.6	0.34	54.14
47000	25.2	3.5	11.71	76.1	87.81	0.4	45.32
48000	17.2	2.38	18.1	65.84	83.94	0.32	58.9

49000	18.8	2.61	18.45	65.29	83.74	0.32	82.45
50000	11.2	1.55	22.76	95.25	118.01	0.45	75.67
51000	8.4	1.16	43.91	118.81	162.72	0.67	95.45
52000	6.8	0.94	15.51	127.44	142.95	0.45	36.17
53000	4.8	0.66	47.96	219	266.96	0.77	52.17

Table 5.5: Summary of capacitive performance data for EDLC employing BCCHME in GCD current density of 5 mAcm⁻², that performed 30,000 charge-discharge cycles.

Life cycle number	Areal capacitance (mF cm ⁻²)	Energy density (μWh cm ⁻²)	R _s (Ω)	R _{ct} (Ω)	ESR (Ω)	IR drop (V)	Coulombic efficiency (%)
1	32	4.44	0.23	5.54	5.77	0.14	78.04
1000	33	4.58	0.24	8.84	9.08	0.15	75
2000	31	4.3	0.24	6.96	7.2	0.12	75.6
3000	50	6.94	0.39	3.86	4.25	0.09	84.74
4000	65	9.02	0.43	2.98	3.41	0.09	80.24
5000	95	13.19	0.46	7.67	8.13	0.14	74.8
6000	85	11.8	0.59	15.65	16.24	0.16	79.43
7000	101	14.02	0.71	15.87	16.58	0.21	70.62
8000	142	19.72	0.77	10.68	11.45	0.17	77.59
9000	200	27.77	0.92	5.75	6.67	0.12	84.03
10000	280	38.88	1.15	4.58	5.73	0.11	87.5
11000	212	29.44	1.2	11.5	12.7	0.17	76.53
12000	378	52.5	2.36	4.21	6.57	0.11	91.08
13000	351	48.75	3.45	6.25	9.7	0.15	81.43
14000	186	25.83	4.77	8.12	12.89	0.18	89.42
15000	227	31.52	5.2	6.71	11.91	0.14	89.72
16000	171	23.75	5.32	8.78	14.1	0.18	86.36
17000	113	15.69	5.88	13.09	18.97	0.23	83.08
18000	94	13.05	5.94	16.33	22.27	0.26	83.18
19000	142	19.72	9.73	11.38	21.11	0.25	92.2

20000	49	6.8	13.75	26.72	40.47	0.38	87.5
21000	57	7.91	12.19	22.02	34.21	0.34	86.36
22000	45	6.25	15.1	25.73	40.83	0.4	86.53
23000	76	10.55	10.34	18.67	29.01	0.29	88.37
24000	76	10.55	11.49	25.74	37.23	0.29	88.37
25000	113	15.69	12.66	41.11	53.77	0.23	83.08
26000	46	6.38	14.53	23.85	38.38	0.37	79.31
27000	58	8.05	11.54	22.77	34.31	0.33	85.29
28000	63	8.75	12.79	19.12	31.91	0.31	88.73
29000	66	9.16	11.27	19.68	30.95	0.31	84.61
30000	45	6.25	14.84	25.95	40.79	0.41	86.53

Detailed electrochemical performance metrics at 1000-cycle intervals are systematically documented in Tables 5.4 and 5.5 for the 2 mA cm^{-2} and 5 mA cm^{-2} conditions, respectively. Representative charge-discharge profiles throughout the operational lifetime are presented in Fig.5.12 (A) and 5.12 (B), while corresponding CV evolution is shown in Fig.5.12 (C) and 5.12 (D). These supplementary data reveal the progressive development of redox-like behaviour within the systems, manifesting as broad pseudocapacitive peaks in the 0-0.3 V potential range. This evolution of CV demonstrates the gradual activation of redox-active functional groups inherent to the chitosan backbone. The amino ($-\text{NH}_2$) and hydroxyl ($-\text{OH}$) groups within the chitosan structure undergo reversible electrochemical transformations that contribute additional Faradaic capacitance beyond the primary electrostatic double-layer mechanism [103]. This pseudocapacitive activation occurs through the sustained interaction between BCCHME components and electrode surfaces during extended cycling, exposing previously inactive functional sites to electrochemical processes. In the EDLC with 2 mA cm^{-2} , the Coulombic efficiency maintained moderate stability at during initial cycles, remaining consistently high until approximately 20,000 cycles before gradually declining to 52 % at end-of-life conditions. But in the EDLC employing 5 mA cm^{-2} , the Coulombic efficiency maintained exceptional stability throughout the total lifespan. This performance trajectory reflects the superior electrochemical reversibility of the BCCHME system while indicating the eventual onset of irreversible processes characteristic of long-term aging at higher current density.

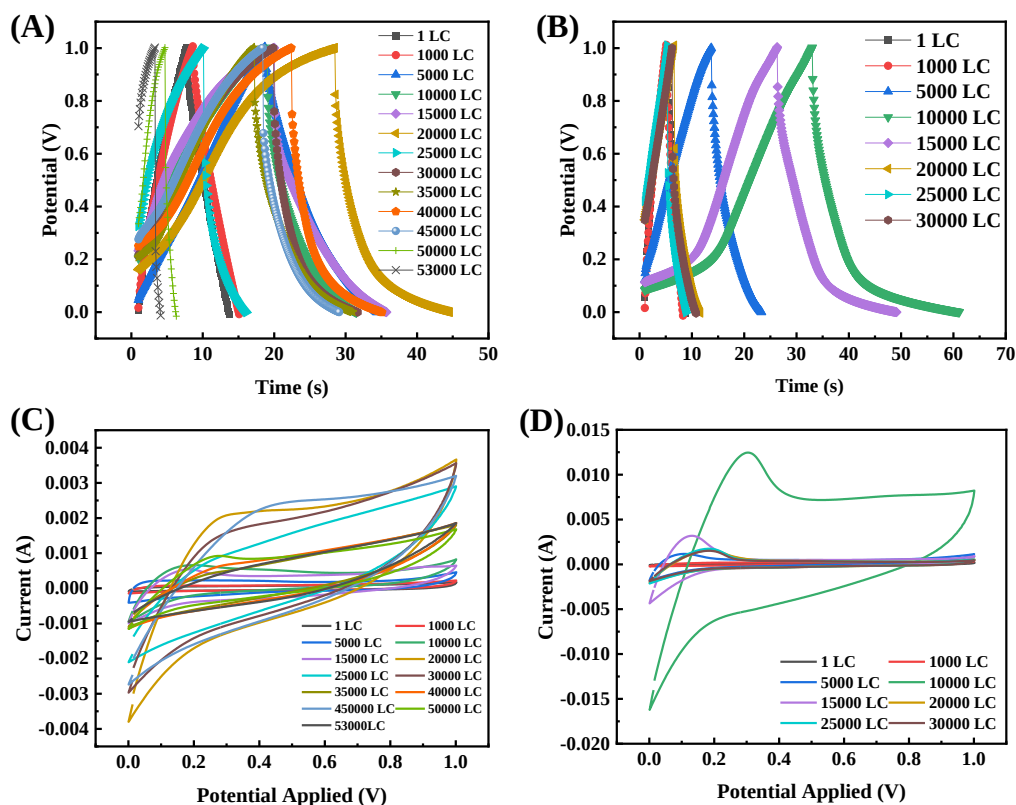


Fig.5.12 (A) Plot of GCDs during life cycle studies of the EDLC tested at 2 mA cm⁻²; (B) Plot of GCDs during life cycle studies of the EDLC tested at 5 mA cm⁻²; (C) Plot of CVs during life cycle studies of the EDLC tested at 2 mA cm⁻²; (D) Plot of CVs during life cycle studies of the EDLC tested at 5 mA cm⁻².

Fig.5.11 (B) and 5.11 (E) present the comprehensive resistance evolution profiles throughout the operational lifetime, providing critical insights into the aging mechanisms specific to the BCCHME framework. The R_s demonstrated exceptional stability, increasing modestly from 0.19 to 47.96 Ω for the 2 mA cm⁻² device, and maintaining values within 0.23 to 14.84 Ω for the 5 mA cm⁻² device throughout 30,000 cycles. The borax crosslinking agent forms a robust yet flexible network that accommodates volumetric changes during cycling without compromising structural integrity. This dual crosslinking mechanism provides optimal balance between mechanical stability and ionic transport efficiency, essential for maintaining long-term electrochemical performance. Comprehensive resistance data are tabulated in Tables 5.4 and 5.5 for EDLCs employing 2 and 5 mA cm⁻², respectively. In contrast to R_s

behaviour, the R_{ct} exhibited progressive increase in both the devices. This gradual R_{ct} evolution indicates interfacial aging processes involving the formation of resistive layers at the electrode-electrolyte interface. The ESR values also followed similar trends. Since ESR represents the summation of R_s and R_{ct} , the predominant contribution to aging arises from interfacial processes rather than bulk electrolyte degradation. This behaviour confirms that the BCCHME maintains its bulk ionic conductivity and structural integrity throughout extended cycling, with performance limitations primarily stemming from electrode-electrolyte interfacial modifications. EIS monitoring throughout the operational lifetime, presented in Fig.5.13, reveals the systematic evolution of semi-circular features in Nyquist plots. Initially, a single semicircle appears in the low-frequency region, followed by the emergence of a second semicircle at lower frequencies as cycling progresses, ultimately merging into a single feature with increased diameter reflecting the dominance of R_{ct} in the overall impedance response [104].

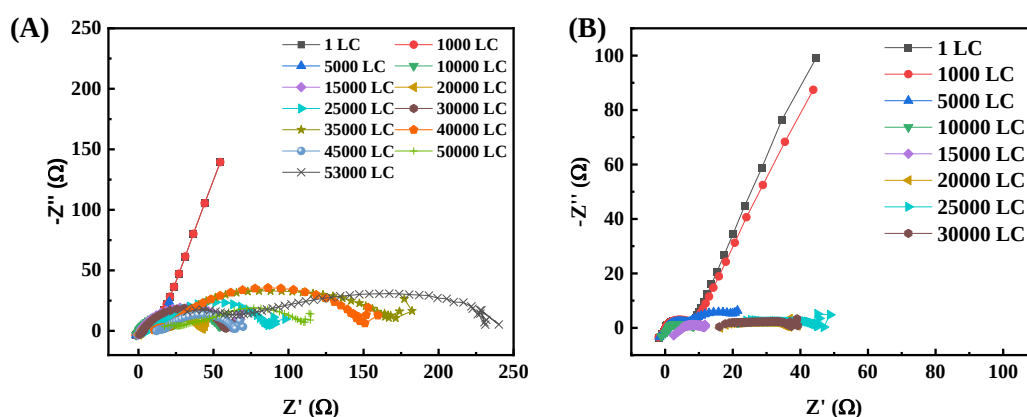


Fig.5.13 (A) Nyquist plots obtained from EIS during life cycle studies of the EDLC tested at 2 mA cm^{-2} ; (B) Nyquist plots obtained from EIS during life cycle studies of the EDLC tested at 5 mA cm^{-2} .

Fig.5.11 (C) and 5.11 (F) demonstrate the IR drop evolution throughout the operational lifetime, providing insights into the power delivery capabilities of BCCHME-based devices. Both the EDLCs exhibited a moderately low IR drop during the initial cycles and gradually increased toward the end of the cycles. The subsequent increase at end-of-life conditions directly correlates with R_{ct} evolution and reflects the progressive

degradation of power delivery capability as interfacial resistance accumulates. The extended period of stable IR drop performance demonstrates the superior power characteristics of the BCCHME system compared to conventional polymer electrolytes.

Table 5.6: Comparison of electrochemical performance metrics for various polymer-based electrolytes reported in recent literature alongside the BCCHME.

Electrolyte	Areal capacitance (mF cm ⁻²)	Energy density (μWh cm ⁻²)	Energy density (μW cm ⁻²)	Cycle life number	Ref.
Polyvinyl alcohol + H ₃ BO ₃	11.24	1.7	55.7	10,000	[105]
Polyvinylidene fluoride-[1-ethyl-3-methylimidazolium bis (trifluoromethyl sulfonyl) Imide]	203	18	660	---	[106]
PVA + NaOH	35.3	---	180	5,000	[107]
PVA + KOH	83.33	4.62	200	200	[108]
PVA + H ₂ SO ₄	5.5	1.1	---	5,000	[109]
PVA + H ₂ SO ₄ + hydroquinone	9.0	---	---	8,000	[110]
PVA + H ₂ SO ₄	40.4	5.61	250	10,000	[111]
Polyvinylpyrrolidone + NaCl	20	---	---	---	[112]
[EMIM][OTF]	1.75	0.205	110	10,000	[113]
PVA- 1-Ethyl-3-Methylimidazolium ethyl sulfate	1.94	0.14	730	5,000	[114]
PVA-1-Ethyl-3-Methylimidazolium ethyl sulfate + hydroquinone	15.1	1.54	920	5,000	[114]
Chitosan- sodium carbonate	260.4	36.16	2016	51,500	[13]
Chitosan-borax	378	52.5	5000	53,000	This work

Table 5.6 presents a comprehensive comparison of electrochemical performance metrics for various liquid, quasi-solid, and SPEs reported in recent literature alongside the BCCHME. The BCCHME-based EDLC demonstrates highly competitive performance characteristics when benchmarked against established electrolyte systems in the literature. The energy density achieved surpasses several reported biopolymer-based electrolytes and approaches values comparable to more complex multi-component polymer systems. Most notably, the exceptional cycling stability demonstrated by the BCCHME system represents a significant advancement over many reported electrolyte systems, indicating superior long-term durability and operational reliability. While liquid electrolyte systems typically demonstrate higher specific capacitance values, they often suffer from safety concerns, potential leakage issues, and limited operational voltage windows that restrict their practical applications. The ability of BCCHME to maintain stable electrochemical performance over extended cycling periods, combined with its environmentally benign composition using only two naturally derived components, positions it as a promising sustainable alternative to conventional electrolyte systems.

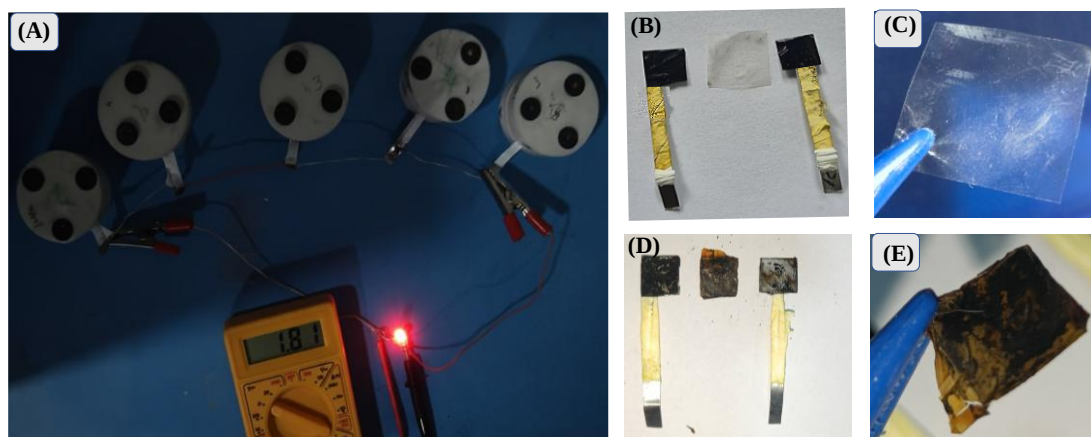


Fig.5.14 (A) Photograph of a red LED illuminated by a prototype device consisting of EDLCs connected in series; (B) Image of the BCCHME along with a pair of BPC-electrodes prior to EDLC assembly; (C) Enlarged view of the BCCHME before assembly; (D) Postmortem image of the BCCHME along with a pair of BPC-electrodes after disassembly following the EDLC cycle life test; (E) Enlarged postmortem view of the BCCHME after cycling.

The outstanding electrochemical performance and long-term cycling stability of the BCCHME-based EDLC motivated the fabrication of a working prototype to demonstrate its practical feasibility. As depicted in Fig.5.14 (A), five individual EDLC cells, each incorporating the BCCHME, were connected in series and charged at a current density of 2 mA cm^{-2} . The assembled device successfully powered a red LED, delivering a total output voltage of 1.81 V with stable illumination sustained for approximately 1.85 minutes. This proof-of-concept clearly establishes the capability of the chitosan-borax membrane to serve as a reliable solid electrolyte for real-world energy storage applications.

Fig.5.14 (B-E) depict the physical and morphological characteristics of the BCCHME before and after device testing. In Fig.5.14 (B), the BCCHME is shown alongside two BPC-coated SS electrodes, highlighting the its uniform thickness and whitish appearance, indicative of homogeneous borate-chitosan network formation. The close-up in Fig.5.14 (C) further confirms the free-standing, flexible nature of the membrane, which is essential for ensuring intimate electrode-electrolyte contact and minimising interfacial resistance in the EDLC assembly. Post-cycling disassembly in Fig.5.14 (D) revealed minor surface discoloration and detachment of the electrode coating on the surface of the BCCHME, which may be attributed to repetitive ion insertion and extraction as well as electrolyte-electrode interfacial reactions during prolonged cycling. The recovered BCCHME, as shown in Fig.5.14 (E) exhibited localized surface roughness and a faint greyish tint, possibly arising from adsorption of electrode-derived species or partial oxidative changes. Notably, despite these surface modifications, the membrane retained its structural integrity, suggesting that the borax-mediated crosslinking provide robust stability and resistance to dissolution, even under extended electrochemical operation.

5.4 Conclusions

In conclusion, BCCHMEs are promising for electrochemical device applications, offering enhanced ion transport and mechanical integrity through dual ionic and covalent crosslinking. An important finding is that borax crosslinking significantly increases dielectric constant while maintaining moderate dielectric loss, which is directly linked to capacitance and thus to charge storage behaviour. The present work demonstrates an EDLC fabricated from a biodegradable, non-toxic electrolyte with high cycling stability, energy density, and power density. FTIR analysis confirms the role of borax in generating both ionic ($-\text{NH}_3^+ \cdots \text{B}(\text{OH})_4^-$) and covalent ($\text{B}-\text{O}-\text{C}$) bonds, increasing the number of free ions available for conduction. The BCCHME achieves an ionic conductivity of $7.03 \times 10^{-4} \text{ S cm}^{-1}$, supported by AC conductivity trends, with a large ion fraction ($t_{\text{ion}} = 0.93$) contributing to the conduction process as determined from transference number measurement. LSV reveals an electrochemical stability window of 2.24 V, and CV confirms that the EDLC stores charge ions via electric double-layer formation without Faradaic reactions. The EDLC exhibits outstanding cycling stability, completing 53,000 and 30,000 cycles at 2 and 5 mA cm^{-2} , respectively, which demonstrates the practical viability of the BCCHME. At 2 mA cm^{-2} , the capacitance increases extraordinarily by 635.59 %, from an initial value of 23.6 mF cm^{-2} to a maximum of 150 mF cm^{-2} after 19,000 cycles. Similarly, at 5 mA cm^{-2} , the device shows a remarkable 1181.25 % enhancement, rising from 32 mF cm^{-2} to 378 mF cm^{-2} within 12,000 cycles. While performance retention is exceptional, prolonged cycling particularly at 2 mA cm^{-2} results in a gradual decline in Coulombic efficiency, likely due to mechanical detachment or accumulation of electrode material on the current collector. Future work will focus on fine-tuning the electrolyte formulation, testing alternative electrode compositions and binders, and improving electrode-current collector adhesion to mitigate such effects. Given its robustness under high current densities, the BCCHME platform also holds strong potential for adaptation in other energy storage and conversion systems, including batteries and fuel cells. The present results firmly establish biodegradable borax-chitosan electrolytes as viable candidates for sustainable, high-performance energy devices.

5.5 References

- [1] B.E. Conway, V. Birss, J. Wojtowicz, The role and utilization of pseudocapacitance for energy storage by supercapacitors, *J Power Sources* 66 (1997) 1–14. [https://doi.org/10.1016/S0378-7753\(96\)02474-3](https://doi.org/10.1016/S0378-7753(96)02474-3).
- [2] D.O. Akinyele, R.K. Rayudu, Review of energy storage technologies for sustainable power networks, *Sustainable Energy Technologies and Assessments* 8 (2014) 74–91. <https://doi.org/10.1016/j.seta.2014.07.004>.
- [3] K. Aanchal, V. Sharma, Urvashi, Green Battery: Sustainable Way of Energy Storage, in: *Electrocatalytic Materials*, Springer Nature Switzerland, Cham, 2024: pp. 619–636. https://doi.org/10.1007/978-3-031-65902-7_20.
- [4] R.T. Abdulwahid, S.B. Aziz, M.F.Z. Kadir, Environmentally friendly plasticized electrolyte based on chitosan (CS): Potato starch (PS) polymers for EDLC application: Steps toward the greener energy storage devices derived from biopolymers, *J Energy Storage* 67 (2023) 107636. <https://doi.org/10.1016/j.est.2023.107636>.
- [5] R.T. Abdulwahid, S.B. Aziz, M.F.Z. Kadir, Environmentally friendly plasticized electrolyte based on chitosan (CS): Potato starch (PS) polymers for EDLC application: Steps toward the greener energy storage devices derived from biopolymers, *J Energy Storage* 67 (2023) 107636. <https://doi.org/10.1016/j.est.2023.107636>.
- [6] N.A. Choudhury, P.W.C. Northrop, A.C. Crothers, S. Jain, V.R. Subramanian, Chitosan hydrogel-based electrode binder and electrolyte membrane for EDLCs: experimental studies and model validation, *J Appl Electrochem* 42 (2012) 935–943. <https://doi.org/10.1007/s10800-012-0469-2>.
- [7] L. Yan, Q. Zhang, Z. Zhang, G.-J. Li, Y. Jin, X.-L. Zhang, Y.-Y. Sun, Hydrogel electrolyte membrane with regulated pore effect to stabilize zinc anode in aqueous zinc-ion batteries, *J Memb Sci* 690 (2024) 122243. <https://doi.org/10.1016/j.memsci.2023.122243>.
- [8] G. Feuillade, Ph. Perche, Ion-conductive macromolecular gels and membranes for solid lithium cells, *J Appl Electrochem* 5 (1975) 63–69. <https://doi.org/10.1007/BF00625960>.

-
- [9] L.T. Khoon, M.-L.W. Fui, N.H. Hassan, M.S. Su'ait, R. Vedarajan, N. Matsumi, M. Bin Kassim, L.K. Shyuan, A. Ahmad, In situ sol–gel preparation of ZrO₂ in nano-composite polymer electrolyte of PVDF-HFP/MG49 for lithium-ion polymer battery, *J Solgel Sci Technol* 90 (2019) 665–675. <https://doi.org/10.1007/s10971-019-04936-1>.
- [10] S.B. Aziz, R.T. Abdulwahid, M.A. Brza, M.B. Ahmed, A.R. Murad, H.B. Tahir, R.M. Abdullah, J.M. Hadi, S.A. Hussien, Exploring the sustainable frontier by investigating structural, electrochemical and ion transport properties of potassium salt-doped PVA-based polymer electrolyte for supercapacitor application, *J Energy Storage* 71 (2023) 108175. <https://doi.org/10.1016/j.est.2023.108175>.
- [11] K.S. Ngai, S. Ramesh, K. Ramesh, J.C. Juan, A review of polymer electrolytes: fundamental, approaches and applications, *Ionics (Kiel)* 22 (2016) 1259–1279. <https://doi.org/10.1007/s11581-016-1756-4>.
- [12] C.P. Jiménez-Gómez, J.A. Cecilia, Chitosan: A Natural Biopolymer with a Wide and Varied Range of Applications, *Molecules* 25 (2020) 3981. <https://doi.org/10.3390/molecules25173981>.
- [13] D. Hazarika, D. Kamei, N. Shijoh, N.A. Choudhury, An ionically cross-linked chitosan hydrogel membrane electrolyte for long-lived electrical double layer capacitors, *J Power Sources* 629 (2025) 236037. <https://doi.org/10.1016/j.jpowsour.2024.236037>.
- [14] J. Qian, X. Wang, J. Shu, C. Su, J. Gong, Z. Xu, J. Jin, J. Shi, A Novel Complex of Chitosan–Sodium Carbonate and Its Properties, *Mar Drugs* 16 (2018) 416. <https://doi.org/10.3390/md16110416>.
- [15] N. Zhang, H. Zhang, R. Li, Y. Xing, Preparation and adsorption properties of citrate-crosslinked chitosan salt microspheres by microwave assisted method, *Int J Biol Macromol* 152 (2020) 1146–1156. <https://doi.org/10.1016/j.ijbiomac.2019.10.203>.
- [16] C. Jeyaseelan, N. Chaudhary, R. Jugade, Sulphate-Crosslinked Chitosan as an Adsorbent for the Removal of Congo Red Dye From Aqueous Solution, Air, Soil and Water Research 11 (2018). <https://doi.org/10.1177/1178622118811680>.

-
- [17] M.M. Beppu, R.S. Vieira, C.G. Aimoli, C.C. Santana, Crosslinking of chitosan membranes using glutaraldehyde: Effect on ion permeability and water absorption, *J Memb Sci* 301 (2007) 126–130. <https://doi.org/10.1016/j.memsci.2007.06.015>.
- [18] C.-Y. Yang, C.-H. Hsu, M.-L. Tsai, Effect of crosslinked condition on characteristics of chitosan/tripolyphosphate/genipin beads and their application in the selective adsorption of phytic acid from soybean whey, *Carbohydr Polym* 86 (2011) 659–665. <https://doi.org/10.1016/j.carbpol.2011.05.004>.
- [19] K. Nowacki, M. Galiński, A genipin-crosslinked chitosan hydrogel as a quasi-solid-state electrolyte for sustainable electrochemical capacitors, *Sustain Energy Fuels* 9 (2025) 3624–3634. <https://doi.org/10.1039/D5SE00223K>.
- [20] A.S. Gupta, K. Mukherjee, T.K. Giri, Borax cross-linked polysaccharide-based self-healing hydrogels for drug delivery and regenerative medicine, *J Drug Deliv Sci Technol* 105 (2025) 106592. <https://doi.org/10.1016/j.jddst.2024.106592>.
- [21] E. Vaughan, C. Santillo, A. Imbrogno, G. Gentile, A.J. Quinn, S. Kaciulis, M. Lavorgna, D. Iacopino, Direct Laser Writing of Chitosan–Borax Composites: Toward Sustainable Electrochemical Sensors, *ACS Sustain Chem Eng* 11 (2023) 13574–13583. <https://doi.org/10.1021/acssuschemeng.3c02708>.
- [22] M. Xu, W. Yue, L. Zhang, K. Chen, S. Li, Y. Xu, Q. Xu, J. Huang, H. Xie, Engineering chitosan into a recyclable and flame-resistant gel electrolyte via a dual cross-linking strategy for flexible supercapacitors, *Green Chemistry* 26 (2024) 918–926. <https://doi.org/10.1039/D3GC04263D>.
- [23] M.B. Lawrence, Influence of cross-linker concentration on the water contained within the pores of poly(vinyl alcohol)-borax hydrogels: a vibrational spectroscopic study, *Polymer Bulletin* 81 (2024) 13783–13801. <https://doi.org/10.1007/s00289-024-05364-0>.
- [24] M. Chen, J. Chen, W. Zhou, J. Xu, C.-P. Wong, High-performance flexible and self-healable quasi-solid-state zinc-ion hybrid supercapacitor based on borax-crosslinked polyvinyl alcohol/nanocellulose hydrogel electrolyte, *J Mater Chem A Mater* 7 (2019) 26524–26532. <https://doi.org/10.1039/C9TA10944G>.

-
- [25] X. Chen, N. Ji, F. Li, Y. Qin, Y. Wang, L. Xiong, Q. Sun, Dual Cross-Linked Starch–Borax Double Network Hydrogels with Tough and Self-Healing Properties, *Foods* 11 (2022) 1315. <https://doi.org/10.3390/foods11091315>.
- [26] K. Lu, X. Lan, R. Folkersma, V.S.D. Voet, K. Loos, Borax Cross-Linked Acrylamide-Grafted Starch Self-Healing Hydrogels, *Biomacromolecules* 25 (2024) 8026–8037. <https://doi.org/10.1021/acs.biomac.4c01287>.
- [27] X. Wan, Q. Xie, H. Song, C. Li, J. Wang, Borax-crosslinked hydrogel electrolyte membranes for quasi-solid state aqueous energy storage devices, *J Memb Sci* 655 (2022) 120606. <https://doi.org/10.1016/j.memsci.2022.120606>.
- [28] S. Tanpichai, F. Phoothong, A. Boonmahitthisud, Superabsorbent cellulose-based hydrogels cross-liked with borax, *Sci Rep* 12 (2022) 8920. <https://doi.org/10.1038/s41598-022-12688-2>.
- [29] B. Myrzakhmetov, A. Akhmetova, A. Bissenbay, M. Karibayev, X. Pan, Y. Wang, Z. Bakenov, A. Mentbayeva, Review: chitosan-based biopolymers for anion-exchange membrane fuel cell application, *R Soc Open Sci* 10 (2023). <https://doi.org/10.1098/rsos.230843>.
- [30] A. Shahab Marf, R. M. Abdullah, S. B. Aziz, Structural, Morphological, Electrical and Electrochemical Properties of PVA: CS-Based Proton-Conducting Polymer Blend Electrolytes, *Membranes (Basel)* 10 (2020) 71. <https://doi.org/10.3390/membranes10040071>.
- [31] S.B. Aziz, S. Al-Zangana, M.A. Brza, S.R. Saeed, R.T. Abdulwahid, M.F.Z. Kadir, Study of Dielectric Properties and Ion Transport Parameters in Chitosan-Barium Nitrate Based Solid Polymer Electrolytes, *Int J Electrochem Sci* 14 (2019) 10580–10595. <https://doi.org/10.20964/2019.12.39>.
- [32] A.K. Arof, S. Amirudin, S.Z. Yusof, I.M. Noor, A method based on impedance spectroscopy to determine transport properties of polymer electrolytes, *Phys. Chem. Chem. Phys.* 16 (2014) 1856–1867. <https://doi.org/10.1039/C3CP53830C>.
- [33] R.T. Abdulwahid, S.B. Aziz, M.F.Z. Kadir, N.M. Sadiq, N.A. Halim, M.H. Hamsan, S.R. Saeed, H.J. Woo, Biodegradable polymer membrane K⁺ ion conductor for electrochemical device application, *J Mater Sci* 57 (2022) 19902–19923. <https://doi.org/10.1007/s10853-022-07825-1>.

-
- [34] D. Kamei, N.A. Choudhury, KI-doped redox-active gelatin chemical hydrogel membrane electrolytes for solid-state electrical double layer capacitors, *Mater Today Chem* 37 (2024) 101891. <https://doi.org/10.1016/j.mtchem.2023.101891>.
- [35] Y. Hu, V. Topolkaraev, A. Hiltner, E. Baer, Measurement of water vapor transmission rate in highly permeable films, *J Appl Polym Sci* 81 (2001) 1624–1633. <https://doi.org/10.1002/app.1593>.
- [36] R. Deivanayagam, R. Shahbazian-Yassar, Electrochemical Methods and Protocols for Characterization of Ceramic and Polymer Electrolytes for Rechargeable Batteries, *Batter Supercaps* 4 (2021) 596–606. <https://doi.org/10.1002/batt.202000221>.
- [37] D. Kamei, D. Hazarika, N.A. Choudhury, Pure and KI-doped glyoxal-crosslinked gelatin hydrogel membrane electrolytes for solid-state EDLCs, *Mater Today Chem* 43 (2025) 102470. <https://doi.org/10.1016/j.mtchem.2024.102470>.
- [38] S. Yeasmin, M. Bora, B.K. Saikia, D. Mahanta, Binder mediated enhanced electrochemical capacitance in sodium silicate-graphite paint coated filter paper electrodes for all-solid-state symmetric electrochemical capacitors, *J Energy Storage* 73 (2023) 108945. <https://doi.org/10.1016/j.est.2023.108945>.
- [39] X. He, T. Zhuang, S. Ruan, X. Xia, Y. Xia, J. Zhang, H. Huang, Y. Gan, W. Zhang, An innovative poly(ionic liquid) hydrogel-based anti-freezing electrolyte with high conductivity for supercapacitor, *Chemical Engineering Journal* 466 (2023) 143209. <https://doi.org/10.1016/j.cej.2023.143209>.
- [40] A.Ch. Lazanas, M.I. Prodromidis, Electrochemical Impedance Spectroscopy—A Tutorial, *ACS Measurement Science Au* 3 (2023) 162–193. <https://doi.org/10.1021/acsmeasuresciau.2c00070>.
- [41] S. Mahmoudi-Qashqay, M.-R. Zamani-Meymian, A. Maleki, A simple method of fabrication hybrid electrodes for supercapacitors, *Sci Rep* 14 (2024) 29105. <https://doi.org/10.1038/s41598-024-80243-2>.
- [42] N. Yadav, N. Yadav, S.A. Hashmi, Ionic liquid incorporated, redox-active blend polymer electrolyte for high energy density quasi-solid-state carbon supercapacitor, *J Power Sources* 451 (2020) 227771. <https://doi.org/10.1016/j.jpowsour.2020.227771>.

-
- [43] T.U. Wani, A.H. Pandith, F.A. Sheikh, Polyelectrolytic nature of chitosan: Influence on physicochemical properties and synthesis of nanoparticles, *J Drug Deliv Sci Technol* 65 (2021) 102730. <https://doi.org/10.1016/j.jddst.2021.102730>.
- [44] I. Aranaz, A.R. Alcántara, M.C. Civera, C. Arias, B. Elorza, A. Heras Caballero, N. Acosta, Chitosan: An Overview of Its Properties and Applications, *Polymers (Basel)* 13 (2021) 3256. <https://doi.org/10.3390/polym13193256>.
- [45] A. Shekhawat, V. Gomase, A. Bambal, M. Khapre, P. Waghe, D. Saravanan, R. Jugade, Chemical functionalization of Chitosan biopolymer with diacetyl monoxime for enhanced Cr(VI) removal from aqueous media, *Int J Biol Macromol* 282 (2024) 137038. <https://doi.org/10.1016/j.ijbiomac.2024.137038>.
- [46] K. Mohan, A.R. Ganesan, P.N. Ezhilarasi, K.K. Kondamareddy, D.K. Rajan, P. Sathishkumar, J. Rajarajeswaran, L. Conterno, Green and eco-friendly approaches for the extraction of chitin and chitosan: A review, *Carbohydr Polym* 287 (2022) 119349. <https://doi.org/10.1016/j.carbpol.2022.119349>.
- [47] J. Pérez-Calderón, M.V. Santos, N. Zaritzky, Synthesis, characterization and application of cross-linked chitosan/oxalic acid hydrogels to improve azo dye (Reactive Red 195) adsorption, *React Funct Polym* 155 (2020) 104699. <https://doi.org/10.1016/j.reactfunctpolym.2020.104699>.
- [48] D. Ishikawa, A. He, Y. Xu, T. Fujii, Y. Ozaki, Evidence for two kinds of hydrogen-bonding networks in ionic solutions by 2D infrared correlation spectroscopy, *Sci Rep* 15 (2025) 16991. <https://doi.org/10.1038/s41598-025-00774-0>.
- [49] M.M. Nofal, S.B. Aziz, J.M. Hadi, R.T. Abdulwahid, E.M.A. Dannoun, A.S. Marif, S. Al-Zangana, Q. Zafar, M.A. Brza, M.F.Z. Kadir, Synthesis of Porous Proton Ion Conducting Solid Polymer Blend Electrolytes Based on PVA: CS Polymers: Structural, Morphological and Electrochemical Properties, *Materials* 13 (2020) 4890. <https://doi.org/10.3390/ma13214890>.
- [50] S.B. Aziz, O.Gh. Abdullah, D.M. Aziz, M.B. Ahmed, R.T. Abdulwahid, Energy Storage Performance of Plasticized PVA-Based Electrolyte: Electrical and Electrochemical Properties, *ACS Appl Electron Mater* 6 (2024) 7763–7780. <https://doi.org/10.1021/acsaelm.4c01040>.

-
- [51] R. Tomar, P. Srivastava, K. Strzałkowski, S. Kumar, M.Z.A. Yahya, N.A. Masmali, P.K. Singh, D. Singh, Novel approach: Simultaneous application of ionic liquid doped polymer electrolyte in supercapacitor and dye-sensitized solar cells, *Journal of Science: Advanced Materials and Devices* 9 (2024) 100729. <https://doi.org/10.1016/j.jsamd.2024.100729>.
- [52] A. Rao, S. Bhat, S. De, V. Cyriac, Improving supercapacitor performance with novel potato starch-PVA solid polymer electrolyte blend modified by sodium perchlorate-glycerol additives, *J Energy Storage* 102 (2024) 113965. <https://doi.org/10.1016/j.est.2024.113965>.
- [53] M.F. Shukur, F.M. Ibrahim, N.A. Majid, R. Ithnin, M.F.Z. Kadir, Electrical analysis of amorphous corn starch-based polymer electrolyte membranes doped with LiI, *Phys Scr* 88 (2013) 025601. <https://doi.org/10.1088/0031-8949/88/02/025601>.
- [54] S.B. Aziz, R.T. Abdulwahid, S. Al-Zangana, P.A. Mohammed, M.B. Ahmed, R.M. Abdullah, D.M. Aziz, H.J. Woo, M.F.Z. Kadir, Electrochemical studies of EDLC device with commercialized properties constructed from biodegradable plasticized PVA based electrolyte: Electrical and energy storage properties, *J Energy Storage* 123 (2025) 116765. <https://doi.org/10.1016/j.est.2025.116765>.
- [55] N.I. Harun, R.M. Ali, A.M.M. Ali, M.Z.A. Yahya, Conductivity studies on cellulose acetate–ammonium tetrafluoroborate based polymer electrolytes, *Materials Research Innovations* 15 (2011) s168–s172. <https://doi.org/10.1179/143307511X13031890748858>.
- [56] M.Z.A. Yahya, A.K. Arof, Conductivity and X-ray photoelectron studies on lithium acetate doped chitosan films, *Carbohydr Polym* 55 (2004) 95–100. <https://doi.org/10.1016/j.carbpol.2003.08.018>.
- [57] S.B. Aziz, M.A. Brza, M.F.Z. Kadir, M.H. Hamsan, Z.H.Z. Abidin, D.A. Tahir, O.Gh. Abdullah, Ion in Chitosan Based Solid Electrolyte, *Int J Electrochem Sci* 14 (2019) 5521–5534. <https://doi.org/10.20964/2019.06.13>.
- [58] S.B. Aziz, M.H. Hamsan, M.F.Z. Kadir, W.O. Karim, R.M. Abdullah, Development of Polymer Blend Electrolyte Membranes Based on Chitosan: Dextran with High Ion Transport Properties for EDLC Application, *Int J Mol Sci* 20 (2019) 3369. <https://doi.org/10.3390/ijms20133369>.

-
- [59] H. Xu, L. Huang, W. Li, S. Gu, D. Zeng, Y. Zhang, Y. Sun, H. Cheng, Shielding the electrostatic attraction by design of zwitterionic single ion conducting polymer electrolyte with high dielectric constant, *J Memb Sci* 651 (2022) 120452. <https://doi.org/10.1016/j.memsci.2022.120452>.
- [60] S.B. Aziz, S.M. Mamand, The Study of Dielectric Properties and Conductivity Relaxation of Ion Conducting Chitosan:NaTf Based Solid Electrolyte, *Int J Electrochem Sci* 13 (2018) 10274–10288. <https://doi.org/10.20964/2018.11.05>.
- [61] S.B. Aziz, S.M. Mamand, The Study of Dielectric Properties and Conductivity Relaxation of Ion Conducting Chitosan:NaTf Based Solid Electrolyte, *Int J Electrochem Sci* 13 (2018) 10274–10288. <https://doi.org/10.20964/2018.11.05>.
- [62] S. Majumdar, R. Ray, Ionic conduction and charge carrier relaxation in chitosan acetate based solid biopolymer electrolyte embedded with LiClO₄, *Journal of Polymer Research* 28 (2021) 157. <https://doi.org/10.1007/s10965-021-02509-x>.
- [63] N.A. Choudhury, J. Ma, Y. Sahai, R.G. Buchheit, High performance polymer chemical hydrogel-based electrode binder materials for direct borohydride fuel cells, *J Power Sources* 196 (2011) 5817–5822. <https://doi.org/10.1016/j.jpowsour.2011.03.004>.
- [64] Y. Xiao, Y. Xiang, R. Xiu, S. Lu, Development of cesium phosphotungstate salt and chitosan composite membrane for direct methanol fuel cells, *Carbohydr Polym* 98 (2013) 233–240. <https://doi.org/10.1016/j.carbpol.2013.06.017>.
- [65] D.M. Correia, M.A. Gámiz-González, G. Botelho, A. Vidaurre, J.L. Gomez Ribelles, S. Lanceros-Mendez, V. Sencadas, Effect of neutralization and cross-linking on the thermal degradation of chitosan electrospun membranes, *J Therm Anal Calorim* 117 (2014) 123–130. <https://doi.org/10.1007/s10973-014-3707-5>.
- [66] T. Mitra, G. Sailakshmi, A. Gnanamani, A.B. Mandal, Studies on Cross-linking of succinic acid with chitosan/collagen, *Materials Research* 16 (2013) 755–765. <https://doi.org/10.1590/S1516-14392013005000059>.
- [67] J. Ma, Y. Sahai, R.G. Buchheit, Evaluation of multivalent phosphate cross-linked chitosan biopolymer membrane for direct borohydride fuel cells, *J Power Sources* 202 (2012) 18–27. <https://doi.org/10.1016/j.jpowsour.2011.11.003>.
- [68] M.E.S. Ahmed, M.I. Mohamed, H.Y. Ahmed, M.M. Elaasser, N.G. Kandile, Fabrication and characterization of unique sustain modified chitosan

- nanoparticles for biomedical applications, *Sci Rep* 14 (2024). <https://doi.org/10.1038/s41598-024-64017-4>.
- [69] C. Santillo, Y. Wang, G.G. Buonocore, G. Gentile, L. Verdolotti, S. Kaciulis, H. Xia, M. Lavorgna, Hybrid Graphenene Oxide/Cellulose Nanofillers to Enhance Mechanical and Barrier Properties of Chitosan-Based Composites, *Front Chem* 10 (2022). <https://doi.org/10.3389/fchem.2022.926364>.
- [70] F. Ferrero, M. Periolatto, Antimicrobial finish of textiles by chitosan UV-curing, *J Nanosci Nanotechnol* 12 (2012) 4803–4810. <https://doi.org/10.1166/jnn.2012.4902>.
- [71] P.G. Gan, S.T. Sam, A.M. Faiq, Tensile Properties and Crystallinity of Crosslinked Nanocrystalline Cellulose/Chitosan Composite, in: *IOP Conf Ser Mater Sci Eng*, Institute of Physics Publishing, 2018. <https://doi.org/10.1088/1757-899X/429/1/012042>.
- [72] S.N.S. Begum, R. Pandian, V.K. Aswal, R.P. Ramasamy, Chitosan - Gold - Lithium nanocomposites as solid polymer electrolyte, *J Nanosci Nanotechnol* 14 (2014) 5761–5773. <https://doi.org/10.1166/jnn.2014.8994>.
- [73] K. Nowacki, M. Galiński, I. Stępnia, Synthesis and characterization of modified chitosan membranes for applications in electrochemical capacitor, *Electrochim Acta* 320 (2019). <https://doi.org/10.1016/j.electacta.2019.134632>.
- [74] S.U. Rahman, S. Bilal, A.U.H. Ali Shah, Synthesis and characterization of polyaniline-chitosan patches with enhanced stability in physiological conditions, *Polymers (Basel)* 12 (2020) 1–13. <https://doi.org/10.3390/polym12122870>.
- [75] D. Baskar, R. Balu, S.S. Kumar, Mineralization of pristine chitosan film through biomimetic process, *Int J Biol Macromol* 49 (2011) 385–389. <https://doi.org/10.1016/j.ijbiomac.2011.05.021>.
- [76] A.S.F.M. Asnawi, S.B. Aziz, I. Brevik, M.A. Brza, Y.M. Yusof, S.M. Alshehri, T. Ahamad, M.F.Z. Kadir, The Study of Plasticized Sodium Ion Conducting Polymer Blend Electrolyte Membranes Based on Chitosan/Dextran Biopolymers: Ion Transport, Structural, Morphological and Potential Stability, *Polymers (Basel)* 13 (2021) 383. <https://doi.org/10.3390/polym13030383>.
- [77] V. Cyriac, Ismayil, K. Mishra, Y.N. Sudhakar, Z.E. Rojudi, S.P. Masti, I.M. Noor, Suitability of NaI complexed sodium alginate-polyvinyl alcohol

- biodegradable polymer blend electrolytes for electrochemical device applications: Insights into dielectric relaxations and scaling studies, *Solid State Ion* 411 (2024) 116578. <https://doi.org/10.1016/j.ssi.2024.116578>.
- [78] S. Valizadeh, M. Naseri, S. Babaei, S.M.H. Hosseini, A. Imani, Development of bioactive composite films from chitosan and carboxymethyl cellulose using glutaraldehyde, cinnamon essential oil and oleic acid, *Int J Biol Macromol* 134 (2019) 604–612. <https://doi.org/10.1016/j.ijbiomac.2019.05.071>.
- [79] F. Jahan, R.D. Mathad, S. Farheen, Effect of mechanical strength on chitosan-pva blend through ionic crosslinking for food packaging application, *Mater Today Proc* 3 (2016) 3689–3696. <https://doi.org/10.1016/j.matpr.2016.11.014>.
- [80] J. Ma, Y. Sahai, R.G. Buchheit, Evaluation of multivalent phosphate cross-linked chitosan biopolymer membrane for direct borohydride fuel cells, *J Power Sources* 202 (2012) 18–27. <https://doi.org/10.1016/j.jpowsour.2011.11.003>.
- [81] K.A. Francis, C.-W. Liew, S. Ramesh, K. Ramesh, S. Ramesh, Ionic liquid enhanced magnesium-based polymer electrolytes for electrical double-layer capacitors, *Ionics (Kiel)* 22 (2016) 919–925. <https://doi.org/10.1007/s11581-015-1619-4>.
- [82] S.B. Aziz, E.M.A. Dannoun, M.H. Hamsan, R.T. Abdulwahid, K. Mishra, M.M. Nofal, M.F.Z. Kadir, Improving EDLC Device Performance Constructed from Plasticized Magnesium Ion Conducting Chitosan Based Polymer Electrolytes via Metal Complex Dispersion, *Membranes (Basel)* 11 (2021) 289. <https://doi.org/10.3390/membranes11040289>.
- [83] S.B. Aziz, A.S.F.M. Asnawi, P.A. Mohammed, R.T. Abdulwahid, Y.M. Yusof, R.M. Abdullah, M.F.Z. Kadir, Impedance, circuit simulation, transport properties and energy storage behavior of plasticized lithium ion conducting chitosan based polymer electrolytes, *Polym Test* 101 (2021) 107286. <https://doi.org/10.1016/j.polymertesting.2021.107286>.
- [84] S. Shiraishi, Electric Double Layer Capacitors, in: *Carbon Alloys*, Elsevier, 2003: pp. 447–457. <https://doi.org/10.1016/B978-008044163-4/50027-9>.
- [85] S.B. Aziz, M.A. Brza, K. Mishra, M.H. Hamsan, W.O. Karim, R.M. Abdullah, M.F.Z. Kadir, R.T. Abdulwahid, Fabrication of high performance energy storage EDLC device from proton conducting methylcellulose: dextran polymer blend

- electrolytes, *Journal of Materials Research and Technology* 9 (2020) 1137–1150. <https://doi.org/10.1016/j.jmrt.2019.11.042>.
- [86] R. Kant, M.B. Singh, Theory of the Electrochemical Impedance of Mesoporous Electrodes Embedded with Heterogeneous Micropores, *The Journal of Physical Chemistry C* 121 (2017) 7164–7174. <https://doi.org/10.1021/acs.jpcc.7b01287>.
- [87] X. Zhang, M. Kar, T.C. Mendes, Y. Wu, D.R. MacFarlane, Supported Ionic Liquid Gel Membrane Electrolytes for Flexible Supercapacitors, *Adv Energy Mater* 8 (2018). <https://doi.org/10.1002/aenm.201702702>.
- [88] C.-W. Liew, S. Ramesh, Electrical, structural, thermal and electrochemical properties of corn starch-based biopolymer electrolytes, *Carbohydr Polym* 124 (2015) 222–228. <https://doi.org/10.1016/j.carbpol.2015.02.024>.
- [89] R.D. Oliveira, C.S. Santos, J.R. Garcia, M. Vidotti, L.F. Marchesi, C.A. Pessoa, IR drop studies of poly(aniline)-based modified electrodes, *Journal of Electroanalytical Chemistry* 878 (2020) 114662. <https://doi.org/10.1016/j.jelechem.2020.114662>.
- [90] V.D. Patake, T.T. Ghogare, A.D. Gulbake, C.D. Lokhande, The electrochemical performance of electrodeposited chitosan bio-nanopolymer in non-aqueous electrolyte: a new anodic material for supercapacitor, *SN Appl Sci* 1 (2019) 1063. <https://doi.org/10.1007/s42452-019-1054-7>.
- [91] C. Portet, P.L. Taberna, P. Simon, C. Laberty-Robert, Modification of Al current collector surface by sol–gel deposit for carbon–carbon supercapacitor applications, *Electrochim Acta* 49 (2004) 905–912. <https://doi.org/10.1016/j.electacta.2003.09.043>.
- [92] S.H. Kwon, E. Lee, B.-S. Kim, S.-G. Kim, B.-J. Lee, M.-S. Kim, J.C. Jung, Preparation of activated carbon aerogel and its application to electrode material for electric double layer capacitor in organic electrolyte: Effect of activation temperature, *Korean Journal of Chemical Engineering* 32 (2015) 248–254. <https://doi.org/10.1007/s11814-014-0215-z>.
- [93] M.E. Orazem, B. Tribollet, *Electrochemical Impedance Spectroscopy*, Wiley, 2008. <https://doi.org/10.1002/9780470381588>.

-
- [94] N. Mahato, T.V.M. Sreekanth, K. Yoo, J. Kim, Semi-Polycrystalline Polyaniline-Activated Carbon Composite for Supercapacitor Application, *Molecules* 28 (2023) 1520. <https://doi.org/10.3390/molecules28041520>.
- [95] U. Mahanta, D. Kundu, R.P. Venkatesh, S. Sujatha, S.A. Ilangoan, T. Banerjee, Electrochemical Performance and Molecular Structure of Diluted 1-Alkyl-3-methylimidazolium Tetrafluoroborate Ionic Liquids and Their Mixture as Electrolytes for Double-Layer Capacitors: An Integrated Approach by Electrochemical Characterization and Molecular Dynamics Simulation, *Ind Eng Chem Res* 58 (2019) 22741–22753. <https://doi.org/10.1021/acs.iecr.9b04350>.
- [96] R. Kötz, M. Carlen, Principles and applications of electrochemical capacitors, *Electrochim Acta* 45 (2000) 2483–2498. [https://doi.org/10.1016/S0013-4686\(00\)00354-6](https://doi.org/10.1016/S0013-4686(00)00354-6).
- [97] S. Mahmoudi-Qashqay, M.-R. Zamani-Meymian, A. Maleki, A simple method of fabrication hybrid electrodes for supercapacitors, *Sci Rep* 14 (2024) 29105. <https://doi.org/10.1038/s41598-024-80243-2>.
- [98] N.O. Laschuk, E.B. Easton, O. V. Zenkina, Reducing the resistance for the use of electrochemical impedance spectroscopy analysis in materials chemistry, *RSC Adv* 11 (2021) 27925–27936. <https://doi.org/10.1039/D1RA03785D>.
- [99] L. Manjakkal, A. Pullanchiyodan, N. Yogeswaran, E.S. Hosseini, R. Dahiya, A Wearable Supercapacitor Based on Conductive PEDOT:PSS-Coated Cloth and a Sweat Electrolyte, *Advanced Materials* 32 (2020). <https://doi.org/10.1002/adma.201907254>.
- [100] C. Kong, Z. Du, J. Song, J. Zhang, S.T. Rahman, S. Wang, G. Wang, Hierarchical porous graphene nanosheets derived from moso bamboo with superior supercapacitor performance, *J Power Sources* 607 (2024) 234574. <https://doi.org/10.1016/j.jpowsour.2024.234574>.
- [101] H. Soltani, H. Bahiraei, S. Ghasemi, M. Hashempour, Rate capability and electrolyte concentration: Tuning MnO₂ supercapacitor electrodes through electrodeposition parameters, *Heliyon* 11 (2025) e41427. <https://doi.org/10.1016/j.heliyon.2024.e41427>.
- [102] J.A. Lee, M.K. Shin, S.H. Kim, H.U. Cho, G.M. Spinks, G.G. Wallace, M.D. Lima, X. Lepró, M.E. Kozlov, R.H. Baughman, S.J. Kim, Ultrafast charge and

- discharge bistructured yarn supercapacitors for textiles and microdevices, *Nat Commun* 4 (2013) 1970. <https://doi.org/10.1038/ncomms2970>.
- [103] C. Jiang, M. Gao, S. Zhang, L. Huang, S. Yu, Z. Song, Q. Wu, Chitosan/graphene oxide hybrid hydrogel electrode with porous network boosting ultrahigh energy density flexible supercapacitor, *Int J Biol Macromol* 225 (2023) 1437–1448. <https://doi.org/10.1016/j.ijbiomac.2022.11.201>.
- [104] P. Forouzandeh, V. Kumaravel, S.C. Pillai, Electrode Materials for Supercapacitors: A Review of Recent Advances, *Catalysts* 10 (2020) 969. <https://doi.org/10.3390/catal10090969>.
- [105] A. Imbrogno, J. Islam, C. Santillo, R. Castaldo, L. Sygellou, C. Larrigy, R. Murray, E. Vaughan, Md.K. Hoque, A.J. Quinn, D. Iacopino, Laser-Induced Graphene Supercapacitors by Direct Laser Writing of Cork Natural Substrates, *ACS Appl Electron Mater* 4 (2022) 1541–1551. <https://doi.org/10.1021/acsaelm.1c01202>.
- [106] G. Bhattacharya, S.J. Fishlock, S.S. Roy, J. McLaughlin, Development of Waste Red-Mud Nanoparticle Decorated Laser-Induced Graphene Flexible Supercapacitor, *ECS Meeting Abstracts* MA2020-01 (2020) 601–601. <https://doi.org/10.1149/MA2020-015601mtgabs>.
- [107] J. Zhao, L. Gao, Z. Wang, S. Wang, R. Xu, Boosting the performance of flexible in-plane micro-supercapacitors by engineering MoS₂ nanoparticles embedded in laser-induced graphene, *J Alloys Compd* 887 (2021) 161514. <https://doi.org/10.1016/j.jallcom.2021.161514>.
- [108] H. Awasthi, H. Renuka, A.K. Srivastava, S. Goel, Laser-induced graphene-based flexible interdigital electrode realizing micro supercapacitor sustainable in different temperatures, *Energy Storage* 5 (2023). <https://doi.org/10.1002/est2.405>.
- [109] J. Lee, J. Jang, H. Zhou, Y. Lee, J. In, Densified Laser-Induced Graphene for Flexible Microsupercapacitors, *Energies (Basel)* 13 (2020) 6567. <https://doi.org/10.3390/en13246567>.
- [110] Z. Peng, J. Lin, R. Ye, E.L.G. Samuel, J.M. Tour, Flexible and Stackable Laser-Induced Graphene Supercapacitors, *ACS Appl Mater Interfaces* 7 (2015) 3414–3419. <https://doi.org/10.1021/am509065d>.

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- [111] M. Khandelwal, C. Van Tran, J. Lee, J. Bin In, Nitrogen and boron co-doped densified laser-induced graphene for supercapacitor applications, *Chemical Engineering Journal* 428 (2022) 131119. <https://doi.org/10.1016/j.cej.2021.131119>.
- [112] M. Reina, A. Scalia, G. Auxilia, M. Fontana, F. Bella, S. Ferrero, A. Lamberti, Boosting Electric Double Layer Capacitance in Laser-Induced Graphene-Based Supercapacitors, *Adv Sustain Syst* 6 (2022). <https://doi.org/10.1002/adsu.202100228>.
- [113] A. Ray, J. Roth, B. Saruhan, Laser-Induced Interdigital Structured Graphene Electrodes Based Flexible Micro-Supercapacitor for Efficient Peak Energy Storage, *Molecules* 27 (2022) 329. <https://doi.org/10.3390/molecules27010329>.
- [114] A. Rao, S. Bhat, S. De, V. Cyriac, A.R. S, Study of [EMIM] [EtSO₄] ionic liquid-based gel polymer electrolyte mediated with hydroquinone redox additive for flexible supercapacitors, *J Energy Storage* 68 (2023) 107716. <https://doi.org/10.1016/j.est.2023.107716>.

CHAPTER 6

Conclusions and future scope

This chapter provides a comprehensive summary and final conclusions of the thesis. It also outlines potential directions for future research and further investigations.

6.1 Summary of key findings

Chapter 1 presented the global energy crisis and highlighted the critical importance of advanced ESSs for enabling a sustainable energy transition. The chapter established that while renewable energy sources like solar and wind offer abundant clean energy, their intermittent nature necessitates robust energy storage solutions to balance supply and demand fluctuations. It provided a comprehensive overview of various electrochemical energy storage technologies, including conventional batteries (lead-acid, Ni-Cd, NiMH, Li-ion), MABs, and RFBs, emphasizing their respective advantages and limitations in the energy-power density trade-off represented by the Ragone plot.

The chapter particularly emphasized the advantages of electrochemical capacitors, specifically EDLCs, for high power applications due to their fast charge-discharge capabilities, exceptional cycle life ($>10^6$ cycles), and high power density. The fundamental charge storage mechanism in EDLCs was explained through the evolution of double-layer models from Helmholtz to Stern to the modern BSK framework. The role of key EDLC components, electrodes, electrolytes, separators, and current collectors, was thoroughly discussed, with special focus on the critical importance of electrolyte selection in determining device performance, safety, and operational voltage window. Among the various electrolyte types, the chapter explored the emergence and advantages of SSEs, particularly biopolymer-based hydrogel electrolytes, for their enhanced safety, flexibility, and environmental sustainability. Chitosan emerged as a particularly promising biopolymer matrix due to its biocompatibility, biodegradability, cationic nature, and film-forming capability. The chapter detailed various hydrogel preparation strategies, with special emphasis on ionic crosslinking as an eco-friendly, tunable, and highly effective approach using multivalent anions such as carbonate, sulfate, phosphate, and citrate ions.

A comprehensive literature survey revealed significant research gaps in the systematic exploration of ICCHs for EDLC applications, particularly using environmentally benign crosslinkers like sodium carbonate. The identified limitations of existing synthetic polymer-based systems and toxic chemical crosslinkers shaped the

motivation and objectives of this study toward developing sustainable, cost-effective, and high-performance biopolymer electrolytes.

Chapter 2 systematically investigated ICCHMEs using sodium carbonate as the crosslinker. The synthesis process successfully addressed the challenge of CO₂ bubble formation during crosslinking through meticulous optimization, resulting in transparent, colorless, and mechanically robust flexible films with thickness of approximately 60 μm . The unique porous structure formed by CO₂ evolution during crosslinking was confirmed through FE-SEM analysis and was found to enhance ion transport pathways.

Comprehensive physicochemical characterization revealed excellent material properties: WU of 226 %, DR of 18.24 % after 6 hours of boiling, and WVTR of 60 g m⁻² h⁻¹. Mechanical testing demonstrated significant improvement in properties compared to UCM, with tensile strength increasing from 30.51 to 53.29 MPa and elongation at break improving from 6.48 % to 11.13 %. XRD analysis showed reduced crystallinity from 19.50 % to 15.02 %, indicating enhanced amorphous character favorable for ionic conductivity. The optimized ICCHME with 0.5 M Na₂CO₃ exhibited remarkable ionic conductivity of 7.89 mS cm⁻¹ with predominantly anionic charge transport and an electrochemical stability window of 0-2.32 V. Ion transport parameter analysis revealed diffusion coefficient of $8.36 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$, ion mobility of $3.24 \times 10^{-5} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$, and ion number density of $1.51 \times 10^{21} \text{ m}^{-3}$, confirming efficient ionic transport within the hydrogel matrix.

EDLCs fabricated using ICCHMEs as both electrolyte and separator with BPC electrodes demonstrated exceptional electrochemical performance. The devices achieved peak areal capacitance of 260.40 mF cm⁻² at 2 mA cm⁻², energy density of 36.17 $\mu\text{Wh cm}^{-2}$, and power density of 2000 $\mu\text{W cm}^{-2}$. Most remarkably, the EDLCs exhibited unprecedented cycle life performance of 51,500 cycles at 2 mA cm⁻² and 33,000 cycles at 5 mA cm⁻², representing some of the longest cycle lives reported for biopolymer-based hydrogel electrolyte systems.

The superior cycling stability was attributed to the constant and very low R_s throughout the entire cycle life, indicating excellent electrolyte stability and minimal water evaporation due to chitosan's hydrophilic nature. Postmortem analysis confirmed structural integrity of the ICCHME after extensive cycling. Finally, a prototype device comprising five EDLCs connected in series successfully powered a red LED bulb for 1.83 minutes, demonstrating the practical viability of these sustainable ESSs.

Chapter 3 presented GCCHMEs synthesized using Na_2CO_3 as the ionic crosslinker, with FTIR confirming effective ionic bonding between chitosan NH_3^+ groups and CO_3^{2-} ions. The gradient crosslinking approach eliminated the need for complex bubble removal optimization required in isotropic crosslinking. WU decreased significantly from 112 to 79 % with increasing Na_2CO_3 concentration from 0.5 M to 3 M, while DR ranged from 16.74 to 11.17 %. Ionic conductivity was highest at 0.5M Na_2CO_3 concentration, achieving $5.41 \times 10^{-4} \text{ S cm}^{-1}$, which decreased to $1.54 \times 10^{-4} \text{ S cm}^{-1}$ at 3M due to denser cross-linked network formation. Mechanical properties showed enhanced tensile strength from 41.22 to 44.34 MPa with increasing crosslinker concentration, though elongation decreased from 8.53 to 7.71 %. Breakdown voltage remained stable across all concentrations.

EDLCs fabricated with GCCHMEs and BPC electrodes demonstrated excellent electrochemical performance. The optimal GCCHME-0.5M achieved an initial areal capacitance of 33.6 mF cm^{-2} at 0.5 mA cm^{-2} , reaching a peak value of 299.4 mF cm^{-2} at 11,000 cycles, while GCCHME-3M showed lower performance with 181 mF cm^{-2} peak capacitance. Energy density values were $41.58 \text{ } \mu\text{Wh cm}^{-2}$ for GCCHME-0.5M and $25.14 \text{ } \mu\text{Wh cm}^{-2}$ for GCCHME-3M, with consistent power density of $1000 \text{ } \mu\text{W cm}^{-2}$ for both systems. Remarkably, both EDLCs sustained excellent cycling stability with GCCHME-0.5M achieving 57,000 charge-discharge cycles and GCCHME-3M completing 26,000 cycles at 1 mA cm^{-2} . Practical application was demonstrated by powering a red LED for 95 seconds using five EDLCs connected in series.

When compared to the findings in **Chapter 2**, it is evident that both isotropic and gradient Na_2CO_3 cross-linked chitosan hydrogels exhibited similar trends in

optimization, but with distinct performance characteristics. Electrolyte prepared via isotropic crosslinking approach used in **Chapter 2** exhibited superior ionic conductivity compared to gradient approach used in **Chapter 3**, attributed to the formation of internal hydrogel voids from CO₂ bubble evolution during bulk crosslinking. However, gradient crosslinking offered notable advantages including simplified synthesis without bubble removal requirements, while achieving comparable or superior cycle lives. The structural differences were crucial: ICCHMEs possessed interconnected void networks that enhanced ion transport but required complex processing, whereas GCCHMEs featured denser, more compact structures with surface-dominated crosslinking that facilitated easier fabrication. This suggests that gradient crosslinking represents a practical advancement toward scalable, environmentally friendly hydrogel electrolyte manufacturing, while isotropic crosslinking provides superior electrochemical properties through optimized internal architecture. Together, these chapters demonstrate how crosslinking strategy significantly influences both the processing complexity and functional properties of chitosan-based hydrogel electrolytes for supercapacitor applications.

Chapter 4 presented the development of OCCHMEs for solid-state EDLCs. The chapter detailed the green synthesis of OCCHMEs via ionic crosslinking of chitosan with potassium oxalate, optimized at 0.5 M oxalate concentration. Physicochemical characterizations showed WU of 208 %, a DR of 17.8 %, and a WVTR of 29.1 g m⁻² h⁻¹. FTIR and XRD analysis confirmed successful ionic crosslinking and a reduced crystallinity of 10.2 %, while FE-SEM and EDX demonstrated a homogeneous, compact morphology with 14.2 wt % K incorporation. Dielectric studies and EIS revealed a high ionic conductivity of 4.84 mS cm⁻¹, an ionic transference number of 0.92, and a breakdown voltage of 2.10 V. Ion transport parameters ($D = 5.09 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$; $\mu = 1.98 \times 10^{-5} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$; $n = 1.53 \times 10^{23} \text{ m}^{-3}$) confirmed efficient ion mobility. Mechanical testing indicated a tensile strength of 55.0 MPa and Young's modulus of 982.9 MPa. EDLC devices with OCCHMEs achieved an areal capacitance of 300.8 mF cm⁻² at 2 mA cm⁻², energy density of 42.11 μWh cm⁻², and power density of 2.02 mW cm⁻². Remarkably, cycle life extended to 46,000 and 32,000 cycles at 2 and 5 mA cm⁻², respectively, with minimal resistance growth (R_s up to 28.5 Ω; ESR to 142.1 Ω).

A five-cell prototype powered a red LED for 1.76 minutes, demonstrating practical viability. The use of an oxalate crosslinker in the **Chapter 4**, instead of the carbonate one from **Chapters 2** and **Chapter 3**, fundamentally alters the hydrogel network architecture of chitosan. This change directly impacts its ion-transport behavior. Oxalate dianions ($\text{C}_2\text{O}_4^{2-}$), with two carbons and four oxygens, form denser, bidentate ionic bridges with protonated $-\text{NH}_3^+$ sites on chitosan, whereas carbonate (CO_3^{2-}) provides planar, monodentate linkages. This tighter oxalate network reduces crystallinity and slightly lowers WU but yields a mechanically stiffer membrane. On the cation side, K^+ being larger and less strongly hydrated than Na^+ diffuses more readily through the oxalate cross-linked matrix, increasing the cationic transference number, while Na^+ in the carbonate cross-linked system remains more immobilized. These combined effects give oxalate-based hydrogels enhanced mechanical strength and selective anion conduction compared to carbonate-based hydrogel systems.

Chapter 5 introduced BCCHMEs fabricated via dual ionic and covalent crosslinking with borate ions. The optimized 0.5 M borax BCCHME exhibited WU of 182 %, a DR of 14.7 %, and WVTR of $20.4 \text{ g m}^{-2} \text{ h}^{-1}$. FTIR confirmed both $\text{NH}_3^+ \cdots \text{B}(\text{OH})_4^-$ ionic bonds and B–O–C ester linkages; XRD revealed reduced crystallinity of 16.6 %. FE-SEM and EDX showed a dense morphology with 13 wt% B and 21 wt% Na. Dielectric analysis and EIS yielded an ionic conductivity of $7.03 \times 10^{-4} \text{ S cm}^{-1}$, $t_{\text{ion}} = 0.93$, $t_{\text{cation}} = 0.08$, and breakdown voltage of 2.24 V. Ion transport studies gave $D = 4.19 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, $\mu = 1.6 \times 10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$, and $n = 1.05 \times 10^{31} \text{ m}^{-3}$. Mechanical testing showed tensile strength of 45.9 MPa and Young's modulus of 1465.5 MPa. EDLCs with BCCHME delivered initial areal capacitances of 23.6 and 32 mF cm^{-2} at 2 and 5 mA cm^{-2} , increasing to maxima of 150 and 378 mF cm^{-2} after 19,000 and 12,000 cycles, respectively. Energy densities reached 17.2 $\mu\text{Wh cm}^{-2}$ at 2 mA cm^{-2} and 52.5 $\mu\text{Wh cm}^{-2}$ at 5 mA cm^{-2} . Devices sustained 53,000 and 30,000 cycles, with R_s stable below 48 Ω and R_{ct} below 219 Ω . A five-cell series prototype powered a red LED for 1.85 minutes.

In comparing with the **Chapter 2**, **Chapter 3** and **Chapter 4**, a clear progression in network chemistry, mechanical robustness, and electrochemical performance emerges.

The carbonate cross-linked membrane from **Chapter 2** achieved the highest ionic conductivity, moderate mechanical strength and lowest interfacial resistance, owing to in situ CO₂ evolution that enhanced porosity, which is further proven by **Chapter 3**. The oxalate cross-linked system in **Chapter 4** delivered a balanced profile with conductivity, breakdown voltage, and superior mechanical stiffness, albeit at the cost of slightly lower hydration and higher interfacial resistance. The borax cross-linked membrane of **Chapter 5** integrates the advantages as well as disadvantages of both previous systems. It achieves lowest ionic conduction, but exhibited superior mechanical properties and longer cycle life at 2 mA cm⁻², attributed to the dual ionic-covalent crosslinking mechanism providing enhanced structural stability. This underscores how the dual ionic-covalent crosslinking afforded by borax yields a simplified, sustainable electrolyte in high-performance solid-state supercapacitors.

Across all four electrolyte membranes, a consistent trend was observed between the degree of crystallinity and the electrochemical functionality. The progressive reduction in crystallinity from 19.50% in the UCM to 15.02%, 11.67%-9.57%, 10.19%, and 16.59% in ICCHME, GCCHME, OCCHME, and BCCHME, respectively, corresponded to systematic improvements in ionic conductivity. This trend is mechanistically explained by the role of amorphous domains in polymer electrolytes: unlike crystalline regions where tightly packed polymer chains and intact hydrogen-bonding networks impede ion movement, amorphous regions offer expanded free volume, greater chain segmental mobility, and lower tortuosity for ion migration pathways. As the crosslinking-induced disruption of crystalline order increases the amorphous fraction, more sites become accessible for ion coordination and transport, thereby raising the ionic conductivity.

The ionic conductivity of the hydrogel electrolyte membranes arises from the dissociation of the incorporated salts within the hydrated chitosan matrix, leading to the formation of mobile ionic species. Specifically, ICCHME and GCCHME systems contain Na⁺ and CO₃²⁻ ions, OCCHME consists of K⁺ and C₂O₄²⁻ ions, while BCCHME contains Na⁺ and B(OH)₄⁻ (tetraborate) ions. It is observed that the anions (CO₃²⁻, C₂O₄²⁻, and B(OH)₄⁻ ions) preferentially interact with the protonated functional groups of chitosan (–NH₃⁺), forming ionic associations within the polymer network.

Despite this interaction, transference number measurements indicate that anions are the dominant charge carriers in these systems. This apparent behavior can be explained by a hopping or exchange mechanism, where anions migrate through the polymer matrix via successive breaking and reformation of ionic interactions between adjacent coordination sites. The presence of a highly hydrated hydrogel network further facilitates this process by enhancing segmental mobility and enabling dynamic ion transport pathways [1,2]. Thus, the ionic conduction in these hydrogel electrolytes is predominantly governed by anion transport through a coordinated hopping mechanism within the hydrated chitosan matrix.

The electrolyte composition plays a significant role in determining the R_{ct} at the electrode-electrolyte interface, primarily through its influence on ion mobility, crosslinking density, and interfacial interactions. In the present study, a clear trend has been observed wherein the carbonate-based ICCHME exhibits the lowest R_{ct} due to its relatively porous structure and higher free volume, which originate from CO_2 evolution during the crosslinking process. This facilitates efficient ion transport and improved accessibility of ions to the electrode surface. In contrast, the oxalate-based OCCHME shows comparatively higher R_{ct} , which can be attributed to the formation of a denser and more compact hydrogel network through bidentate coordination of oxalate ions with the chitosan matrix, thereby restricting ion mobility. Furthermore, systems with higher crosslinking density, such as GCCHME at higher salt concentration and BCCHME with dual crosslinking, exhibit relatively higher interfacial resistance due to reduced free volume and increased ionic interactions within the polymer network. Thus, an increase in crosslinking density generally leads to an increase in charge transfer resistance.

6.2 Significance of the study

This research has established that the nature of the ionic crosslinker profoundly affects both the physicochemical and electrochemical properties of chitosan-based hydrogel membrane electrolytes. By systematically comparing carbonate, oxalate, and borate crosslinkers, we demonstrated tailored control over WU, mechanical integrity, and ionic conductivity without resorting to synthetic polymers or toxic chemical agents. The optimized carbonate cross-linked membranes achieved exceptional cycle life in

EDLCs, while oxalate and borate cross-linked variants offered complementary trade-offs between flexibility and electrochemical stability. These findings underscore the versatility of chitosan, an abundant, biodegradable biopolymer, as a sustainable platform for designing SSEs. Moreover, the simple, scalable fabrication methods and use of low-cost, environmentally benign crosslinkers position these materials as promising candidates for next-generation, eco-friendly energy storage devices.

6.3 Limitations of the study

Despite the encouraging performance, several limitations must be acknowledged. First, the ionic conductivity of hydrogel membranes remains lower than that of liquid electrolytes, imposing a ceiling on achievable power density. Second, long-term dimensional stability under extreme thermal cycling and mechanical deformation was not fully explored, leaving open questions about durability in harsh environments. Third, the study focused on proof of concept EDLCs; integration into hybrid or battery-type systems may introduce interfacial compatibility challenges with non-carbon electrodes. Fourthly, the sudden decrease of Coulombic efficiencies in all the EDLCs has to be solved by altering the electrode materials. Finally, the influence of residual acetic acid or unbound crosslinker ions on membrane aging and self-discharge behavior warrants further examination.

6.4 Future scope

Building on these insights, future work can pursue several directions:

- Crosslinker combinations and gradients: implementing spatial or temporal gradients of multiple ionic crosslinkers may enable membranes with surface-tuned stiffness and core-optimized conductivity, enhancing interface kinetics.
- Hybrid electrode architectures: pairing chitosan hydrogel electrolytes with redox-active or pseudocapacitive electrode materials (e.g., transition metal oxides, conducting polymers) could boost overall energy density while retaining cycle life.
- Green hydrogen and fuel-cell integration: given chitosan's proton conductivity, these hydrogel membranes could serve as SSEs or separator layers in proton-exchange membrane fuel cells and electrolyzers for green hydrogen

generation. Their leak-proof nature and broad electrochemical window make them ideal for next-generation proton exchange membrane systems.

- Biopolymer blends and nanocomposites: blending chitosan with other natural polymers (e.g., cellulose, alginate) or incorporating conductive nanofillers (graphene, MXenes) may synergistically enhance ion transport pathways and mechanical resilience.
- Environmental and lifecycle assessments: comprehensive life-cycle analyses and biodegradability testing will be essential to quantify environmental impact and guide sustainable manufacturing.
- Advanced modeling and in-situ characterization: molecular dynamics and in-situ spectroscopy could reveal crosslinking kinetics, ion solvation structures, and transport mechanisms at the molecular level, informing rational design.

6.5 Concluding remarks

In conclusion, this work has demonstrated green, cost-effective route to robust chitosan hydrogel membrane electrolytes via simple ionic crosslinking strategies. The resulting materials combine high WU, mechanical strength, and ion conductivity without toxic reagents or complex synthesis. When employed in EDLCs, carbonate cross-linked membranes delivered longer cycle lives, while oxalate and borate variants provided complementary performance profiles. These outcomes validate chitosan hydrogels as a versatile, sustainable platform for solid-state energy storage and pave the way toward broader applications in green hydrogen electrolyzers, fuel cells, and hybrid supercapacitors. The insights gained herein establish a foundation for future innovations in biopolymer-based electrolytes that meet the dual imperatives of high performance and environmental stewardship.

APPENDIX-1

PLAGARISM REPORT



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DEPARTMENT OF CHEMISTRY

Headquarters: LUMAMI, ZUNHEBOTO DISTRICT-798627, NAGALAND, INDIA

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Title of the Ph.D. thesis	<i>Syntheses and Characterizations of Novel Polymer Membrane Electrolytes Comprising of Ionically Cross-Linked Chitosan Hydrogels for Application in Supercapacitors</i>
Name and institutional address of the supervisor	Dr. Nurul Alam Choudhury Department of Chemistry Nagaland University, Lumami, Nagaland - 798627, India.
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Dipankar Hazarika

Dipankar Hazarika
(Scholar)

Place: Lumami
Date: 22/04/2026

Name & Signature of the Supervisor: *Dr. Nurul Alam Choudhury*
with seal

Dr. Nurul A. Choudhury
Assistant Professor
Department of Chemistry
Nagaland University
Head Quarters-Lumami

(Name & Signature of the Head):
with seal

Ambrish Singh

वर्षागाध्यक्ष / Head

रसायन विज्ञान विभाग / Department of Chemistry
नागालैण्ड विश्वविद्यालय / Nagaland University
लुमामी / Lumami-798627



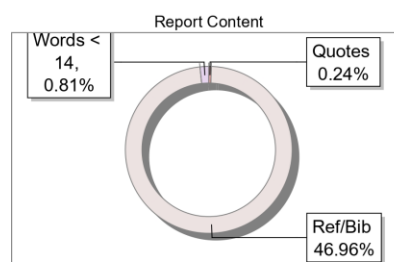
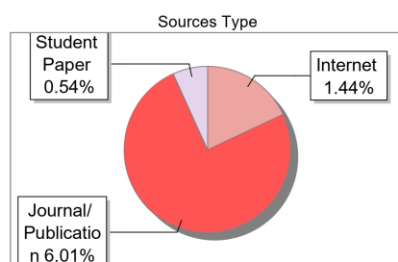
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Author Name	Dipankar Hazarika
Title	Syntheses and Characterizations of Novel Polymer Membrane Electrolytes Comprising of Ionically Cross-Linked Chitosan Hydrogels for Application in Supercapacitors
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Submission Date	2025-10-22 00:28:05
Total Pages, Total Words	390, 98278
Document type	Thesis

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Language	English
Student Papers	Yes
Journals & publishers	Yes
Internet or Web	Yes
Institution Repository	Yes

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APPENDIX-2

CURRICULUM VITAE

Dipankar Hazarika

Permanent Address:

Vill: Jorhatia Gaon,

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ACADEMIC QUALIFICATIONS

2021-Current	Ph.D. in Chemistry, Nagaland University
2019-2021	M.Sc. in Chemistry, Nagaland University Dissertation title: <i>A Review of Polymer Electrolytes for Redox Flow Batteries</i> CGPA: 8.36
2016-2019	B.Sc. (Hons. in Chemistry), North Lakhimpur College (autonomous) affiliated to Dibrugarh University CGPA: 7.36
2014-2016	HS (Science), AHSEC Board, North Lakhimpur College, Assam Percentage: 79.20
2014	HSLC, SEBA Board, Pichala National Academy, Lakhimpur, Assam Percentage: 90.17

AWARDS/ACHIEVEMENTS

1. Awarded **International Travel Support (ITS)** by ANRF, Government of India, to attend the **9th Nano Today Conference (Elsevier), Singapore**, September 22–25, 2025. (File No.: ITS/2025/003536).
2. Awarded the **Royal Norwegian Embassy Fellowship Grant** for Innovations in Battery Energy Storage in India (2025) — *selected as one of 13 innovators across India*.
3. Awarded **TIDE 2.0 Grant** by the **Ministry of Electronics & Information Technology** (MeitY), Govt of India, under **IIT Bombay**.
4. Selected for official incubation under NSRCEL, IIM Bangalore, as part of Cohort Launchpad 29 (2025); chosen among 31 start-ups from a total of 542 applications.
5. Finalist of **Maruti Suzuki Nurture Cohort-3**, All India edition, organized by **IIM, Kolkata & Maruti Suzuki** (Ranked under top 11).
6. Selected for **fully sponsored one-year incubation** under the Technology Incubation Center, **Indian Institute of Technology Guwahati**, for my startup *Amplite Energy* (2025).
7. Secured **1st Position** in the *Business Model Canvas (BMC) Presentation* at IIT Guwahati Technology Incubation Centre (2025).
8. Received **Best Oral Presentation Award** (sponsored by the **Royal Society of Chemistry**) at the *International Conference on Chemistry in Multidisciplinary Research (ICCMR-2025)*, Nagaland University, March 25–27, 2025.
9. Awarded **Ishan Uday Scholarship**, University Grants Commission, Government of India (2016–2019).
10. Received the **Anundoram Barooah Award**, Government of Assam, for meritorious performance in HSLC examination (2014).

RESEARCH PUBLICATIONS

1. **Hazarika, D.**, Shijoh, N., Kichu M. A., & Choudhury, N. A. (2025). Sustainable and Robust Oxalate-Crosslinked Quasi-Solid Chitosan Hydrogel Membrane Electrolyte for Durable Solid-State Electrical Double Layer Capacitors, *International Journal of Biological Macromolecules*, Volume

350, March 2026, 150864, <https://doi.org/10.1016/j.ijbiomac.2026.150864>, (IF: 8.5).

2. **Hazarika, D.**, Kamei, D., Shijoh, N., & Choudhury, N. A. (2025). An ionically cross-linked chitosan hydrogel membrane electrolyte for long-lived electrical double layer capacitors. *Journal of Power Sources*, 629(236037), <https://doi.org/10.1016/j.jpowsour.2024.236037>. (IF: 8.1)
3. Kamei, D., **Hazarika, D.**, & Choudhury, N. A. (2025). Pure and KI-doped glyoxal-crosslinked gelatin hydrogel membrane electrolytes for solid-state EDLCs. *Materials Today. Chemistry*, 43(102470), <https://doi.org/10.1016/j.mtchem.2024.102470>. (IF: 6.7)
4. Kichu, M. A., **Hazarika, D.**, Kamei, D., & Choudhury, N. A. (2025). *Ultra-long Lifespan of EDLC Using Ionotropically Gelled Chitosan Membrane Electrolyte*. *Journal of Power Sources*, 659(238435), <https://doi.org/10.1016/j.jpowsour.2025.238435> (IF: 7.9)
5. Shijoh, N., **Hazarika, D.**, Kichu M. A., Kamei D., & Choudhury, N. A. (2025). *Al(III)-crosslinked Gelatin Hydrogel Membrane Electrolytes for Long-lived EDLCs*. *Journal of Power Sources*, 659(238409), <https://doi.org/10.1016/j.jpowsour.2025.238409> (IF: 7.9)
6. Kichu, M. A., Shijoh N., **Hazarika, D.**, & Choudhury, N. A. (2025). HPO42--Crosslinked Chitosan Hydrogel Membrane as Quasi-Solid Electrolyte for Durable Electric Double Layer Capacitors. *Electrochimica Acta*, 147665, <https://doi.org/10.1016/j.electacta.2025.147665> IF: 5.4
7. Kamei, D., Kichu M. A., **Hazarika, D.**, Shijoh, N., & Choudhury, N. A. (2025). Glutaraldehyde-Glyoxal Co-Crosslinked Gelatin Hydrogel Electrolytes with KI/HQ Dopant for Solid-State Electric Double Layer Capacitors. *Journal of Physics and Chemistry of Solids*, 113332, <https://doi.org/10.1016/j.jpcs.2025.113332> IF: 4.9

MANUSCRIPTS UNDER REVISION

1. **Hazarika, D.**, Kichu, M. A., Shijoh, N., Kamei, D., & Choudhury, N. A. (2025). Structure–property Insights into CO₃²⁻-crosslinked Chitosan Hydrogel

Membranes: Facile Synthesis via Gradient Crosslinking of Quasi-solid Electrolytes for EDLCs with Remarkable Cycle Lives. *Journal of Power Sources*, (Manuscript Number: POWER-D-25-03572) (IF: 7.9)

PATENTS

1. Ionically Cross-linked Chitosan Hydrogel Membrane Electrolyte for Long-lived Electrical Double Layer Capacitors, **D. Hazarika**, D. Kamei, N. Shijoh, N. A. Choudhury, Indian patent, Patent No.: 570972; Application No.: 202431059207; **Granted** on: 22/09/2025.
2. Ionotropically Gelled Chitosan Membrane Electrolytes synthesized using Sodium Thiosulfate for Ultra-Long Lifespan of Supercapacitors, M. A. Kichu, **D. Hazarika**, D. Kamei, N. A. Choudhury, *Indian patent*, Patent No.: 569370, Application No.: 202431059206; **Granted** on: 30/07/2025.
3. KI-doped Glyoxal-Crosslinked Gelatin Hydrogel Membrane Electrolytes for Supercapacitors, D. Kamei, **D. Hazarika**, and N. A. Choudhury, *Indian patent*, Patent No.: 570983; Application No.: 202431068469; **Granted** on: 30/07/2025.
4. Borax Crosslinked Chitosan Hydrogel Electrolyte for all Solid-State Supercapacitors, **D. Hazarika**, M. A. Kichu, N. Shijoh, and N. A. Choudhury, *Indian patent*, Application No.: 202531080607; Published on: 20/09/2024.
5. Oxalate–Crosslinked Quasi-Solid Chitosan Hydrogel Membrane Electrolyte for Durable Supercapacitors, **D. Hazarika**, M. A. Kichu, N. Shijoh, and N. A. Choudhury, *Indian patent*, Application No.: 202531080608; Published on: 05/09/2025.
6. HPO_4^{2-} -Crosslinked Chitosan Hydrogel Membrane as Quasi-Solid Electrolyte for Durable Electric Double Layer Capacitors, M. A. Kichu, N. Shijoh, **D. Hazarika**, and N. A. Choudhury, *Indian patent*, Application No.: 202531080606; Published on: 05/09/2025.
7. Cationically-Linked Gelatin Hydrogel Electrolyte Membrane for Supercapacitor, **D. Hazarika**, N. Shijoh, D. Kamei, M. A. Kichu, and N. A. Choudhury, *Indian patent*, Application No.: 202431068468; Published on: 20/09/2024.

START-UP EXPERIENCE

Founder, Amplyte Energy (July 2025 – Present)

1. Developing and commercializing **polymer electrolyte technologies** for sustainable energy storage devices.
2. Selected for **1-year fully sponsored incubation** under the Technology Incubation Center, **IIT Guwahati**.
3. Recognized among the **Top 3 Start-ups of North East India** and incubated under the **Indian Institute of Management, Kolkata (IIM-K)**.
4. Recipient of **Meity EIR 2.0** (2025).

CONFERENCE PRESENTATIONS

1. **Oral presentation** on the topic “*Surface-crosslinked Chitosan Hydrogel Membrane Electrolytes for High-performance EDLC: Optimized Ionic Conductivity and Durability*” in the International Conference on Chemistry in Multidisciplinary Research, 2025, organized by the Department of Chemistry, Nagaland University, held during March 25-27, 2025.
2. **Oral presentation** on the topic “*Biopolymer derived Quasi solid Electrolytes Comprising of Ionically crosslinked Chitosan Hydrogels for Applications in EDLCs*” in the International Conference on Advances in Sustainable Solutions for Energy Transitions (ASSET-2025), organized by the School of Energy Science and Engineering, IIT Guwahati, held during January 2-4, 2025.
3. **Oral presentation** on the topic “*A Mechanically Strong Chitosan Hydrogel Membrane Electrolyte for Solid-State Electrical EDLCs*” in the National Seminar on Application of Chemical Science for Sustainable Solution in Energy, Health and Environment, organized by the Dept. of Chemistry, Moinul Haque Choudhury Memorial Science College, Algapur, Hailakandi, Assam, held on September 19, 2024.
4. **Oral presentation** on the topic “*An Ionically Crosslinked Chitosan Hydrogel Membrane Electrolyte with Low Solution-Resistance for Solid-State Electrical*”

Double Layer Capacitors Exhibiting Long Cycle-life” in the International Conference on Hydrogen Energy and Advanced Materials (ICHEAM-2024), organized by the Dept. of Physics, Institute of Science, Banaras Hindu University, Varanasi – 221005, held during April 22-24, 2024.

5. **Oral presentation** on the topic “*A Novel and Cost-effective Crosslinked Chitosan Hydrogel Membrane Electrolyte for Solid-State Electrical Double Layer Capacitors*” in the 68th Annual Technical Session of Assam Science Society and National Seminar on “Recent Breakthroughs and Innovations in Science and Technology”, organized by Assam Science Society & Assam Down Town University, Assam, held on March 30, 2024.

WORKSHOPS/ WEBINARS ATTENDED

1. Participated in the Webinar on “*AI Applications in Academia*”, organized by the Department of Environmental Science, Nagaland University, held on *April 25, 2025*.
2. Participated in National Seminar on “*Application on Gen AI*”, organized by Indian Institute of Innovation and Science (IIISc), held on *February 4, 2025*.
3. Participated in National Seminar on “*AI Innovation 2025*”, organized by Indian Institute of Innovation and Science (IIISc), held on *January 28, 2025*.
4. Participated in one-day workshop on “*Elevating the research productivity through Scopus*”, organized by Elsevier, held on May 28, 2024.
5. Participated in one-day workshop on “*Quality improvement parameters in research publications*”, Organized by Department of Chemistry and IQAC, Nagaland University, held on April 19, 2023.
6. Participated in one-day workshop on “*Improving research writing using Grammarly*”, organized Central library of Nagaland University in collaboration with BridgePeople, held on March 30, 2022.
7. Participated in the International E-conference on “*Molecules to Materials for Sustainability in XXI Century, MMS-2021*”, organized by Dept. of Chemistry,

Institute of Science, GITAM Deemed to be University, Visakhapatnam, held on March 8-9, 2021.

8. Participated in the National e-seminar on “*Chemistry in emerging trends of interdisciplinary research (NeSCETIR-2020)*”, organized by Dept. of Chemistry, Nagaland University, held on November 18-20, 2020.
9. Participated in the webinar on “*Water conservation: strategies and challenges*”, organized by Dept. of EVS, Sri Aurobindo College, University of Delhi, held September 7, 2020.

OTHER COURSES AND CERTIFICATES

1. Participated in four days “**Research Development Programme for Young Researchers**” organized by IQAC, Nagaland University, held during 24th to 28th March, 2025.
2. One-year **Advance Diploma in Computer Application (ADCA)** from Institute of Advance computer science, Recognized by Govt. of India (**Percentage: 67%**).
3. Participated and got an “A” grade in a one-week Online **National Faculty Development Program** on “**e-Content Development**”, organized by Guru Angad Dev Malaviya Mission Teacher Training Centre, SGTB Khalsa College, University of Delhi, held from 10th October to 16th October 2023.
4. Participated and got an “A+” grade in a one-week Online **National Faculty Development Program** on “**Basics of Research Methodology and Issues in Plagiarism (An Interdisciplinary Approach)**”, organized by Guru Angad Dev Teaching Learning Centre, a Centre under the Pandit Madan Mohan Malaviya National Mission on Teachers and Teaching (PMMMNMTT) of the Ministry of Education and Department of Business Economics, SGTB Khalsa College, University of Delhi, held on 31st May to 06th June 2022.

SKILLS

Software: MS Office, Origin, Nova (Metrohm Autolab), MATLAB

Instrumentation: Metrohm Autolab electrochemical workstation, 8-channel Battery Analyzer, Vibrating Viscometer, FT-IR spectrometer, Mass spectrometer.

Proposal Writing: Experience with ANRF, MNRE, and Norwegian Embassy grant proposals; skilled in writing funding applications, GeM procurements, and innovation documentation.

Project Management: Experience in project administration, progress reporting, and completion monitoring of funded research projects.

APPENDIX-3

PAPERS PUBLISHED



An ionically cross-linked chitosan hydrogel membrane electrolyte for long-lived electrical double layer capacitors

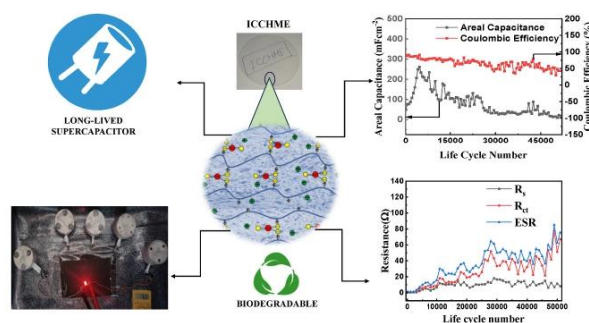
Dipankar Hazarika , Duangailung Kamei , Nuphizo Shijoh, Nurul Alam Choudhury

Laboratory for Polymer Materials and Renewable Energy, Department of Chemistry, Nagaland University, Lumami-798627, Zunheboto, Nagaland, India

HIGHLIGHTS

- Chitosan was ionically cross-linked with Na_2CO_3 to synthesize ICCHME.
- The tensile strength of the ICCHME was found to be 53.29 MPa.
- The EDLC with ICCHME showed a peak areal capacitance of 260.40 mFcm^{-2} .
- The EDLC showed 51,500 and 33000 charge-discharge cycles at 2 and 5 mAcm^{-2} , respectively.
- The areal capacitance increased by 529.26 % and 425 % during life cycle studies.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Chitosan
Sodium carbonate
Ionic crosslinking
Hydrogel membrane electrolyte
Electrical double layer capacitor
Long cycle life

ABSTRACT

An Ionically Crosslinked Chitosan Hydrogel Membrane Electrolyte (ICCHME) has been prepared by crosslinking chitosan with sodium carbonate (Na_2CO_3). The ICCHME has been characterized by physicochemical and electroanalytical techniques. It possesses water uptake and dissolution ratio of 226 % and 18.24 %, respectively. Shifts in band positions of -NH and -OH in the Fourier transform infra-red (FTIR) spectrum of ICCHME indicated ionic crosslinking between chitosan and Na_2CO_3 . The XRD studies reveal that the ICCHME is semi-crystalline with 15.02 % crystallinity. FESEM reveals a uniform porous structure for ICCHME. The EDX spectrum of ICCHME shows the presence of Na, C, N, and O. It has exhibited an ionic conductivity of 7.89 mS cm^{-1} . A solid-state Electrical Double Layer Capacitor (EDLC) assembled using ICCHME as electrolyte and Black Pearls carbon as electrode has exhibited an areal capacitance of 260.40 mFcm^{-2} at 2 mAcm^{-2} . The EDLC has exhibited an energy density of 36.16 μWhcm^{-2} and a power density of 2000 μWcm^{-2} . The EDLC has shown a low solution resistance (R_s) of 0.24 Ω . The EDLC has exhibited excellent cycle lives of 51,500 and 33,000 cycles at 2 and 5 mAcm^{-2} , respectively. While attaining peak performance stage, the areal capacitance has increased by 529.26 % and 425 % during life cycle studies at 2 and 5 mAcm^{-2} , respectively. During the cycle life test, the EDLC has

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Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

journal homepage: www.elsevier.com/locate/ijbiomac

Sustainable and robust oxalate-crosslinked quasi-solid chitosan hydrogel membrane electrolyte for durable solid-state electrical double layer capacitors

Dipankar Hazarika, Nuphizo Shijoh, Marjo A Kichu, Nurul Alam Choudhury*

Laboratory for Polymer Materials and Renewable Energy, Department of Chemistry, Nagaland University, Lumami-798627, Zunheboto, Nagaland, India

ARTICLE INFO

Keywords:

Chitosan
Oxalate crosslinker
Hydrogel membrane electrolyte
Ionic crosslinking
Electrical double layer capacitor

ABSTRACT

The development of safe, sustainable, and high-performance electrolytes remains a major bottleneck in advancing solid-state electrochemical double-layer capacitors (EDLCs). Conventional synthetic polymer electrolytes often exhibit limited ionic conductivity and poor environmental compatibility, highlighting the need for bio-derived alternatives with improved electrochemical performance. In this work, a green and scalable chitosan-based hydrogel electrolyte was developed using potassium oxalate as an ionic crosslinker to form an oxalate-crosslinked chitosan hydrogel membrane electrolyte (OCCME). The crosslinking mechanism, structure, and properties of the OCCME were systematically investigated through spectroscopic, morphological, and electrochemical analyses. Ionic complexation between oxalate ions and protonated chitosan chains generated uniform, semi-crystalline membranes with enhanced amorphous content, water retention, and mechanical stability. The optimized OCCME exhibited high ionic conductivity (4.84 mS cm^{-1}), a wide electrochemical stability window of 2.10 V, and an ionic transference number of 0.92. When employed in EDLCs, the OCCME delivered an areal capacitance of 300.8 mF cm^{-2} , energy density of 42.1 μWh cm^{-2} , and remarkable cycling durability over 46,000 cycles. A prototype EDLC successfully powered a red LED bulb, further demonstrating its practical applicability. These findings demonstrate the potential of oxalate-based ionic crosslinking as a green and efficient strategy for designing next-generation biopolymer electrolytes for sustainable energy storage applications.

1. Introduction

The global energy landscape is undergoing a paradigm shift driven by the urgent need to transition from fossil fuels toward sustainable, renewable energy sources. This transition is accompanied by a growing demand for efficient, reliable, and environmentally benign energy storage systems capable of stabilizing the intermittency of renewable power generation [1]. Among various energy storage technologies, electrochemical double-layer capacitors (EDLCs) have attracted increasing attention due to their high power density, rapid charge-discharge rates, and outstanding cycling stability, making them indispensable for hybrid energy systems, electric vehicles, and flexible electronics [2]. Unlike batteries, which rely on faradaic redox reactions, EDLCs store energy through the electrostatic accumulation of ions at the electrode-electrolyte interface, thereby ensuring longer operational lifespans and higher safety. However, the overall performance of EDLCs depends critically on the properties of their constituent components,

particularly the electrolyte, which governs ionic transport, electrochemical stability, and interfacial compatibility [3]. Conventional EDLCs typically employ liquid electrolytes (aqueous, organic, or ionic liquid systems) owing to their high ionic conductivities and facile processability [4]. Nevertheless, these liquid systems suffer from several inherent limitations such as electrolyte leakage, evaporation, flammability, and limited operational temperature windows, which hinder their long-term practical applicability [5]. To overcome these drawbacks, gel polymer electrolytes (GPEs) and hydrogel polymer electrolytes (HPEs) have emerged as promising alternatives that combine the ionic transport efficiency of liquids with the mechanical integrity of solids [6]. Hydrogels, in particular, offer advantages such as high-water content, mechanical flexibility, biocompatibility, and facile fabrication, rendering them highly attractive for flexible, wearable, and sustainable energy storage devices [7].

In this context, natural materials, especially biopolymers, have gained remarkable attention as sustainable components in energy

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Pure and KI-doped glyoxal-crosslinked gelatin hydrogel membrane electrolytes for solid-state EDLCs

Duangailung Kamei , Dipankar Hazarika , Nurul Alam Choudhury

Laboratory for Polymer Materials and Renewable Energy, Department of Chemistry, Nagaland University, Lumami, 798627, Zunheboto, Nagaland, India

ARTICLE INFO

Keywords:

Gelatin
Glyoxal
Hydrogel membrane Electrolyte
Redox-active dopant
Activation energy for hydrogel synthesis
Electrical double layer capacitor

ABSTRACT

Polymer hydrogels are three-dimensional solid materials with large amounts of water or aqueous solution absorbed in their networks. Hydrogels are utilized as solid electrolytes in energy devices such as Electrical Double Layer Capacitors (EDLCs). Glyoxal-crosslinked pure and 0.1 M KI-doped Gelatin Hydrogel Membrane Electrolytes (GNHMEs) have been prepared by reacting gelatin (GN) and glyoxal (GLY) in aqueous media. Water uptake (WU) of GNHMEs decreases from 717 to 319 % as the concentration of GLY increases from 3.13 to 40 %. Dissolution ratio of pure GNHME in boiling water is 49.0 %. The FTIR spectra of pure and doped GNHMEs show bands at 1731 and 1730 cm^{-1} corresponding to C=O stretching of aldehyde group except for pure GN which contain no aldehyde groups. T_g values for pure and doped-GNHMEs are 72.16 and 63.45°C, respectively. GNHME doped with KI possesses significantly lower stiffness (25.57 MPa) and tensile strength (40.47 MPa) while dramatically increasing the elongation percentage (63.60 %). The GNH synthesis reaction has activation energy of 13.39 kJ mol^{-1} . Pure and doped-GNHMEs exhibit ionic conductivities of 6.66×10^{-4} and $1.71 \times 10^{-3} \text{ S cm}^{-1}$, respectively. Specific capacitances of 3.5 and 10.7 F g^{-1} have been obtained at 5 mVs^{-1} for EDLCs using pure and doped-GNHMEs, respectively. EDLCs using pure and doped-GNHMEs have exhibited cell resistances of 2.75 and 1.05 Ω , respectively; energy densities of 0.17 and 1.28 Wh kg^{-1} , respectively. EDLCs using both pure and doped-GNHMEs have shown 4000 charge/discharge cycles at 1 mA cm^{-2} . Prototype power devices with five EDLCs of each type connected in series have been assembled and tested. A 1 V LED bulb has been powered by the device for 80 s.

1. Introduction

Majority of the current energy requirement is met by fossil fuels. The quick exhaustion of fossil fuel supplies and the detrimental effects on health as well as environment that happens from the usages of such fuels have warranted for the fast advancement of alternative sources of energy. Renewable energy is sporadic [1–4]. Renewable energy is intermittent [1–4]. Therefore, electrochemical supercapacitors (ESs) and battery R&D must be focused rapidly to fully harness renewable energy sources. ESs are of two primary categories, viz. Pseudo capacitors (PCs) and EDLCs [5,6]. Electricity storage by EDLCs takes place by forming double layers of electrical charges on the interfaces of electrode and electrolyte. In contrast, electricity storage by PCs takes place due to Faradaic processes, viz. redox reactions, underpotential deposition, intercalation, etc. taking place on electrode surfaces at a suitable electrode voltage [2,3]. High surface-area materials, such as activated carbon and carbon nanotube are used as electrodes in EDLCs. To the

contrary, redox-active materials, such as transition metal oxides and electrically conducting polymers, are used as electrodes in PCs [7]. EDLCs have some advantages compared to rechargeable batteries and are used in hybrid devices for battery-powered cars, high-load starting aid for diesel locomotives, electrical vehicles, as well as medical equipment [8,9]. The EDLC possesses a few merits over secondary batteries, viz. higher power densities and longer cycle lives [10].

One of the most important components in regulating the ion transfer efficiency, potential window, energy density, and safety concerns is electrolytes [11,12]. Electrolytes used in EDLCs can be either aqueous or non-aqueous. Both liquid and solid electrolytes are used in EDLCs. Liquid electrolytes encounter many issues, including packing failure and leaks. Solid electrolytes have the benefits of being dependable, compact, and leak-proof [3,4,13]. On the other hand, owing to issues such as limited ionic conductivity, poor ion accessibility, and a small electrolyte-electrode contact area, the EDLCs using solid electrolytes perform less well capacitatively [14,15]. One type of solid electrolyte that has ions

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Available online 17 December 2024

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Ultra-long lifespan of electric double layer capacitor using ionotropically gelled chitosan membrane electrolyte

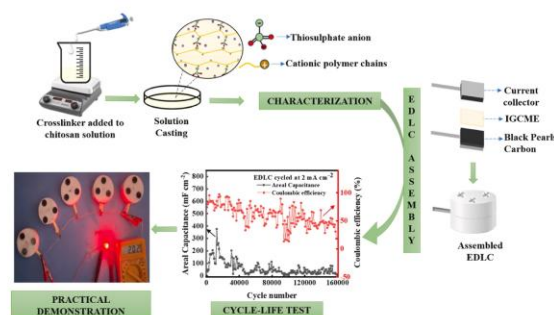
Marjo A. Kichu, Dipankar Hazarika , Duangailung Kamei, Nurul Alam Choudhury

Laboratory for Polymer Materials and Renewable Energy, Department of Chemistry, Nagaland University, Lumami, 798627, Zunheboto, Nagaland, India

HIGHLIGHTS

- IGCME was prepared by ionotropic gelation of chitosan using $\text{Na}_2\text{S}_2\text{O}_3$ crosslinker.
- The average activation energy for the gelation was found to be $15.25 \text{ kJ mol}^{-1}$.
- EDLC showed 505.5 mF cm^{-2} capacitance, $70.2 \text{ } \mu\text{Wh cm}^{-2}$ energy, and 3 mW cm^{-2} power.
- EDLC exhibited a cycle life of 158,924 charge-discharge cycles at 2 mA cm^{-2} .
- Five EDLCs powered a red LED for 40 min, showcasing practical applicability.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Chitosan
Sodium thiosulphate crosslinker
Ionotropic gelation
Hydrogel membrane electrolyte
Electrical double-layer capacitor
High cycle life

ABSTRACT

The transition from conventional liquid electrolytes to quasi-solid-state electrolytes is essential for improving the safety and long-term stability of energy storage systems. In this study, a hydrogel electrolyte is fabricated using the ionotropic gelation method for application in Electric double-layer capacitors (EDLCs). Chitosan is ionically crosslinked with sodium thiosulfate to form an Ionotropically Gelled Chitosan Membrane Electrolyte (IGCME). The successful crosslinking is confirmed through Fourier Transform Infrared Spectroscopy, X-ray Diffraction, and Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy. The IGCME exhibits a high ionic conductivity of $7.07 \times 10^{-3} \text{ S cm}^{-1}$ and an ionic transference number of 0.958 with anion-dominated conductivity. Electrochemical stability up to 2.2 V is confirmed via Linear Sweep Voltammetry. When integrated with Black Pearls Carbon electrodes, the EDLC demonstrates an areal capacitance of 505.5 mF cm^{-2} and an energy density of $70.2 \text{ } \mu\text{Wh cm}^{-2}$ at 3 mA cm^{-2} . The EDLC shows remarkable durability, lasting through 158,924 charge-discharge cycles at 2 mA cm^{-2} , surpassing previous records for hydrogel electrolytes. In a practical demonstration, five EDLCs are connected in series to power a red LED bulb for 40 min. These results highlight the effectiveness of ionotropic gelation in developing hydrogel electrolytes for energy storage applications.

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Al³⁺-crosslinked gelatin hydrogel membrane: A high-stability electrolyte for durable electrical double layer capacitors

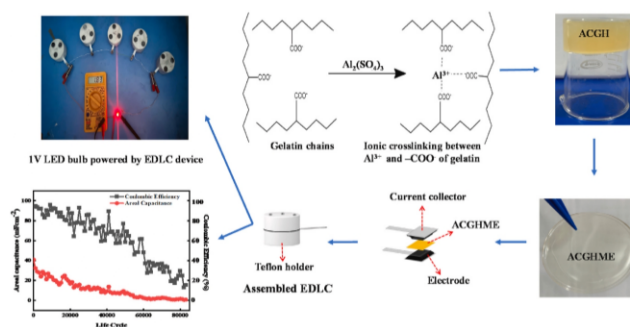
Nuphizo Shijoh, Dipankar Hazarika , Marjo A Kichu, Duangailung Kamei ,
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HIGHLIGHTS

- ACGHME was prepared by ionically crosslinking gelatin with Al³⁺.
- The activation energy for the crosslinking process was 52.03 ± 1.91 kJ mol⁻¹.
- EDLC with ACGHME showed areal capacitance of 46.2 mF cm⁻² at 0.5 mA cm⁻².
- EDLC showed a total cycle life of 83,000 and a peak Coulombic efficiency of 92.9 %.
- Five EDLCs connected in series powered a 1V LED for 2.83 min.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Gelatin
Al³⁺ crosslinker
Ionic crosslinking
Hydrogel membrane electrolyte
Electrical double layer capacitor

ABSTRACT

Hydrogels, with their high-water content and flexibility, have emerged as promising candidates as quasi-solid electrolytes for energy storage systems. This study presents an Aluminium (3+) Crosslinked Gelatin Hydrogel Membrane Electrolyte (ACGHME) synthesized via ionic crosslinking of gelatin with Al³⁺ ions. The ACGHME exhibits a water uptake of 1109 % and a water vapor transmission rate of 54.78×10^{-3} g m⁻² h⁻¹. The tensile strength of ACGHME is 56.93 MPa and its elongation percentage is 6.50 %. The room-temperature ionic conductivity of ACGHME is 1.73 mS cm⁻¹. The ionic and electronic transference numbers of ACGHME are 0.98 and 0.02, respectively. Further analysis shows that ACGHME possesses an ion mobility of 2.33×10^{-5} m² V⁻¹ s⁻², diffusion coefficient of 6.01×10^{-7} m² s⁻¹, and a charge-carrier number density of 1.91×10^{21} m⁻³. The ACGHME also exhibits a stable electrochemical potential window of 2.2 V. When integrated into solid-state Electrical Double Layer Capacitor (EDLC) with Black Pearls Carbon electrodes, the ACGHME demonstrates an areal capacitance of 46.2 mF cm⁻² and an energy density of 6.4 μWh cm⁻² at 0.5 mA cm⁻². Remarkably, the EDLC exhibits an

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journal homepage: www.journals.elsevier.com/electrochimica-acta

HPO₄²⁻-Crosslinked chitosan hydrogel membrane as quasi-solid electrolyte for durable electric double layer capacitors

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ARTICLE INFO

Key words:

Chitosan hydrogel membrane electrolyte
Disodium hydrogen phosphate
Ionic crosslinking
Quasi-solid Electrolyte
Electric double layer capacitor

ABSTRACT

Chitosan, a biopolymer known for its biocompatibility and ionic gelation behaviour, has been widely explored in biomedical applications but remains underutilized in energy storage systems. In this study, we repurpose a well-established chitosan hydrogel system formed via ionic crosslinking between chitosan and disodium hydrogen phosphate (DSHP), resulting in a stable, three-dimensional hydrogel network to develop a quasi-solid Chitosan Hydrogel Membrane Electrolyte (CaHME) for Electric Double Layer Capacitor (EDLC) applications. The CaHME exhibits a high ionic conductivity of 4.07 mS cm⁻¹, a dominant ionic transference number of 0.98, and a breakdown voltage of 2.5 V, confirming excellent ion transport and electrochemical stability. The assembled EDLCs employing CaHMEs show outstanding performance, with a peak areal capacitance of 619 mF cm⁻², energy density of 85.97 μWh cm⁻², and power density of 5000 μW cm⁻² at 5 mA cm⁻². Another EDLC using CaHME cycling at 6 mA cm⁻² demonstrates an areal capacitance of 380.4 mF cm⁻², energy density of 52.23 μWh cm⁻², and power density of 6000 μW cm⁻². Long-term cycling tests showed excellent durability, with 57,000 and 36,000 cycles at 5 and 6 mA cm⁻², respectively. A practical demonstration involving five EDLCs connected in series successfully powered a red LED bulb for 2 min and 25 s, showcasing real-world applicability. These results highlight the untapped potential of CaHME as a sustainable, high-performance electrolyte for next-generation EDLCs.

1. Introduction

The increasing emphasis on eco-conscious technologies has underscored the critical need for sustainable and high-efficiency materials in energy storage [1]. Among energy storage devices, Electric Double Layer Capacitors (EDLCs) have gained prominence due to their rapid charge/discharge capability and extended cycle life [2]. The electrolyte is pivotal to device performance, as it facilitates efficient ion transport between the electrodes [3]. Although conventional liquid electrolytes are commonly employed, they pose several challenges, including leakage hazards, flammability, and adverse environmental impact. Solid or quasi-solid polymer electrolytes provide an effective alternative, offering improved safety and stability [4]. Hydrogels, a class of quasi-solid materials, consist of polymer networks capable of retaining significant water content while maintaining structural integrity [5]. Their adaptability and tunable properties have led to widespread applications in biomedicine, controlled drug release, and environmental remediation [6]. Among natural biopolymers, chitosan stands out for its biocompatibility, biodegradability, and ease of modification [7]. Derived from

chitin through deacetylation, chitosan exhibits excellent film-forming ability, attributed to its polycationic nature, which facilitates ionic crosslinking. This property enables the formation of hydrogels with desirable physicochemical characteristics suitable for various applications [8]. In ionic crosslinking, the positively charged amine groups of chitosan electrostatically interact with crosslinker anions, leading to the formation of a structured hydrogel network [9]. This process enables precise modulation of the structural and physicochemical properties of the hydrogel, including mechanical strength, swelling behaviour, and ionic transport pathways. Such tunability makes ionically crosslinked hydrogels highly versatile, with applications spanning from biomedicine [10,11] to energy storage technologies [12,13], where optimized conductivity and stability are essential. While extensive research has explored ionically crosslinked chitosan hydrogels for biomedical applications, their potential as hydrogel membrane electrolytes for energy storage systems, including EDLCs, has yet to be fully explored [12,13]. A crosslinker that has been reported for chitosan hydrogel formation is disodium hydrogen phosphate (DSHP).

Yang et al. [14] reported the development of a novel chitosan-based

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APPENDIX-3

PATENTS



INTELLECTUAL
PROPERTY INDIA
PATENTS | DESIGNS | TRADE MARKS
GEOGRAPHICAL INDICATIONS



सत्यमेव जयते

क्रम सं/SL No. 033139021



पेटेंट कार्यालय, भारत सरकार
The Patent Office, Government Of India

पेटेंट प्रमाण पत्र | **Patent Certificate**

(पेटेंट नियमावली का नियम 74) | (Rule 74 of The Patents Rules)

पेटेंट सं. / Patent No. 570972

आवेदन सं. / Application No. 202431059207

फाइल करने की तारीख / Date of Filing 06/08/2024

पेटेंटी / Patentee Nagaland University

आविष्कारकों का नाम / Name of Inventor(s) 1.Dipankar Hazarika 2.Duangailung Kamei 3.Nuphizo Shijoh 4.Nurul Alam Choudhury

प्रमाणित किया जाता है कि पेटेंटी को, उपरोक्त आवेदन में यथाप्रकटित *Ionicallly Cross-linked Chitosan Hydrogel Membrane Electrolyte for Long-lived Electrical Double Layer Capacitors* नामक आविष्कार के लिए, पेटेंट अधिनियम, 1970 के उपबंधों के अनुसार आज तारीख अगस्त 2024 के छठे दिन से बीस वर्ष की अवधि के लिए पेटेंट अनुदत्त किया गया है।

It is hereby certified that a patent has been granted to the patentee for an invention entitled *Ionicallly Cross-linked Chitosan Hydrogel Membrane Electrolyte for Long-lived Electrical Double Layer Capacitors* as disclosed in the above mentioned application for the term of 20 years from the 6th day of August 2024 in accordance with the provisions of the Patents Act,1970.

अनुदान की तारीख : 22/09/2025
Date of Grant :



Controller of Patents

टिप्पणी - इस पेटेंट के नवीकरण के लिए फीस, यदि इसे बनाए रखा जाना है, अगस्त 2026 के छठे दिन को और उसके पश्चात प्रत्येक वर्ष में उसी दिन देय होगी।
Note. - The fees for renewal of this patent, if it is to be maintained, will fall / has fallen due on 6th day of August 2026 and on the same day in every year thereafter.



The Patent Office, Government Of India

Patent Certificate

(Rule 74 of The Patents Rules)

569370

202431059206

06/08/2024

Nagaland University

1.Marjo A Kichu 2.Duangailung Kamei 3.Dipankar Hazarika

It is hereby certified that a patent has been granted to the patentee for an invention entitled *Ionotropically Gelled Chitosan Membrane Electrolytes synthesized using Sodium Thiosulfate for Ultra-Long Lifespan of EDLCs* as disclosed in the above mentioned application for the term of 20 years from the 6th day of August

2024 in accordance with the provisions of the Patents Act, 1970. انٲس آف ڈی، انٲیٲسار سٲاٲٲٲ اٲٲٲٲ

[illegible]

भारत सरकार, बौद्धिक संपदा कार्यालय, भारत सरकार, Intellectual Property Office, Government of India, बौद्धिक सम्पत्ति
नियंत्रण विभाग, नया दिल्ली-११००६९, भारत

अनुदान की तारीख
Date of Grant: 30/07/2025

Date of Grant : _____

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[illegible]



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PATENTS | DESIGNS | TRADE MARKS
GEOGRAPHICAL INDICATIONS



सत्यमेव जयते

क्रम सं/SL No :033139024



पेटेंट कार्यालय, भारत सरकार
The Patent Office, Government Of India

पेटेंट प्रमाण पत्र | Patent Certificate
(पेटेंट नियमावली का नियम 74) | (Rule 74 of The Patents Rules)

पेटेंट सं. / Patent No. 570983

आवेदन सं. / Application No. 202431068469

फाइल करने की तारीख / Date of Filing 11/09/2024

पेटेंटी / Patentee Nagaland University

आविष्कारकों का नाम /Name of Inventor(s) 1.Duangailung Kamei 2.Dipankar Hazarika 3.Nurul Alam Choudhury

प्रमाणित किया जाता है कि पेटेंटी को, उपरोक्त आवेदन में यथाप्रकटित **KI-doped Glyoxal-Crosslinked Gelatin Hydrogel Membrane Electrolytes for Supercapacitors** नामक आविष्कार के लिए, पेटेंट अधिनियम, 1970 के उपबंधों के अनुसार आज तारीख सितम्बर 2024 के ग्यारहवें दिन से बीस वर्ष की अवधि के लिए पेटेंट अनुदत्त किया गया है।

It is hereby certified that a patent has been granted to the patentee for an invention entitled **KI-doped Glyoxal-Crosslinked Gelatin Hydrogel Membrane Electrolytes for Supercapacitors** as disclosed in the above mentioned application for the term of 20 years from the 11th day of September 2024 in accordance with the provisions of the Patents Act,1970.



अनुदान की तारीख : 22/09/2025
Date of Grant :

डिप्टी - इस पेटेंट के नवीकरण के लिए फीस, यदि इसे बनाए रखा जाना है, सितम्बर 2026 के ग्यारहवें दिन को और उसके पश्चात प्रत्येक वर्ष में उसी दिन देय होगी।
Note. - The fees for renewal of this patent, if it is to be maintained, will fall / has fallen due on 11th day of September 2026 and on the same day in every year thereafter.

पेटेंट नियंत्रक
Controller of Patents

(12) PATENT APPLICATION PUBLICATION

(19) INDIA

(22) Date of filing of Application :06/08/2024

(21) Application No.202431059207 A

(43) Publication Date : 09/08/2024

(54) Title of the invention : Ionically Cross-linked Chitosan Hydrogel Membrane Electrolyte for Long-lived Electrical Double Layer Capacitors

(51) International classification :H01G0011860000, A61K0009200000, H01G0011320000, H01G0011340000, C08L0005080000

(86) International Application No :NA
Filing Date :NA

(87) International Publication No : NA

(61) Patent of Addition to Application Number :NA
Filing Date :NA

(62) Divisional to Application Number :NA
Filing Date :NA

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4)Nurul Alam Choudhury

Address of Applicant :Laboratory for Polymer Materials and Renewable Energy, Department of Chemistry Nagaland University, Lumami Headquarters, Zunheboto district Zunheboto -----

(57) Abstract :

The invention is an Ionically Crosslinked Chitosan Hydrogel Membrane Electrolyte (ICCHME) prepared by crosslinking chitosan with Na₂CO₃. The ICCHME has a water uptake of 226% and a dissolution ratio of 18.24%, along with an ionic conductivity of 7.89 mS_{cm}⁻¹. An EDLC using ICCHME as electrolyte and Black Pearls carbon as electrode exhibits a specific capacitance of 18.41 Fg⁻¹ at 5 mVs⁻¹ and 17.71 Fg⁻¹ at 2 mAc_m⁻², with energy and power densities of 2.50 Whkg⁻¹ and 138.25Wkg⁻¹ respectively, and low solution resistance (Rs) of 0.24 Ω. It has cycle lives of 51,500 and 33,000 cycles at 2 and 5 mAc_m⁻², and during the cycle life test, it maintains almost constant Rs.

No. of Pages : 20 No. of Claims : 7

(12) PATENT APPLICATION PUBLICATION

(21) Application No.202431068468 A

(19) INDIA

(22) Date of filing of Application :11/09/2024

(43) Publication Date : 20/09/2024

(54) Title of the invention : Cationically-Linked Gelatin Hydrogel Membrane Electrolyte for Supercapacitors

(51) International classification :C07D0487040000, C07D0403140000, A61K0031519000, A61P0015100000, C07D0401140000

(86) International Application No :NA
Filing Date :NA

(87) International Publication No : NA

(61) Patent of Addition to Application Number :NA
Filing Date :NA

(62) Divisional to Application Number :NA
Filing Date :NA

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(57) Abstract :

The invention relates to a novel hydrogel membrane electrolyte that is cost-effective, environmentally benign and prepared by ionically crosslinking gelatin with Aluminium (III) ion and characterized by physicochemical and electrochemical methods. Water Vapor Transmission rate (WVTR) of Ionically Crosslinked Gelatin Hydrogel Membrane Electrolyte (ICGHME) and pure gelatin hydrogel membranes vary within a narrow range of $54.784 \times 10^{-3} \text{ gm}^{-2} \text{ h}^{-1}$ and $80.85 \times 10^{-3} \text{ gm}^{-2} \text{ h}^{-1}$ respectively. The water uptake of Ionically crosslinked gelatin hydrogel has been found to be 1109%. The ICGHME has an ionic conductivity of 1.73 mScm^{-1} .

No. of Pages : 27 No. of Claims : 6

(12) PATENT APPLICATION PUBLICATION

(19) INDIA

(22) Date of filing of Application :26/08/2025

(21) Application No.202531080607 A

(43) Publication Date : 05/09/2025

(54) Title of the invention : Borax Crosslinked Chitosan Hydrogel Electrolyte for all Solid-State Supercapacitors

(51) International classification :C08J0005220000, H01M0010056500, B01D0071820000, H01M0008101800, H01G0011320000		(71)Name of Applicant : 1)Nagaland University Address of Applicant :Nagaland University, Lumami, Nagaland India Pin - 798627 Zunheboto -----
(86) International Application No	:NA	Name of Applicant : NA
Filing Date	:NA	Address of Applicant : NA
(87) International Publication No	: NA	(72)Name of Inventor :
(61) Patent of Addition to Application Number	:NA	1)Dipankar Hazarika
Filing Date	:NA	Address of Applicant :Department of Chemistry, Nagaland University, Nagaland, India, 798627 Zunheboto -----
(62) Divisional to Application Number	:NA	2)Marjo A Kichu
Filing Date	:NA	Address of Applicant :Department of Chemistry, Nagaland University, Nagaland, India, 798627 Zunheboto -----
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		4)Nurul Alam Choudhury
		Address of Applicant :Department of Chemistry, Nagaland University, Nagaland, India, 798627 Zunheboto -----

(57) Abstract :

The present invention relates to a green, single-step synthesis of a borax-crosslinked chitosan hydrogel membrane electrolyte (BCCHME), achieved through dual ionic and covalent crosslinking. The optimized BCCHME demonstrates 182% water uptake, 14.65% dissolution ratio, and 16.59% crystallinity. FTIR and elemental analysis confirm its composition. It exhibits high ionic conductivity (7.03×10^{-4} S cm⁻¹), a transference number of 0.93, and electrochemical stability up to 2.24 V. A solid-state EDLC using BCCHME and Black Pearls carbon electrodes achieves a maximum areal capacitance of 378 mF cm². The invention successfully powers a 1 V LED for 1.83 minutes. These results emphasize BCCHME's potential as a biodegradable and efficient electrolyte for sustainable energy storage solutions.

No. of Pages : 29 No. of Claims : 9

(12) PATENT APPLICATION PUBLICATION

(21) Application No. 202531080608 A

(19) INDIA

(22) Date of filing of Application : 26/08/2025

(43) Publication Date : 05/09/2025

(54) Title of the invention : Oxalate–Crosslinked Quasi-Solid Chitosan Hydrogel Membrane Electrolyte for Durable Supercapacitors

(51) International classification : H01G0011620000, H01G0011600000, H01G0011320000, H01G0011520000, C08G0018320000

(86) International Application No : NA

Filing Date : NA

(87) International Publication No : NA

(61) Patent of Addition to Application Number : NA

Filing Date : NA

(62) Divisional to Application Number : NA

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(57) Abstract :

The present invention relates to a sustainable oxalate-crosslinked chitosan membrane electrolyte (OCCME) is created using Potassium oxalate without the need for further ingredients. High water uptake (208%), a dissolution ratio of 17.80%, and a tensile strength of 55.04 MPa are characteristics of the membrane. Its semi-crystalline shape, thermal stability, and ionic complexation are confirmed by FTIR, XRD, SEM, and TGA investigations. The OCCME has an electrochemical stability window of 2.10 V and remarkable ionic conductivity (4.84 mS cm⁻¹). OCCME-based electric double layer capacitors (EDLCs) have a long cycling durability (46,000 cycles at 2 mA cm⁻²) and a high areal capacitance of 300.80 mF cm⁻². A 1V LED light is successfully powered by the EDLC prototype, demonstrating its usefulness as an energy storage device.

No. of Pages : 27 No. of Claims : 7

(12) PATENT APPLICATION PUBLICATION

(21) Application No. 202531080606 A

(19) INDIA

(22) Date of filing of Application : 26/08/2025

(43) Publication Date : 05/09/2025

(54) Title of the invention : HPO42--Crosslinked Chitosan Hydrogel Membrane as Quasi-Solid Electrolyte for Durable Electric Double Layer Capacitors

(51) International classification : H01G9/022, H01G9/035, H01G11/56, H01G11/64, H01G11/72, C08B37/08, C08K3/011, C08L5/08
(86) International Application No : NA
Filing Date : NA
(87) International Publication No : NA
(61) Patent of Addition to Application Number : NA
Filing Date : NA
(62) Divisional to Application Number : NA
Filing Date : NA

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(57) Abstract :
The present invention relates to a stable, three-dimensional hydrogel network is created by ionic crosslinking a chitosan hydrogel system with disodium hydrogen phosphate (DSHP). This system is utilized in electric double layer capacitors (EDLCs) as a quasi-solid chitosan hydrogel membrane electrolyte (CsHME). The CsHME exhibits a breakdown voltage of 2.3 V, a high ionic conductivity of 4.07 mS cm⁻¹, and an ionic transference number of 0.98. The energy density of 85.97 μW h cm⁻², power density of 5000 μW cm⁻², and peak areal capacitance of 619 mF cm⁻² are among the remarkable metrics attained by EDLCs employing CsHME. A 1-volt LED bulb is effectively powered for more than two minutes during long-term cycles, demonstrating exceptional durability and suggesting its potential as a sustainable electrolyte for next-generation EDLCs

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