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Master of Science Thesis

**Bio-Based Cellulose Acetate Membranes for
Sustainable Processes: Synthesis, Characterisation,
and Technological Applications**



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*To my grandmother,
with whom I hold the promise of this degree,
wherever you may be.*

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Abstract

Polymeric membranes are widely used across various industrial sectors, ranging from separation processes to energy storage systems. However, conventional membranes are typically fabricated from fossil-derived polymers and involve the use of toxic, hazardous solvents. Due to increasing environmental concerns and more stringent regulations, significant research is directed towards the development of sustainable polymeric membranes. In this context, cellulose acetate (CA) represents a highly promising bio-based alternative owing to its renewable origin, biodegradable nature, and excellent film-forming properties.

This thesis focuses on the preparation and characterisation of sustainable CA membranes, as well as their evaluation in different technological applications. The membranes were synthesised via the phase inversion method, specifically non-solvent induced phase separation (NIPS). To ensure an eco-friendly approach, traditional solvents were replaced by green solvents, namely dimethyl sulfoxide (DMSO) and γ -valerolactone (GVL). Furthermore, the influence of operational parameters and the addition of citric acid (CAc) as a bio-based additive on the resulting membrane properties was investigated.

Initially, the precursor solutions were analysed through viscosity measurements and Relative Energy Density (RED) calculations. Subsequently, the synthesised membranes underwent morphological and chemical characterisation using Scanning Electron Microscopy (SEM) and Attenuated Total Reflectance Fourier-Transform Infrared (ATR-FTIR) spectroscopy.

Based on the preliminary electrochemical evaluation, a clear distinction was made for the subsequent technological applications depending on the casting solvent employed. On one hand, membranes fabricated using DMSO were selected and investigated for energy storage applications. These were evaluated as sustainable separators for supercapacitors, examining their performance via cyclic voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS), and a float test. Additionally, the CA polymer was directly cast onto Lithium Manganese Oxide (LMO) electrodes to prevent the dissolution of active material, with the coating performance evaluated using SEM, EIS, and CV. On the other hand, membranes prepared with GVL were evaluated for potential use in reverse electrodialysis systems. This separation performance was assessed by EIS and the open-circuit voltage (OCV) in an H-cell configuration, utilising different concentrations of potassium chloride (KCl) solutions in each half-cell.

Overall, this research systematically correlates the formulation of CA membranes with their structural and performance characteristics, investigating the specific suitability of DMSO-based formulations for energy-storage applications and GVL-based systems for salinity gradient energy conversion.

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Chapter 1

Introduction

The escalation of global temperatures and the disruption of climatic patterns are largely driven by anthropogenic activities, most notably the extensive reliance on fossil fuels [1]. To mitigate these impacts, international frameworks, such as the Paris Agreement, have established ambitious targets to limit the global temperature increase to 1.5 °C. These commitments include reducing greenhouse gas emissions by 45% by 2030 and achieving net-zero emissions by 2050 [2–4]. Realising these environmental objectives requires a fundamental transition towards sustainable energy systems, where energy storage and generation technologies are essential for integrating intermittent renewable resources and enhancing grid stability[5,6].

Among the various technologies driving this green transition, energy storage devices—such as supercapacitors and batteries—and energy harvesting systems play a pivotal role [6,7]. However, their overall sustainability is often compromised by the materials comprising their internal components. Elements such as polymeric membranes, used as separators and barrier layers, frequently rely on non-renewable, petroleum-derived resources and hazardous processing compounds. To truly align with global sustainability goals, there is a critical need to develop eco-friendly alternatives across the entire device architecture [8,9].

In this context, cellulose - the most abundant biopolymer on Earth – emerges as an ideal candidate for this purpose, offering a unique combination of renewability, non-toxicity, and intrinsic chemical stability [6,10]. In particular, cellulose acetate (CA), a highly processable derivative, has demonstrated excellent potential in the fabrication of robust, functional, and sustainable membranes [9].

However, the fabrication of CA membranes often involves toxic, dipolar aprotic solvents such as N,N-dimethylformamide (DMF) or 1-methyl-2-pyrrolidone (NMP), which are increasingly scrutinised for their environmental impact [8]. Consequently, this thesis investigates the development of sustainable CA membranes fabricated via the non-solvent induced phase separation (NIPS) method, employing green, bio-derived solvents such as dimethyl sulfoxide (DMSO) and γ -valerolactone (GVL) [9,11].

Furthermore, this research examines the influence of incorporating citric acid (CAc) as a renewable additive to strategically tailor membrane porosity, structural cross-linking, and mechanical resilience [[5,12]. Finally, to validate their practical viability, the fabricated membranes are evaluated across diverse technological applications related to energy storage and harvesting.

The thesis is structured as follows:

Chapter 2 provides a comprehensive review of the state of the art, detailing the transition from conventional to sustainable polymeric membranes, the fundamental principles of the phase inversion process, and the properties and characterisation of cellulose acetate, focusing on its role in diverse technological fields such as supercapacitors for energy storage and reverse electrodialysis for energy harvesting.

Chapter 3 details the materials and experimental techniques utilised during this research, encompassing the membrane fabrication process with green solvents and the subsequent physicochemical, morphological, and electrochemical characterisation methods.

Chapter 4 presents the experimental results and discussion. It evaluates the thermodynamic and rheological behaviour of the precursor solutions and assesses the impact of solvent choice and additive concentration on the final membrane morphology. The chapter concludes by discussing the performance of the membranes when integrated into the target devices.

Chapter 5 sets out the principal conclusions derived from the experimental findings of this thesis. Furthermore, it outlines prospective directions for future research, identifying opportunities to further refine the membrane characteristics and advance their integration into sustainable technologies.

Chapter 2

State of the art

Cellulose acetate has emerged as a promising eco-friendly alternative to fossil-based polymers, combining biodegradability and renewable origins with excellent flexibility and film-forming properties ideal for sustainable membrane fabrication [10,13]. Current research focuses on optimizing the fabrication of these CA membranes by replacing hazardous solvents with green alternatives [14,15] and employing advanced phase separation techniques to precisely control membrane structure [6,9]. Understanding the interplay between polymer concentration, solvent parameters and fabrication conditions is crucial for tailoring the morphological and physical characteristics to meet rigorous industrial standards [9,16]. The resulting membranes can find applications in diverse areas including energy generation and storage, gas separation processes and water remediation [17].

2.1. Membranes

Fundamentally, a membrane is a thin, selective interface that regulates the transport of chemical species between two contacting phases. Membranes can be grouped into dense (symmetric) and porous types. Porous membranes can further be classified according to their pore size (macro-, meso-, or microporous) or by the uniformity of their structure, being either fully porous and symmetric or asymmetric. The most widely used materials in membrane fabrication are organic polymers, but inorganic materials (such as glasses, metals, ceramics, carbon and zeolites) can also be used [14,16]. The most relevant membrane types are described in the following section.

2.1.1. Types of Membranes

Isotropic membranes

Isotropic membranes are characterised by uniform structural transport properties throughout their entire thickness. Within this category, microporous membranes and dense (non-porous) membranes are the two principal types. Microporous membranes contain interconnected pores with a defined size distribution and achieve separation primarily by molecular or particulate size exclusion, making them suitable for microfiltration and ultrafiltration processes. In contrast, dense membranes lack discrete pores, and mass transport occurs through a solution-diffusion mechanism driven by pressure,

concentration, or electrical potential gradients. Selectivity in dense membranes depends on the relative solubility and diffusivity of permeating species within the membrane material, enabling the separation of molecules with similar sizes, as in gas separation, pervaporation and reverse osmosis applications[16].

Anisotropic membranes

Anisotropic membranes exhibit a non-uniform structure composed of an ultrathin selective layer supported by a thicker, porous substructure that provides mechanical stability. The separation performance and permeation flux are governed exclusively by the thin active layer, while the support minimizes transport resistance. Anisotropic membranes can be classified into integrally skinned membranes, in which the selective layer and support are formed from the same material in a single fabrication step, and composite membranes, where the selective layer and the support are made from different material and manufactured separately. Owing to their high permeability and efficient use of material, anisotropic membranes are employed in most industrial membrane separation processes[16].

2.1.2. Conventional Polymeric Membranes

Polymers are typically categorized based on their origin (bio-based or fossil-based) and their biodegradability, as illustrated in *Figure 2.1*. Currently, membrane fabrication relies predominantly on synthetic polymers such as polysulfone (PSf), polypropylene (PP) and polyvinylidene fluoride (PVDF), among others. These synthetic materials belong to the class of fossil-based, non-biodegradable polymers and have historically dominated membrane fabrication due to their superior structural integrity, mechanical strength, and flexibility. Furthermore, their good chemical stability, specifically their tolerance to broad pH ranges and high chlorine concentrations, have made them the material of choice [15,18].

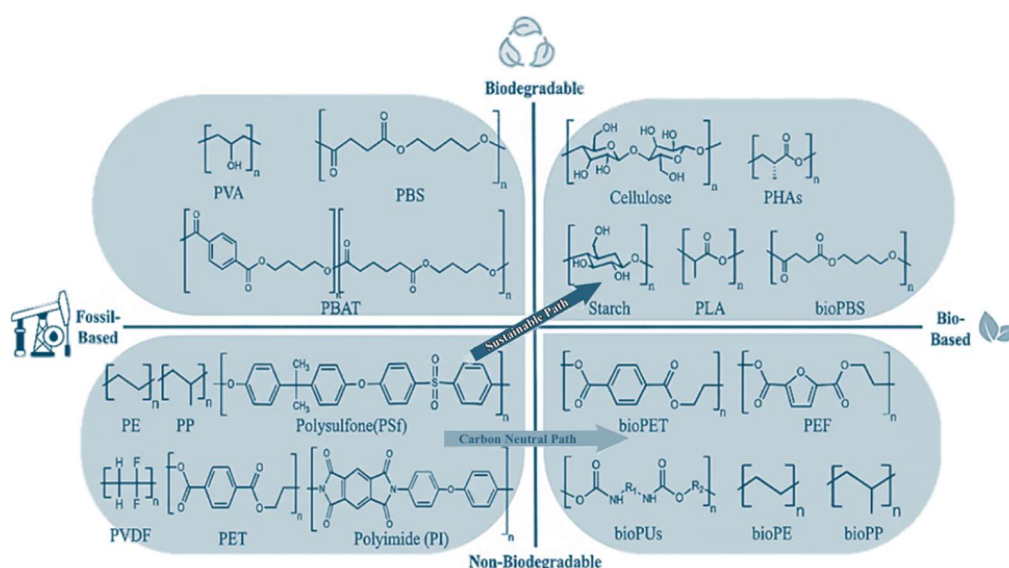


Figure 2.1. Classification of polymers used for membrane fabrication: biodegradable versus non-biodegradable; bio-based versus fossil-based (Adapted from Kim et al., 2024).

Transitioning from fossil-derived polymers to bio-based alternatives represents a step toward carbon neutrality; however, the most sustainable strategy is achieved by shifting toward materials that are both bio-based and biodegradable [15].

2.1.3. Sustainable Polymeric Membranes

Bio-based and biodegradable polymers that are currently being studied for the green transition include cellulose, starch, chitin, polyhydroxyalkanoates (PHAs), polylactide (PLA), and bioderived poly(butylene succinate) (bioPBS) [15,18].

As cellulose, one of the most abundant polymers in nature, represents a promising alternative material due to its specific properties, it is examined in greater detail in the following section. Particular emphasis is placed on one of its derivatives, cellulose acetate, which is the selected material for membrane synthesis of this thesis.

Cellulose and cellulose acetate

Cellulose ((C₆H₁₀O₅)_n) is the most prevalent polysaccharide on the world, serving as the primary structural component of plant cell walls. This high molecular weight homopolysaccharide is made up of linear β-1,4-linked D-glucose units, and its structure contains numerous hydroxyl (-OH) groups. These functional groups allow the polymer chains to form both intra- and intermolecular interactions, leading to strong networks of hydrogen bonds (*Figure 2.2*). These strong hydrogen bonds, within and between chains, largely determine the resulting properties of cellulose and its derivatives [10,19].

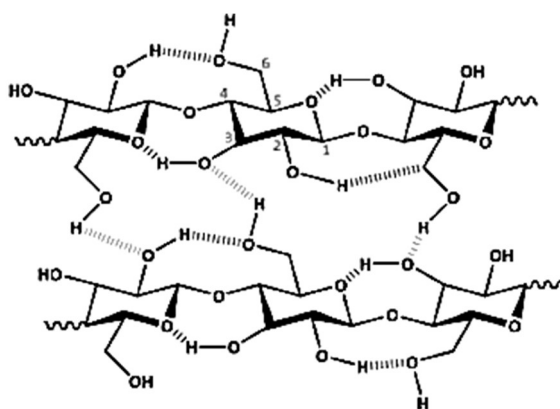


Figure 2.2. Chemical structure of native cellulose [19].

Cellulose lack of toxicity and favourable chemical and physical properties, such as low density, high porosity and a large specific surface area, make it stand out as a promising alternative of the most widely polymers used to date, for instance polyether sulfone (PES) and polyvinylidene fluoride (PVDF), which derive from non-renewable fossil sources. However, one limiting factor for its processability and industrial-scale application is its limited solubility in water and other common solvents due to the strong hydrogen bonds. In this regard, the presence of hydroxyl groups may give the possibility to be functionalized by specific chemical modification to achieve requested properties. Among these, cellulose acetate stands out as the most widely used and industrially relevant [9,19].

Cellulose acetate (CA) is an insoluble cellulose derivative obtained by the partial acetylation of cellulose with an acetyl content ranging from 29% to 44.8%, encompassing mono-, di-, and triacetate forms. It is

the most significant cellulose ester and is obtained by chemical reaction of cellulose, acetic anhydride and acetic acid in the presence of sulfuric acid (H_2SO_4) (Figure 2.3). A range of CA molecular weights is commonly used for membrane fabrication, typically including $30.000 \text{ g.mol}^{-1}$, $50.000 \text{ g.mol}^{-1}$ and $60.000 \text{ g.mol}^{-1}$ [9,17,20].

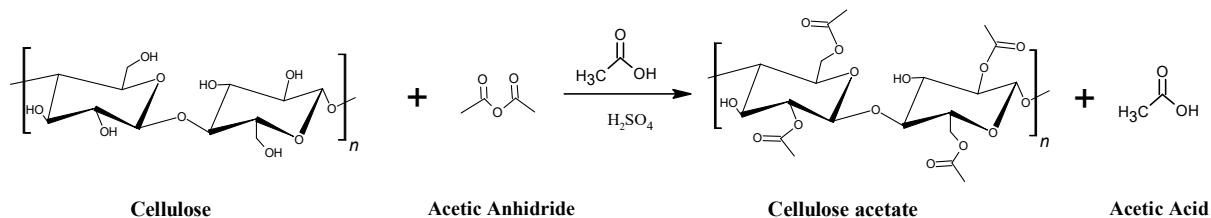


Figure 2.3. Preparation and chemical structure of cellulose acetate (Adapted from [20])

Challenges of Sustainable Polymeric Membranes

To date, a major challenge is the development of bio-based and biodegradable membranes whose attributes for industrial applications are competitive with those of conventional fossil-based polymers. This includes achieving low manufacturing cost, excellent thermal and chemical stability, good mechanical resistance, and high versatility [18]. Furthermore, to meet a sustainable process, these properties must be achieved using alternative, environmentally friendly solvents, thereby moving away from conventional membrane manufacturing, which relies on toxic, dipolar aprotic and petroleum-based solvents [21].

2.2. Cellulose acetate membranes

Characterised by its flexibility, biodegradability, environmental friendliness and nontoxic behaviour, CA is the most preferred biopolymer in membrane manufacturing. It stands out for its exceptional selectivity, good hydrophilicity, water permeability, porosity, low fouling tendency, strong mechanical properties and ease of processing. In particular, the possibility of dissolving CA in green solvents enables the production of fully bio-based membranes through the phase inversion technique [9,10,17].

The previously mentioned characteristics, together with its relative low cost, make cellulose acetate membranes suitable for different applications in a wide range of industries such as water and wastewater treatment, pharmaceutical and biotechnology industries, food industries, biomedical applications and energy generation. Their applications include processes such as microfiltration, ultrafiltration, nanofiltration, forward osmosis, reverse osmosis, gas separation, pervaporation, ion exchange membranes, etc [13,17].

2.2.1. Cellulose acetate membranes synthesis: phase inversion methods

Several methods are available for membrane preparation, depending on the desired form (plate, tube, film, hollow fiber) and structure. For the fabrication of polymeric membranes, phase inversion methods are among the most widely used techniques. Phase inversion refers to the transition from a single-phase casting solution to a two-phase system consisting of a polymer-rich phase, which forms the solid

membrane matrix, and a polymer-lean phase, which will lead to the formation of pores in the solidified material [13,22].

Four main phase inversion techniques can be distinguished: solvent evaporation induced phase separation (EIPS), vapor-induced phase separation (VIPS), thermally induced phase separation (TIPS), and non-solvent induced phase separation (NIPS). Combination of these methods are also employed [8,9]. These different membrane fabrication techniques are briefly presented in this section, with particular emphasis on non-solvent induced phase separation (NIPS), which is widely regarded as the dominant method to produce polymeric membranes, and is adopted on the experimental part of this thesis. Special attention is given to solvent selection and pore morphology control.

Solvent evaporation induced phase separation (EIPS)

In this process, the polymer is dissolved in a mixture of solvent and non-solvent until a homogeneous solution is obtained. The solvent must exhibit a higher volatility than the non-solvent, as its evaporation triggers phase separation leading to the formation of a porous film because of the de-mixing within the solvent-non-solvent mixture. By adjusting the polymer concentration and the composition of the solvent-non-solvent mixture, the resulting pore structure can be controlled. Although this method offers good reproducibility, a key limitation lies in the difficulty of identifying suitable solvent and non-solvent pairs [8].

Vapor-induced phase separation (VIPS)

In VIPS process, the freshly cast polymer film is exposed to a vapor atmosphere composed of a non-solvent, which is sometimes saturated with part of the original solvent to slow down the onset of precipitation. Phase separation is triggered as the non-solvent vapor is first adsorbed on the surface of the film and then diffuses into it. This controlled diffusion typically leads to membranes with a more symmetric architecture and a higher degree of microporosity compared to those produced by direct immersion precipitation [22].

Thermally induced phase separation (TIPS)

Pore generation in TIPS relies on controlled removal of thermal energy. In this approach, the polymer solution is heated to a temperature above the polymer's melting point (T_m) and subsequently cooled in a regulated manner to induce phase separation, leading to the formation of a continuous polymer-rich phase. The dispersed phase grows through droplet coalescence until the system reaches the solidification temperature. Once solidified through polymer crystallization, the diluent is extracted using an appropriate extraction medium. It is recommended to use solvents that combine high boiling temperatures with low vapor pressures [19]. The ultimate pore structure is governed by the thermodynamic properties of the polymer-diluents system manifested in the dope during the quenching process, which may lead to liquid-liquid (L-L) or solid-liquid (S-L) phase separation. Specifically, strong polymer-diluent interactions typically promote S-L phase separation, resulting in the formation of spherulitic structures, whereas weaker interaction favour L-L de-mixing, giving rise to cellular or network-like morphologies that may be closed or partially open. In contrast to L-L phase separation, S-L phase separation occurs at considerably lower temperatures and involves a comparatively simpler membrane formation process. Compared to NIPS method, membranes fabricated using TIPS usually exhibit superior mechanical strength, a more uniform pore size distribution, and greater controllability of the microstructure [23].

Non-solvent induced phase separation (NIPS)

In the NIPS process, the polymer is first dissolved, and the resulting solution is deposited onto a substrate, after which it is immediately transferred to a coagulation bath. The non-solvent acts as pore former as solvent molecules diffuse outward, ultimately producing a thermodynamically stable porous network. Then, the membrane film is collected and dried in an oven to eliminate any remaining solvent residues. This method typically yields materials with porosities of around 70%, pores smaller than 1 μm and high tensile strength. However, the membranes obtained are typically asymmetric, consisting of a dense skin layer and a porous substructure [19].

The kinetics of this method are primarily driven by the chemical potential gradient across the interface, which affects the exchange rate of solvent outflow and non-solvent inflow. Upon the immersion of the casting solution in the coagulation bath, the chemical potential gradient is the largest at the polymer-non-solvent interface, resulting in a rapid initial exchange rate. However, this rate declines over time due to two main factors: the levelling of concentration profiles (*Figure 2.4*) and the formation of a dense top-layer that creates a barrier to mass transfer. Furthermore, the exchange kinetics are governed by physical properties such as the molecular size of the diffusing species and the viscosity of the surrounding medium. There are two possible pathways that liquid-liquid de-mixing can follow after contact of the polymer solution with the non-solvent (*Figure 2.5*): if phase separation is triggered immediately upon contact with the bath, the process is referred to as “instantaneous” de-mixing. In contrast, “delayed” de-mixing is characterised by an induction period, during which the film accumulates sufficient non-solvent prior to the formation of pores. While instantaneous de-mixing leads to membranes with a porous skin and a sub-layer characterised by large, finger-like macro voids, “delayed” de-mixing promotes the formation of a dense top layer and sponge-like formations at the substructure [14,22,24].

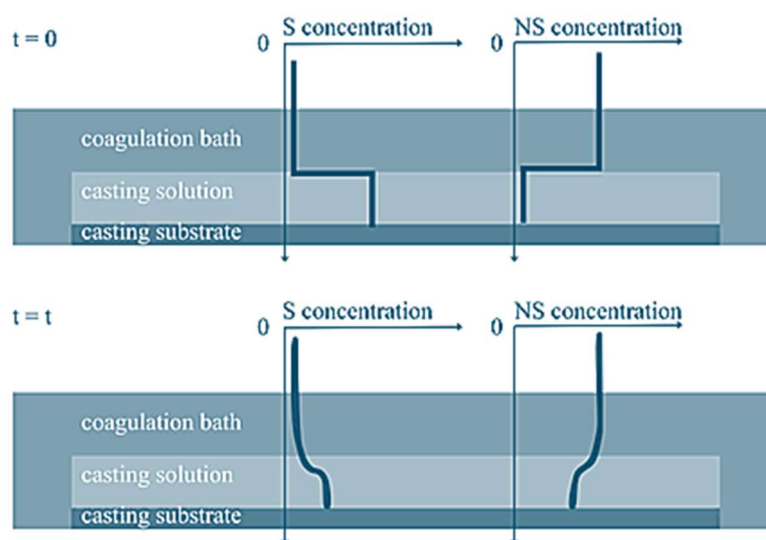


Figure 2.4. Concentration profiles of solvent (S) and non-solvent (NS) during immersion precipitation, immediately after immersion in the non-solvent (top) and after a time t (bottom) for a casting solution that contains some NS. (Adapted from [22])

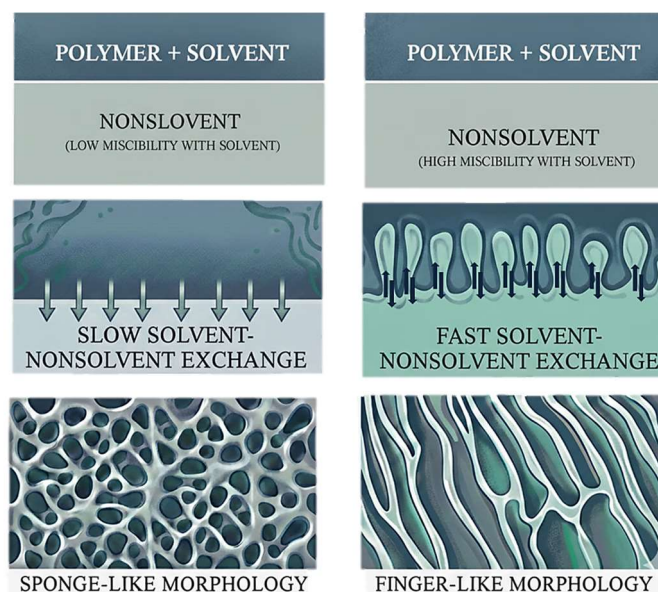


Figure 2.5. Two kinds of membrane structures obtained using different solvent/non-solvent exchange rates (Adapted from [14]).

2.2.2. Operational parameters

Independently of which phase inversion technique is adopted, the pore's dimension and morphology are influenced by a wide range of parameters, including the polymer concentration, the temperature of the polymer solution, the type of solvent and non-solvent employed, the thickness of the cast polymer film, the conditions of the environment or coagulation bath, the composition of the polymer mixture and use of additives, the presence of added salts, the exposure time to air humidity and the nature of the support material [13,20]. In particular, careful attention must be given to the selection of solvent for polymer dissolution, as it plays a critical role in determining the final membrane characteristics, directly affecting membrane properties such as morphology, porosity, mechanical strength and pore size [21].

2.2.3. Traditional solvents and green solvents

Traditional solvents

The most used solvents for membrane preparation at both industrial and laboratory scales to date are organic amide solvents such as N,N-dimethylformamide (DMF), 1-methyl 2-pyrrolidone (NMP) and N,N-dimethylacetamide (DMAc) due to their good solubility of common membrane polymers. However, these petroleum derived solvents are classified by the European Chemical Agency (ECHA) as substance of very high concern, particularly because of their reproductive toxicity, and are subject to restrictions under REACH Annex XVII for manufacture, use and commercialization [11,25].

This makes it evident that, in order to achieve a greener membrane preparation, attention must be directed toward the solvent selected to perform the phase inversion method. This is not a minor factor, considering that membrane application in industrial processes is steadily growing. In fact, the actual annual production of contaminated wastewater in membrane manufacturing reaches over 50 billions of litres [9,11].

Green solvents as alternatives for traditional solvents

To be in concordance with principles 5 and 7 of the 12 principles of green chemistry, safer solvents and auxiliaries together with the use of renewable feedstock should be implemented [11,14].

Bio-based solvents fundamentally differ from traditional ones on its chemical structure. While petroleum-derived solvents consist mainly of hydrocarbons, bio-feedstocks are generally characterised by a high oxygen content. These green solvents are produced by chemically or physically converting plant-derived feedstocks such as sugars, starches, oils and lignocellulosic materials originating from forestry, agricultural crops or organic waste. They are nontoxic, carbon-neutral and environmentally friendly [14].

As the characteristics of the solvent (density, viscosity, polarity) highly impacts on the final structure and properties of the membrane, the alternative solvents must reach the desired solvent power, membrane morphology and performance. A green solvent used for membrane fabrication should ensure a uniform polymer dope solution without affecting the casting process or the optimized membrane preparation protocol (functionality). It should rely on reusable resources whenever possible and be water soluble to enable polymer precipitation via the phase inversion technique. Therefore, it is important to determine whether the thermodynamic and kinetic properties of the phase separation process with the selected solvent achieve the morphology required to meet the desired membrane properties and performance for a given application [14,26].

There are different categories of bio-based solvents proposed to replace the conventional ones, such as cellulose and sugar-based, non-ionic synthetic organic solvents, organic carbonates, lactic acid derivatives and green solvent mixtures, such as ionic liquids and deep eutectic solvents [14].

This thesis will further study the performance of membranes fabricated with two different alternative solvents: γ -valerolactone (GVL) and dimethyl sulfoxide (DMSO), whose characteristics are described in the following paragraphs.

GVL is part of the cellulose and sugar-based solvents, as it is a bio-derived molecule of lignocellulosic biomass. It is a polar aprotic solvent, which makes it soluble in water, and it presents a high boiling point of 208 °C at 1 atm. As shown in *Figure 2.6*, the solvent can be produced by two principal synthetic pathways: (i) the conversion of cellulose-derived hydroxymethylfurfural (HMF) into levulinic acid, and (ii) the production of levulinic acid via furfural derived from hemicellulose. As a drawback, its application in membrane preparation is limited to relatively low temperatures due to its instability in the presence of water at temperatures around 100 °C, where it can directly form 4-hydroxyvaleric acid (4-HVA) [14,27].

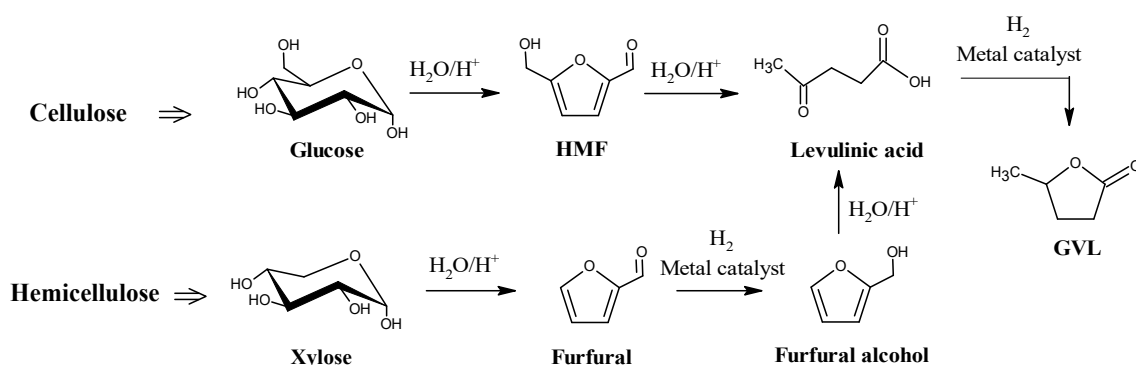


Figure 2.6. Synthetic pathways for GVL production from lignocellulosic biomass (adapted from [27]).

DMSO is a non-ionic synthetic organic solvent. It is a polar aprotic solvent, miscible in water, and a low-volatility compound due to its high boiling point of 189 °C at 1 atm and low vapor pressure (0.6 mmHg at 25 °C). Industrially, DMSO is produced by the controlled oxidation of dimethyl sulfide (DMS), which is primarily obtained as a by-product of the Kraft pulping process of lignocellulosic biomass in the paper industry (*Figure 2.7*). This solvent is structurally similar to conventional aprotic solvents like DMF, NMP and DMAc, but its biodegradability and low intrinsic toxicity for animal and human health make it a comparatively greener alternative [28–30].

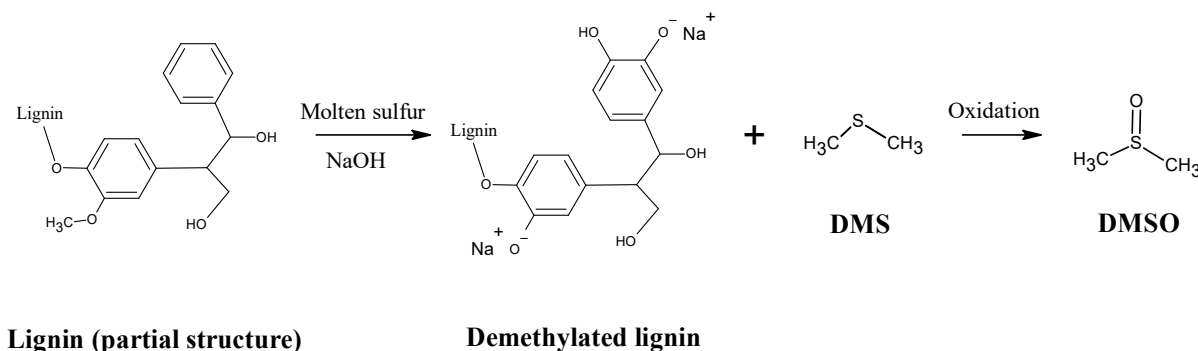


Figure 2.7. Reactions for DMSO production from lignin [30].

2.2.4. Additives

One challenge to address when producing membranes by NIPS is the formation of macro voids, which can severely compromise the mechanical stability of the separator. To tailor the final membrane structure and performance, various organic or inorganic components can be introduced as additives to the casting solution. Depending on their specific nature and concentration, these additives can alter the viscosity and thermodynamics of the polymer solution, effectively acting as pore-forming agents or suppressing macro void formation by delaying the de-mixing process [9,22].

A promising organic additive for this role is citric acid (CAc). As an environmentally friendly and renewable compound that is extracted from fermented citrus fruits, CAc functions synergistically as both a plasticizer and a cross-linking agent within the CA matrix. During the NIPS process, the hydrophilic properties of citric acid facilitate the penetration of water when used as non-solvent, which plays a pivotal role in the resulting porous structure [5,12].

The interplay between CAc concentration and membrane porosity has been recently investigated. It was found that higher concentrations of the additive enhance the pliability of the CA chains through a pronounced plasticisation effect, which results in increased overall porosity and the formation of larger pore sizes. Conversely, at lower concentrations, citric acid disperses more uniformly within the polymer network, subtly altering the solvent/non-solvent exchange kinetics and leading to a denser structure with smaller pores. Furthermore, the incorporation of CAc leads to the esterification of the hydroxyl groups – particularly under elevated temperatures-, which induces enduring cross-linking. This reaction significantly improves the thermal stability and mechanical resilience of the resulting membranes[12].

2.3. Cellulose acetate membranes applications

The excellent film-forming capabilities, high tensile strength, and remarkable chemical stability of CA make it a highly promising alternative for more sustainable processes. This section reviews the main applications of cellulose acetate reported in the literature. Given the scope of this thesis, particular attention is paid to its use in energy-related applications, specifically in supercapacitors and reverse electrodialysis systems.

2.3.1. Supercapacitors

Supercapacitors (SCs) are devices that have emerged as a key technology in the field of energy storage systems (ESSs), of particular interest for dealing with the intermittence of renewable energy sources. They are an efficient alternative to traditional batteries in applications requiring high power density ($5\text{--}50\text{ kW kg}^{-1}$), fast charge/discharge cycles (in seconds), and long service life ($>10^4$ cycles). However, this is achieved at the expense of lower energy densities ($3\text{--}40\text{ Wh kg}^{-1}$) than Li-ion batteries. The major difference is that SCs store charge electrostatically at the electrode-electrolyte interface. This process store energy without involving chemical reactions, such as those in batteries, allowing for significantly faster energy transfer and higher cycle life [31,32].

A diagram of a common SC setup is shown in *Figure 2.8*. It consists of two electrodes with a porous separator placed between them, all immersed in a liquid electrolyte. The primary limitation of this design is the mobility of ions through both the separator and the electrodes [32,33].

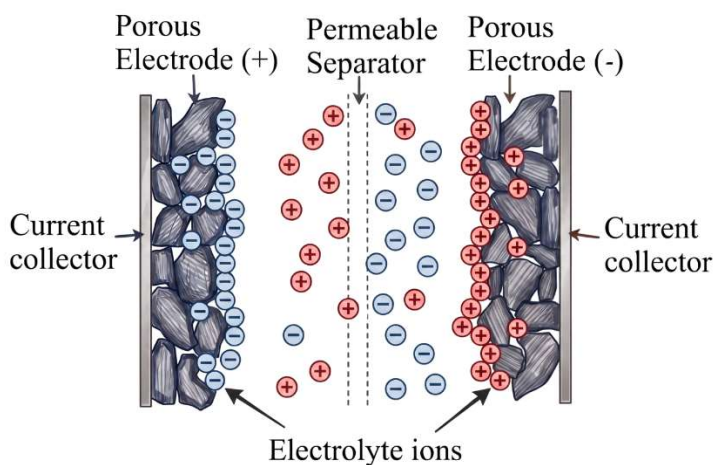


Figure 2.8. Schematic diagram of a supercapacitor configuration and distribution of ions at the charged state (Adapted from [33]).

SCs can be classified into three categories based on their charge storage mechanism: electric double-layer capacitors (EDLCs), pseudocapacitors, and hybrid capacitors.

EDLCs store energy through the formation of an electronic double layer at the interface between high surface area electrodes, commonly carbon-based materials, and the electrolyte. The electrodes material

plays a fundamental role as its surface area influences directly on the achieved capacitance. On the other hand, the choice of the electrolyte has a direct impact on the performance of the supercapacitor. When a potential is applied, electrolyte ions diffuse through the separator and accumulate on the electrode surface that is oppositely charged. This redistribution of charges occurs simultaneously on both electrodes, creating joined double layers that are electrostatically balanced. Therefore, the distance between opposite charge distributions is reduced and, as it is inversely proportional, capacitance is increased. This non-faradaic mechanism enables very fast ion adsorption and desorption, resulting in high power density but relatively low energy density [32].

According to the Stern model (Figure 2.9), which combines Helmholtz model and Gouy-Chapman model, the electric double layer consists of two distinct regions: the compact or Stern layer, that can be subdivided into the inner Helmholtz plane (IHP) and the outer Helmholtz plane (OHP), and the diffuse layer. The IHP corresponds to the layer of specially adsorbed ions that are in direct contact with the electrode surface. Beyond this region lies the OHP, which represents the plane of closest approach of solvated ions that are attracted to the electrode by electrostatic forces but are not specifically adsorbed. This region also delimitates the beginning of the diffuse layer, which as described by Gouy and Chapman, consists of a continuous distribution of ions driven by thermal motion [34].

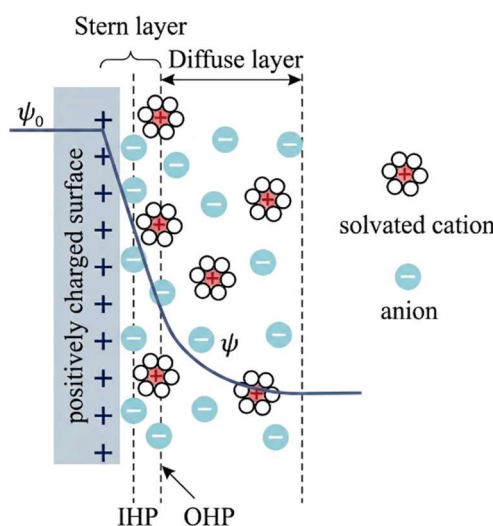


Figure 2.9. Stern model, showing the electric double layer. ψ_0 and ψ are the potentials at the electrode surface and the electrode/electrolyte interface, respectively (Adapted from [34]).

The separation distance between the electronic charges on the electrode and the ionic charges in the IHP and OHP, together with the dielectric properties of the electrolyte, determines the capacitance of the electric double layer. A smaller charge separation distance and higher accessible surface area result in higher capacitance [32].

Pseudocapacitors employ fast and reversible faradaic redox reactions occurring at or near the electrode surface, in addition to electrostatic charge accumulation. Typically, transition metal oxides (e.g., RuO_2 , MnO_2)/sulfides or conducting polymers (e.g., polyaniline) are employed as electrodes, enabling charge storage via redox processes without the phase transformations characteristics of batteries. This mechanism allows to achieve 10-100 times higher specific capacitance than EDLC, resulting in improved energy density while maintaining high power capability. However, the repeated volumetric expansion and contraction of the electrode material during charge-discharge cycling can lead to limited mechanical stability and operational lifetime [7,32].

Hybrid supercapacitors aim to combine the advantageous properties of both EDLCs and pseudocapacitors into a single device. This can be achieved through several designs, where the goal is to synergistically enhance both the energy density (from the faradaic component) and the power density and cyclability (from the capacitive component), for overcoming the traditional energy density of supercapacitors without sacrificing their high-power performance [32,33].

Regardless of the type of SC, performance is critically influenced by diverse factors such as the electrode materials, the electrolyte, separator and current collectors [7].

Cellulose acetate in supercapacitors

In recent years, CA has gained particular attention as a promising material for flexible supercapacitors (FSCs), driven by the growing demand for safe, compact and mechanically durable energy storage devices (ESDs) in portable and wearable electronics. The biggest challenge in this application is to find energy storage materials able to exhibit improved energy and power densities, larger lifetimes and sustainability, while preserving mechanical flexibility and cost-effectiveness at industrial scale. Advanced membrane materials, like cellulose acetate, present opportunities for a wide range of applications including electrodes, binders, electrolytes, separators and in the case of sandwich-shaped FSCs, as current collectors substrate, potentially enabling more efficient and environmentally friendly SC designs [10]. Even if this thesis focuses on its use as separator and as electrode coating, other prevalent roles of CA in FSC reported in the literature are detailed below.

- **Electrodes:** Cellulose and its derivatives can act as effective precursors or structural matrices precursors for the addition of active materials or for direct conversion into carbon-based materials. As seen on Section 2.3.1, the electrode material depends on the type of SC. For EDLCs, carbon-based materials (such as graphene, carbon nanotubes and activated carbon) are commonly used. On this approach, a recent proof-of-concept demonstrated that CA films can be used as precursors for laser-induced graphene (LIG), where local photothermal effects result in in-situ conductive graphene with a 3D interconnected pore structure [35]. This alternative resolves the undesired phenomena of graphene's self-stacking between nanosheets, which affects the electrochemical performance. For pseudocapacitors, transition metal oxides/sulfides are commonly utilised for FSCs. Nonetheless, the propensity to aggregate of oxides and sulfides limits their commercial viability as electrode materials. Incorporation of cellulose has been shown to mitigate aggregation and reveal a greater exposed specific surface area, producing a substantial improvement in electrochemical performance [10].
- **Coating:** Transition metal oxides demonstrate excellent characteristics for supercapacitor applications, notably low electrical resistance and high specific capacitance. Nevertheless, the degradation of these electrodes is driven by multiple factors, including structural deterioration, binder or electrolyte decomposition, and transition metal dissolution[36]. To address these challenges and extend the lifespan of the device, this thesis investigates the use of cellulose acetate (CA) as an innovative coating for LMO-based electrodes. This protective layer aims to suppress the dissolution of metal ions into the electrolyte, thereby mitigating active material loss and the subsequent capacity fading of the electrode.
- **Separator:** hydrophilicity, high chemical stability, low environmental impact, and other advantageous characteristics make CA an interesting material to be employed as separator. The separator is a critical component on a supercapacitor, which prevents physical contact between the electrodes while enabling ionic transport and blocking electron transport. As a result, the

physicochemical characteristics of the separator influence the energy density, power density, cycle stability and safety [10,37].

Currently, commercial cellulose-based separators (Nippon Kodoshi Corp., TF40-30) are among the most used for SCs. Their advantages include high porosity, good thermal stability and environmental friendliness. However, their relatively large pore size often leads to high self-discharge rates, which limits its applicability. To overcome the limitations of commercial separators, significant progress has been made in developing advanced separator materials that align with the green transition. Among these, plant-based materials play a key role, with CA offering the best compromise between environmental capability and electrochemical performance for SCs separators. Furthermore, they are of interest for the development of gel polymer electrolytes (GPEs) for FSCs, which are integrated components that serve simultaneously as both the electrolyte and the separator [37].

- **Electrolyte:** Following common classifications, an electrolyte can be classified by its physical state (liquid, gel, or solid) or its chemical composition (aqueous, organic, or ionic liquid) [37]. In this context, CA can be employed to obtain gel polymer electrolytes (GPE) or solid polymer electrolytes (SPE). These represent an alternative to address material and chemical limitations of conventional liquid electrolytes, such as electrolyte leakage during assembly and reduced durability outside narrow operating temperatures ranges due to their inherent instability. As integrated components, they serve simultaneously as both the electrolyte and the separator. In particular, GPEs can be used for flexible devices, and, unlike SPE, they immobilize liquid electrolytes within the polymer matrix that physically separates the electrodes. Moreover, they minimize interfacial resistance and enable broader operating temperature windows. In addition, they can expand the electrochemical stability window to approximately 4-6 V, far exceeding that of aqueous electrolytes. To date, the biggest challenges of GPEs are overcoming poor compatibility at the gel-electrode interface and improving performance under extreme conditions. Furthermore, the water content in the gel electrolyte significantly influences its operating voltage and energy density [10].

The ability of CA of forming stable gels combined with its sustainability makes it a polymer of growing interest in this field. For example, a highly transparent CA-based bio gel for electrochemical devices has been investigated. On this experimental work, the optimized formulation (10 wt% CA and 1.4 M LiClO₄) exhibited high optical transparency (85% in the visible range), a wide electrochemical stability window, and an ionic conductivity of 2.3×10^{-4} S.cm⁻¹ at 25 °C, increasing to 3.0×10^{-4} S.cm⁻¹ at 80°C, matching with the minimum ideal order of magnitude. Cyclic voltammetry revealed nearly ideal capacitive behaviour, and the bio gel maintained electrochemical stability over 400 cycles. These results demonstrate the potential of CA as a sustainable GPE for supercapacitor-type applications[38].

2.3.2. Reverse Electrodialysis

Reverse electrodialysis is a technique that relies on the conversion of salinity-gradient energy - also referred to as ‘blue energy’- into electric energy. A typical reverse electrodialysis configuration consists of an alternating series of cation and anion exchange membranes positioned between an anode and a cathode. The compartments separating these membranes are alternately filled with high-salinity and low-salinity solutions. This concentration gradient establishes a potential difference across each membrane, generating an individual membrane potential. The total electric potential difference across the entire membrane stack is the sum of these individual potentials [39].

Driven by this gradient, ions undergo selective permeation from the concentrated solution to the diluted solution. Consequently, cations migrate through the cation exchange membranes towards the cathode, while anions pass through the anion exchange membranes towards the anode. To maintain electroneutrality within the electrode compartments, oxidation occurs at the anode surface, and reduction takes place at the cathode surface. As a result, electrons are transferred from the anode to the cathode via an external electric circuit. This electrical current, combined with the potential difference across the electrodes, can be harnessed to deliver electrical power to an external load [39].

Because reverse electrodialysis systems rely heavily on the performance of ion exchange membranes, these materials must exhibit high permselectivity, low resistance, and minimal fouling. Cellulose-based membranes are increasingly gaining attention in reverse electrodialysis as sustainable alternatives to conventional petroleum-based polymers. This growing interest is primarily due to their environmental friendliness, chemical stability, mechanical robustness, and ease of chemical modification[40]. Building upon this, this thesis evaluates the viability of bio-based cellulose acetate as a sustainable cation exchange membrane for such systems.

2.3.3. Other energy related applications

In lithium-ion batteries (LIBs), CA has been investigated as a component in separators because its functional groups (-OH) improve electrolyte wettability and ionic conductivity compared with conventional polyolefin separators. Incorporated into polymer matrices (e.g. polyacrylonitrile/CA with nano-hydroxyapatite), CA resin improves the mechanical performance of the separator and so, the cycle performance of the lithium-ion cells relative to traditional separators [41]. Furthermore, CA's abundant oxygen-containing functional groups contribute to improved interaction with Li^+ ions and electrolyte uptake capability, facilitating uniform lithium transport and potentially mitigating dendrite formation when combined with functional additives such as polyoxometalates [34]. The potential of CA for this application is demonstrated by work such as Arundati et al. [6], who synthesized a CA-based separator by a combination of non-solvent and thermally induced phase separation (N-TIPS). This membrane exhibited far better properties than the commercial Celgard separator.

In fuel cells, CA has been explored as a polymer matrix for proton exchange membranes due to its ability to form composite membranes with tailored proton transport properties when functionalized, for example, with sulfonic groups. In this way, the inherently low proton conductivity of unmodified CA is increased while maintaining its mechanical stability and dimensional integrity [42,43].

2.3.4. Filtration and separation applications

CA membranes are widely employed across various pressure-driven membrane processes, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), and forward osmosis (FO), depending on pore dimension and applied pressure [20].

Among these, nanofiltration – which typical pore size is between 1 nm and 5 nm - has garnered significant attention for water treatment and molecular separation by enabling the passage of certain monovalent salts while retaining larger solutes. These membranes are extensively applied in

desalination, heavy metal removal, and domestic wastewater treatment, owing to CA's intrinsic resistance to chlorine and various chemical agents [20].

For instance, nanofiltration membranes based on CA have been successfully produced using GVL as green solvent via NIPS, exhibiting a high rejection efficiency for the dye rose Bengal [11]. Similarly, the use of ethyl lactate (EL) as a biodegradable solvent, combined with polyvinylpyrrolidone (PVP) as the pore-forming agent, has proven effective in tailoring the porosity of CA membranes. Specifically, when the morphology was tailored toward the ultrafiltration range, the membranes demonstrated high efficiency in the removal of the organic dye methylene blue [9].

Despite these advantages, a primary operational challenge for pristine CA membranes in aqueous applications remains membrane fouling, which causes a significant decline in permeate flux over time. Due to the susceptibility of unmodified CA to foulant deposition and microbial attachment, extensive research in literature focuses on mitigating this issue. Various surface and matrix modification strategies, such as the incorporation of hydrophilic additives or protective coatings, are commonly explored to enhance antifouling resistance and extend the operational lifespan of the membranes[20].

Chapter 3

Materials and Methods

3.1. Materials

Cellulose acetate (CA) powder (average $M_n \sim 30,000$, 39.8 wt.% acetyl content), γ -valerolactone (GVL, BioRenewable, $\geq 99\%$), and anhydrous acetic acid were purchased from Sigma-Aldrich (USA). Dimethyl sulfoxide (DMSO, $\geq 99.9\%$, ACS grade) was obtained from Riedel-de Haën™ (Honeywell, Germany). All chemicals and reagents were of analytical grade and used as received without any further purification.

Sulphuric acid (H_2SO_4 , ACS reagent, 95-98%), sodium hydroxide (NaOH, reagent grade, $\geq 98\%$, anhydrous pellets), and sodium sulphate (Na_2SO_4 , ACS reagent, $\geq 99\%$, anhydrous free-flowing granules) were procured from sigma Aldrich. These reagents were employed as received to prepare aqueous electrolyte solutions with concentrations of 0.5M H_2SO_4 , 1M NaOH, and 0.5M Na_2SO_4 . Deionised water, also supplied by Sigma-Aldrich, was utilised as the universal solvent for all preparations.

3.2. Membrane Preparation

Membrane synthesis, schematically represented in *Figure 3.1*, was conducted via the non-solvent induced phase separation (NIPS) process. The procedure consisted in dissolving 10, 15 and 20 wt% of the CA powder in both DMSO and GVL. In some cases, citric acid was added in this instance in a mass ratio citric acid/CA equal to 0.04.

The mixture was stirred continuously for 3 hours at room temperature until a homogeneous solution was obtained, and then left rest until no air bubbles were observed. Subsequently, the polymeric membranes were prepared by doctor blade casting with a thickness of 220 μm onto a glass plate substrate, followed by immediate immersion in the non-solvent bath, which consisted of distilled water at room temperature. For CA20_DMSO membranes, the casting was also made directly onto LMO based electrodes, followed by the immersion in non-solvent as previously described.

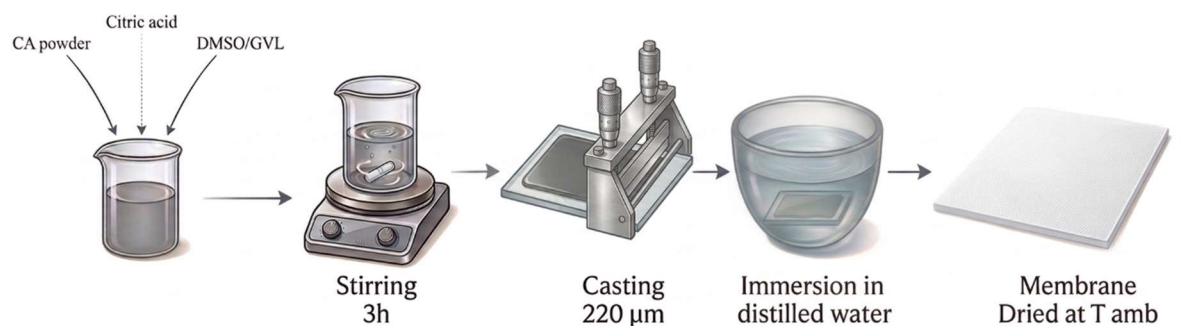


Figure 3.1. Schematic representation of the procedure followed to fabricate the cellulose acetate (CA) membranes via NIPS on a laboratory scale.

Details of the membranes produced are shown in *Table 3.1*. Each membrane ID indicates the concentration of the polymer, the solvent, and the presence of citric acid (CAc) as an additive when applicable.

Table 3.1. List of produced Membranes with their respective composition

Membrane ID	CA (wt%)	Solvent
pCA10_DMSO	10	DMSO
pCA15_DMSO	15	DMSO
pCA15_GVL	15	GVL
pCA15_DMSO_CAc	15	DMSO
pCA15_GVL_CAc	15	GVL
pCA20_DMSO	20	DMSO
pCA20_GVL	20	GVL

3.3. Electrodes preparation

Activated carbon electrodes were prepared by mixing 85 wt% activated carbon (AC) (YP 50F, Kuraray), 10 wt% carbon black (CB) (C65, Imerys) and 5 wt% hydroxypropyl cellulose (HPC) (Sigma Aldrich) in DI water and stirred until uniform dispersion. The ink was coated over a 15 µm titanium foil with wet thickness of 300 µm and dried under fume hood convection.

Lithium manganese oxide (LMO) based electrodes were prepared by mixing 75 wt% LMO powder (Sigma Aldrich) with 20 wt% CB and 5 wt% HPC in DI water and stirred until uniform dispersion. The ink was coated over a 15 µm titanium foil with wet thickness of 150 µm and dried under fume hood convection.

Electrodes were cut in 12 mm diameter, compatibly with Swagelok cells, by means of a laser cutter.

Big Fat Electrodes (BFE) were prepared by mixing 85 wt% activated carbon (AC) (YP 50F, Kuraray), 10 wt% carbon black (CB) (C65, Imerys) and 5 wt% polytetrafluoroethylene (PTFE) (60wt% dispersion in H₂O, Sigma Aldrich) in ethanol. The mixture was initially stirred at 70 °C and then mixed manually. Finally, the resulting material was pressed into sheets using a calender machine.

3.4. Characterization Tests

3.4.1. Relative Energy Density (RED)

To evaluate the miscibility of CA within the selected solvents and ensure a proper polymer dissolution prior to the phase inversion process, the relative energy density (RED) was theoretically estimated. The RED value serves as a qualitative indicator of the solubility of the polymer-solvent system, where a value below unity typically suggests favourable dissolution. RED is defined in *Equation 3.1* as the ratio of the solubility parameter distance (R_a) to the interaction radius of the polymer (R_0):

$$RED = \frac{R_a}{R_0} \quad \text{Equation 3.1}$$

In this expression, R_0 represents the radius of the Hansen solubility sphere for the polymer, which can be obtained from literature or experimental data. The solubility parameter distance, R_a , is theoretically estimated based on the Hansen Solubility Parameters (HSP) of both the polymer and the solvent according to the *Equation 3.2*:

$$R_a = \sqrt{4(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{h1} - \delta_{h2})^2} \quad \text{Equation 3.2}$$

Where δ_d , δ_p , and δ_h correspond to the energy densities arising from dispersion forces, polar interactions, and hydrogen bonding, respectively. The values of these parameters for CA, GVL, DMSO and H₂O have been taken from literature [11,29].

Thermodynamic compatibility between the polymer and the solvent is inversely proportional to the R_a value; hence, a reduction in this distance signifies enhanced solubility. The solubility envelope of a polymer is defined by R_0 . Consequently, in order to have good affinity towards a polymer, the R_a value of the solvent must be smaller than R_0 . *Figure 3.2* illustrates the case of good solubility when $R_a < R_0$ (green dot) and poor solubility when $R_a > R_0$ (red dot) [14,15,28,29].

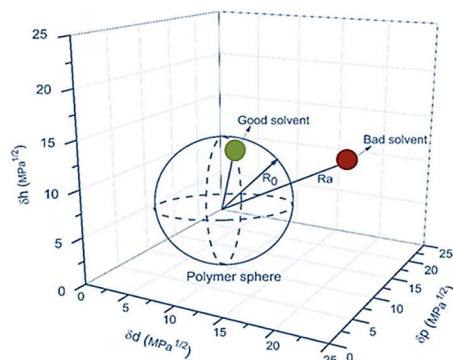


Figure 3.2. Representation of radius of Hansen solubility sphere and R_a . [29]

3.4.2. Viscosity Measurements

The rheological behaviour of the prepared CA solutions using GVL and DMSO as solvent polymer concentrations of 10, 15 and 20 wt% was characterised to assess their processability and influence on the subsequent membrane formation morphology.

Measurements were performed using a modular compact rheometer (MCR 302, Anton Paar, Austria) equipped with a Peltier temperature control system, which maintained the samples at a constant temperature of 20.0 ± 0.1 °C. A parallel-plate geometry (D-PP25, 25mm diameter) was employed, and the measuring gap between the upper plate and the bottom stationary plate was strictly set to 0.6 mm.

The dynamic viscosity was determined by conducting steady-state flow curve tests in rotational mode. A logarithmic shear rate ramp ranging from 0.1 to 1000 s^{-1} was applied, recording 10 data points per measurement interval to accurately capture the flow profile. Data acquisition and processing were managed through the Start Rheoplus Software.

3.4.3. Scanning Electron Microscopy

Scanning electron Microscopy (SEM) was employed to investigate the morphological properties of the fabricated CA membranes. SEM is a surface imaging technique based on the interactions of a focused beam of high-energy electrons with a solid specimen. The instrument operates by serially scanning this primary electron beam across the sample surface and the resulting signals emitted from each point are collected and translated into a high-resolution, magnified image.

The primary beam is generated by an electron gun and focused by electromagnetic lenses to the specimen. The beam-sample interaction results in both elastic and inelastic scattering within a characteristic interaction volume, generating several useful signals [44]:

- Secondary electrons (SE) are low-energy electrons ($<50 \text{ eV}$) ejected due to inelastic collision of the beam with the specimen's outermost surface layer (0,5-5 nm), providing topographic

contrast. SE imaging is highly sensitive to local surface angle, making edges and inclined surfaces appear brighter.

- Backscattered electrons (BSE) are high-energy electrons that escape from a greater depth, providing compositional (Z-contrast) as their intensity increases with the specimen's average atomic number. Consequently, regions composed of heavier elements appear brighter in the image.
- Auger electrons are low-energy electrons emitted from the outermost atomic layers (1-3 nm) that provide surface-sensitive chemical state information.
- Characteristic X-rays are high-energy photons resulting from inner-shell electron transitions that enable qualitative and quantitative elemental analysis (EDS).
- Cathodoluminescence (CL) consists of low-energy photons emitted from semiconductors or insulators. It provides information about crystal defects and optoelectronic properties.

In this study, cross-sectional view was used to evaluate the internal bulk morphology, pore connectivity, and the overall symmetry of the membrane structure. Furthermore, top and bottom surface views were acquired to analyse the surface porosity and to identify potential asymmetries between the air-interface (top) and the substrate-interface (bottom).

Prior to imaging, all specimens were mounted onto substrates using conductive carbon tape and subsequently secured onto the SEM specimen holder. Due to the non-conductive nature of the polymer, it was essential to perform a sputter-coating with a thin layer of platinum using a Q150T ES sample preparation system (Quorum Technologies Ltd). The micrographs were obtained using a Zeiss Supra 40 Field Emission Scanning Electron Microscope (FESEM) equipped with a Gemini column (Carl Zeiss, Germany). Imaging was conducted at an accelerating voltage of 5 kV and an aperture size of 30 μm .

Pore size distribution analysis

For membranes exhibiting a porous, sponge-like structure, cross-sectional SEM images were utilised to estimate the pore size distribution. Pore size quantification was performed using ImageJ software. Following spatial calibration to establish the pixel-to-micron ratio, representative regions with distinct pore structures were selected to ensure analytical accuracy. The images were subsequently binarized by applying a threshold algorithm, with manual adjustments to accurately delineate the pore boundaries. At this instance, it was necessary to perform a manual adjustment to cover the pores. Pore areas (A) were computed using the 'Analyse Particles' function, with the size parameter set from zero to infinity, and circularity constrained between 0.0 to 1.0. This procedure is graphically shown in *Figure 3.3*, with the images being from one of the analysed samples. The equivalent disk diameter (D_{eq}) of each identified pore was calculated from its projected area using *Equation 3.3*.

$$D_{\text{eq}} = 2 \sqrt{\frac{A}{\pi}} \quad \text{Equation 3.3}$$

The resulting data were used to obtain the pore size distribution and to calculate the mean and median pore diameters for each membrane formulation.

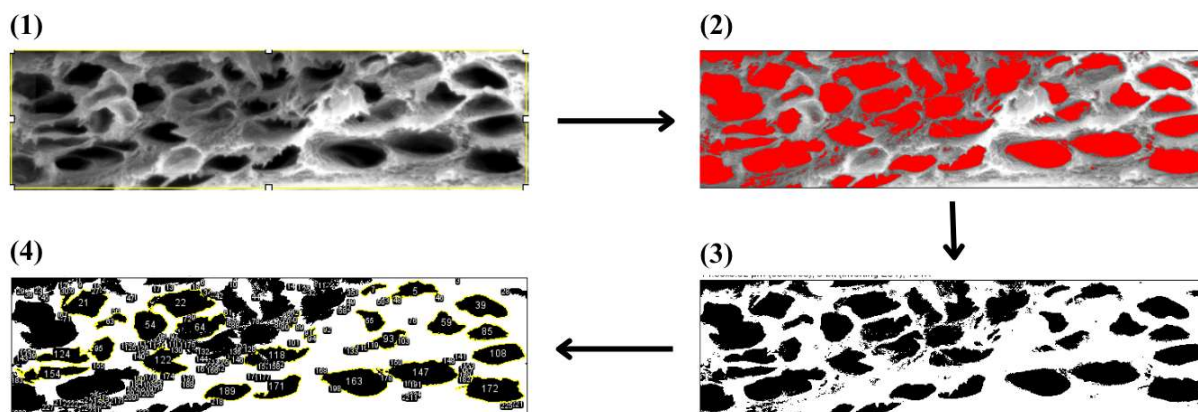


Figure 3.3. Step-by-step procedure for image analysis on ImageJ software: (1) selection of a clear and representative micrograph; (2) application of a threshold algorithm, manually adjusted to accurately delineate the pores; (3) image binarization; and (4) resulting image after applying the “Analyze particles” function.

To complement the structural analysis, the through-pores—which directly govern ion flow and often exhibit different dimensions than those observed in cross-sectional imaging—were systematically evaluated. Initially, the maximum pore size and overall pore size distribution were characterised via capillary flow porometry using a Porometer 3G (Anton Paar) based on an automated liquid displacement technique. Due to the limitations of the available pressure regulator, the maximum applied pressure was restricted to approximately 6.3 bar, corresponding to a minimum detectable pore size of roughly 100 nm. Additionally, ultramicroporosity was quantified using a Micromeritics ASAP 2020 Plus surface area analyser. The samples were degassed under dynamic vacuum at 30 °C for 5 h prior to the CO₂ adsorption measurements. Finally, the pore size distribution was derived utilizing a Density Functional Theory (DFT) model with a regularization parameter set to 0.1.

3.4.4. ATR-FTIR

To identify the characteristic functional groups of cellulose acetate and assess potential chemical differences between the varying membrane compositions, Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) was employed.

ATR is an advanced sampling technique that overcomes the sample preparation challenges associated with traditional transmission FTIR, making it suitable for the direct analysis of solid polymer membranes. The fundamental principle of ATR relies on the phenomenon of total internal reflection. During the analysis, the sample is pressed into direct physical contact with an ATR crystal. This crystal must be an optically dense material, meaning it possesses a significantly higher refractive index than the organic sample being analysed (typical crystal materials include diamond, germanium, or zinc selenide).

When the propagating wave travels through the crystal and hits the crystal-sample interface at an angle greater than the critical angle (as defined by Snell’s law), the light is totally internally reflected. It must

be noted that the infrared (IR) beam does not exit the surface of the crystal at the crystal-sample interface. Instead, the electric component of this wave extends beyond the crystal surface and penetrates the adjacent sample. This protruding energy is known as an ‘evanescent wave’.

The penetration depth of this evanescent wave is typically on the order of a few micrometres, depending on the wavelength of the incident light, the angle of incidence, and the refractive indices of both the crystal and the sample. As the evanescent wave interacts with the sample, specific IR frequencies are absorbed based on the molecular composition and functional groups that are present. This absorption attenuates the totally reflected IR beam. The spectrometer then measures this attenuated light to generate the characteristic FTIR spectrum of the sample surface [45].

For this study, ATR-FTIR measurements of the CA membranes were performed using a Thermo Scientific Nicolet Apex spectrometer. The membranes were placed directly in contact with the diamond ATR crystal without any prior sample preparation. All spectra were recorded at room temperature over a wavenumber range of 4000-400 cm^{-1} , and were subsequently background-corrected and normalised prior to analysis.

3.4.5. Electrolyte Compatibility and Stability Screening

Prior to the electrochemical testing, a preliminary stability screening was conducted to evaluate the resilience of the fabricated CA membranes across a range of pH conditions. This stage was critical for determining the suitability of various electrolytic media for subsequent performance evaluations.

Membrane samples were immersed in three distinct solutions for a duration of three hours to observe their physical and chemical responses: an acidic medium (0.5M H_2SO_4), a neutral medium (0.5M Na_2SO_4), and an alkaline medium (1M NaOH).

3.4.6. Electrochemical Characterization

To comprehensively evaluate the viability of the cellulose acetate membranes as sustainable separators in diverse applications, a multi-tiered electrochemical characterization approach was adopted. The testing methodology consisted in preliminary electrochemical screenings, followed by specific evaluations depending on the application under investigation. All electrochemical characterisations were performed using a VMP3 multichannel potentiostat (BioLogic, France).

Preliminary Electrochemical Screening

The ionic resistance of all membranes was assessed using an H-type cell configuration equipped with Ag/AgCl electrodes. Measurements were conducted independently in the two previously selected electrolytic media: 0.5 M H_2SO_4 and 0.5 M Na_2SO_4 .

For each sample, the experimental protocol consisted of an initial Open Circuit Voltage (OCV) measurement to monitor the thermodynamic stability of the membranes in the electrolyte over time, followed by Electrochemical Impedance Spectroscopy (EIS) to assess the intrinsic ionic resistance and conductivity of the membranes.

EIS is a technique utilised to characterise the impedance of an electrochemical system. The method involves applying a low-amplitude alternating potential perturbation across a broad spectrum of frequencies, which consequently generates a phase-shifted AC current response. The resulting data are commonly visualised using a Nyquist plot. In this representation, the x-axis displays the real component of impedance (Z') whereas the y-axis displays the negative imaginary component ($-Z''$), which reflects the capacitive and inductive phenomena[46,47].

In this specific liquid-electrolyte H-cell configuration, the membrane acts merely as a physical separator and there is no blocking interface to restrict ion flow. This cell, as schematically represented in *Figure 3.4*, corresponded to a four-electrode configuration with the working (WE) and the counter (CE) electrodes made of titanium, and the reference (RE) and working sense (WS) potential probes consisting of Ag/AgCl. The latter were placed strictly on either side of the separator; consequently, the measured potential drop exclusively reflects the processes occurring within the membrane and the surrounding liquid electrolyte [47].

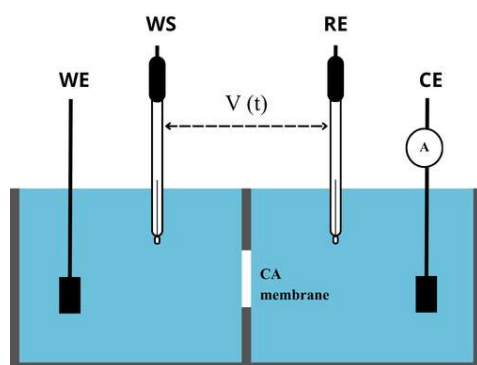


Figure 3.4. 2-compartment cell (H-cell) for measurements of the ionic conductivity of the CA membrane in a four-electrode configuration with the working (WE), working sense (WS), counter (CE), and reference (RE) electrodes (Adapted from [47]).

The electrical response of the system can be modelled using an idealised equivalent circuit comprising discrete electrical components. Within the linear response regime, the membrane system behaves predominantly as a simple parallel RC circuit. The porous matrix filled with the conductive electrolyte provides a pathway for ionic transport, which is represented by a bulk ohmic resistance (R_m). Simultaneously, the polymeric material itself acts as a dielectric, generating a geometric capacitance (C_g). As shown in *Figure 3.5*, when plotted on a Nyquist plot, the parallel RC circuit response consists of a single semicircular arc that terminates on the real axis (Z') as the system behaves as a pure ohmic resistor. In a practical experimental setup, this semicircle does not pass through the origin. At extremely high frequencies, the geometric capacitor effectively behaves as a short circuit, bypassing the complex

porous structure. Consequently, the leftmost intercept of the arc (R_s) with the real axis represents the baseline electrical resistance of the liquid electrolyte situated between the RE and WS electrodes [47,48].

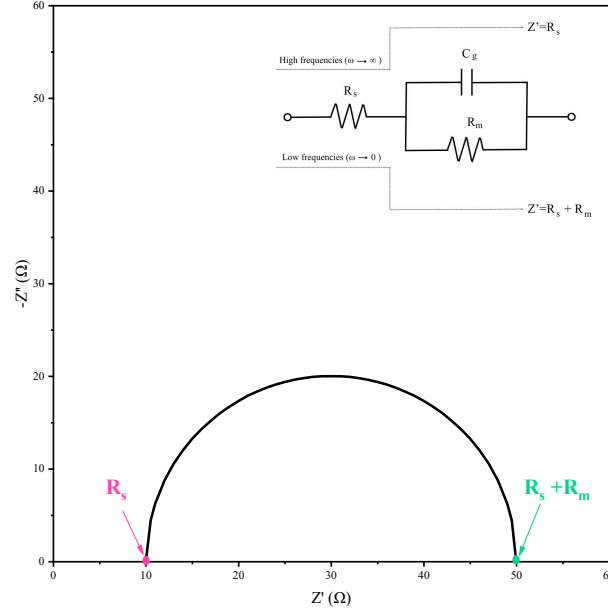


Figure 3.5. Nyquist plot for a liquid-electrolyte H-cell used in polymer membrane conductivity measurements, and its corresponding idealised equivalent circuit (Adapted from [48])

To accurately quantify this baseline resistance and avoid potential fitting errors caused by the depressed semicircles often observed with heterogeneous porous membranes, an independent blank measurement was performed. This control test involved filling the H-cell exclusively with the liquid electrolyte to obtain a direct and reliable value for R_s .

Subsequently, the intrinsic resistance of the membrane (R_m) was calculated by subtracting the resistance of the pure electrolyte solution (R_s) from the total resistance of the cell (R_t), as indicated in Equation 3.4 [47].

$$R_m (\Omega) = R_t - R_s \quad \text{Equation 3.4}$$

Finally, the ionic conductivity (σ) can be obtained using the geometric parameters of the membrane (Equation 3.5)

$$\sigma (\text{S.cm}^{-1}) = \frac{1}{R_m \cdot A} \quad \text{Equation 3.5}$$

Where l represents the thickness of the membrane and A denotes the effective area exposed to the electrolyte, which was 1.13 cm^2 for all samples [49].

To execute these characterisations, the experimental parameters were systematically defined. Initially, the OCV was recorded at 1-second intervals. The measurement was maintained until a stable resting potential was achieved, defined by a voltage drift (dE/dt) criterion of $\leq 1 \text{ mVh}^{-1}$.

Subsequently, EIS was carried out to determine the total ohmic resistance of the system. The impedance spectra were recorded over a frequency range from 1 MHz to 10 mHz, applying a sinusoidal amplitude of 5 mV around the OCV.

Based on the sample's performance on the previous characterisations, some membranes were studied as supercapacitor components, whereas other membranes were selected to be tested for reverse electrodialysis applications.

3.4.7. Electrochemical characterization for supercapacitor applications

The membranes with lowest resistance to ion flow, identified during the preliminary electrochemical screening, were investigated for application in two specific supercapacitor components: as separators and as coatings for LMO-based electrodes.

To evaluate the CA membranes as separators, the procedure consisted in first instance in the assembly of a Swagelok cell with a three-electrode configuration using 0.5 M H_2SO_4 as the aqueous electrolyte. The setup consisted of AC/HPC@Ti as the working electrode, BFE as the counter electrode, and an Ag/AgCl as reference electrode. The experimental protocol included performing OCV, EIS and Cyclic Voltammetry (CV) to the assembled cells.

Subsequently, measurements were conducted using a two-electrode symmetric Swagelok cell, employing AC/HPC@Ti as electrodes and 0.5 M H_2SO_4 as electrolyte. Given that the electrochemical stability of these electrodes under the applied operating conditions has been previously established [50], this configuration enabled the direct evaluation of the synthesised membranes stability. The electrochemical characterization consisted in performing OCV, EIS, and CV, followed by a float test.

These two distinct cell configurations were employed to serve complementary diagnosis purposes. The three-electrode setup was initially utilised to isolate the working electrode interface and establish the electrochemical stability window (ESW) of the membrane-electrolyte system. In contrast, the two-electrode configuration was designed to evaluate the comprehensive performance of the device under the previously determined potential window [51].

To evaluate the performance of the CA membrane as an electrode coating, the characterisation was conducted using a three-electrode Swagelok cell. This set-up employed a CA-coated LMO/HPC@Ti as the working electrode, BFE as the counter electrode, and a standard Ag/AgCl reference electrode, along

with a glass fiber separator and a 2 M Li_2SO_4 aqueous electrolyte. The electrochemical characterization included OCV, EIS, and CV measurements.

It should be noted that, in the case of supercapacitors, the EIS plot differs from that of a liquid-electrolyte H-cell configuration, as illustrated in *Figure 3.6*. In this case, the total measured impedance is the result of several distinct contributions, including the bulk resistance of the liquid electrolyte, the intrinsic electrical resistance of the active electrode material, the physical contact resistance at the interface between the active material and the current collector, and the mass-transport diffusion resistance encountered by electrolyte ions as they penetrate the porous carbon network.

These resistive elements can be conceptually divided based on their physical origins. The intrinsic resistance of the bulk electrolyte ($R_{\text{electrolyte}}$) and the internal diffusion resistance (R_{diff}) are predominantly dictated by the physicochemical properties of both the electrolyte and the electrode materials. In contrast, boundary or interfacial resistances are highly dependent on the manufacturing process and can be systemically controlled and minimized during electrode fabrication. Because these phenomena operate on distinctly different time scales, their individual contributions can be decoupled and modelled using a representative equivalent electrical circuit. From a practical perspective, the high-frequency intercept where the impedance curve crosses the x-axis is of critical importance. This specific point represents the Equivalent Series Resistance (ESR), which is a cumulative measure that encapsulates the purely ohmic resistances of the system, including the bulk ionic resistance of the electrolyte, the intrinsic electronic resistance of the active materials, and the contact resistance at the interfaces[46].

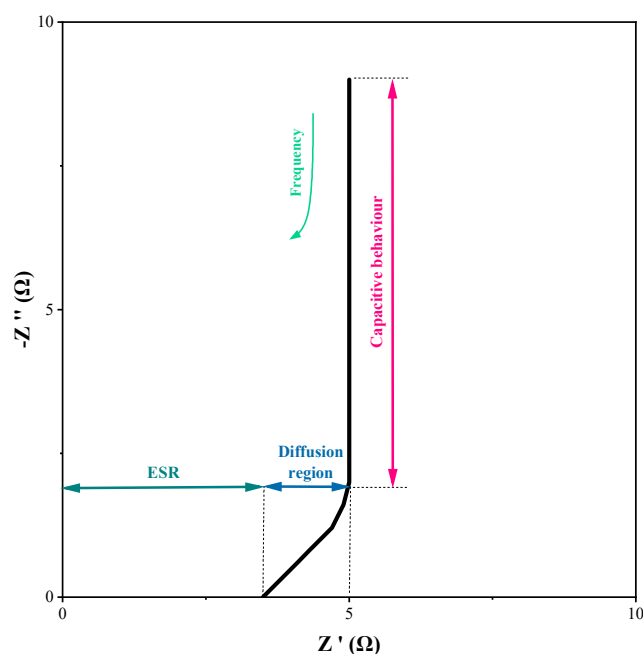


Figure 3.6. Typical Nyquist plot for an EDLC based on porous carbonaceous material. The high-frequency intercept with the real axis (Z') represents the equivalent series resistance (ESR), which accounts for the combined ohmic resistances of the system. Moving from high to medium frequencies, the plot exhibits a characteristic diffusion region, resulting from the electrolyte resistance through the electrode pores. At lower frequencies, a near-vertical line illustrates the capacitive behaviour of the device (Adapted from [46]).

In CV, the current response of the device is recorded when a potential is applied. This technique is widely employed to evaluate the capacitive behaviour and interface kinetics of energy storage devices. During CV, the applied potential is varied linearly over time at a constant scan rate ($v = dV/dt$) up to a predefined upper limit, after which the sweep direction is reversed to return to the initial voltage. The current response (I) is recorded in a current-potential graph.

The shape of the cyclic voltammogram serves as a primary indicator of the dominant charge storage mechanism, as illustrated in *Figure 3.7*. For an ideal EDLCs, the current ($I = dQ/dt$) remains constant for a given scan rate (v), yielding a perfect rectangular CV response. Conversely, if the system incorporates pseudocapacitive materials, charge storage is additionally governed by fast, reversible Faradaic redox reactions, which manifests as distinct anodic and cathodic peaks on the CV plot. In practical devices, however, the CV profiles slightly deviate from ideal geometry due to side electrochemical reactions, which typically rounds the corners upon potential reversal. Furthermore, at excessively high scan rates, ion diffusion limitations and internal resistance become prominent; consequently, the CV curve adopts the form of an ellipse with sharp edges, inclined toward the potential axis[52–54].

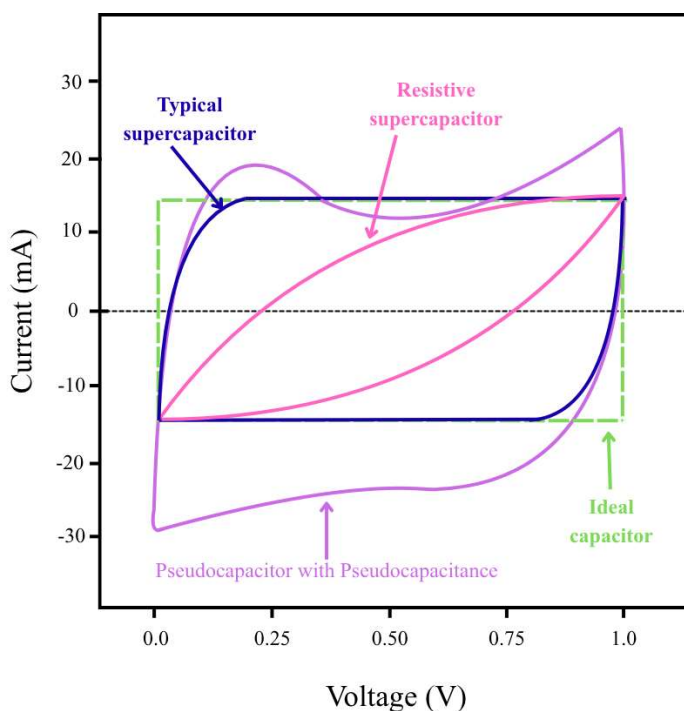


Figure 3.7. Comparative CV profiles illustrating various charge storage behaviours. For ideal EDLCs's (green line) the response is a perfect rectangle. For a typical supercapacitor (blue line) the CV curve slightly deviates due to side electrochemical reactions. If the device features a substantial pseudocapacitive contribution (purple line), the occurrence of surface reactions transforms the characteristic rectangular baseline into a boarder, considerable wavier curve. When evaluating highly resistive devices (pink curve), the CV profile typically collapses, causing the shift of the CV charging-discharging corners towards the centre of the curve (Adapted from[54]).

For electrochemical evaluations, the accurate approach depends on whether it is a two-electrode or a three-electrode cell configuration, as the potential windows and mass normalisations differ significantly. To consider non-ideal behaviours and the dependence of capacitance on potential, the method to calculate specific capacitance (C_{specific}) from CV data is by integrating the voltametric discharge curve as shown in the general *Equation 3.6*:

$$C_{\text{specific}} (\text{F} \cdot \text{g}^{-1}) = \frac{\int i \, dt}{\Delta V \cdot m} \quad \text{Equation 3.6}$$

Where i is the instantaneous current, t is the discharge time, ΔV is the potential or voltage window, and m is the normalizing mass [51].

For material characterisation, the three-electrode configuration isolates the WE, ensuring its potential is measured accurately against a stable RE without interference of the CE. Here ΔV corresponds to the potential span of the WE (ΔV_{WE}), and m is strictly the mass of the active material on the WE (m_{WE}).

For ESW validation and device performance evaluation, a symmetric two-electrode configuration is necessary as it is more complex and closer to final application. Here both electrodes have an identical mass and capacitance ($C_{\text{el}} = C_{\text{anode}} = C_{\text{cathode}}$), and the total cell capacitance (C_{cell}) is equivalent to two capacitors in series, meaning $C_{\text{cell}} \approx C_{\text{el}}/2$. Consequently, when normalising the total mass of both electrodes ($m_{\text{cell}} = 2 \cdot m_{\text{el}}$), the full cell specific capacitance can be calculated using *Equation 3.7* [51,54].

$$C_{\text{cell,specific}} (\text{F} \cdot \text{g}^{-1}) = \frac{C_{\text{el}}}{4 \cdot m_{\text{el}}} \quad \text{Equation 3.7}$$

For a comprehensive evaluation of the device stability and long-term endurance, conducting a voltage floating test is highly adequate, as it provides an accurate simulation of continuous operational stress. The protocol, as illustrated in *Figure 3.8*, consists of a galvanostatic charge/discharge (GCD) step to monitor the device capacitance alternated with a constant voltage period retained for a prolonged period (10-20 h) at the device rated voltage.

Analysing the voltage-time profile generated during GCD testing (*Figure 3.9*) allows for the direct extraction of the equivalent series resistance (ESR). This parameter is derived from the abrupt potential drop observed at the onset of the discharge phase, graphically manifesting as a vertical shift in the graph. While theoretically, an equivalent instantaneous voltage jump occurs at the onset of the charge phase – and is assumed to be of equal magnitude – the discharge potential drop is conventionally used for calculations. [51].

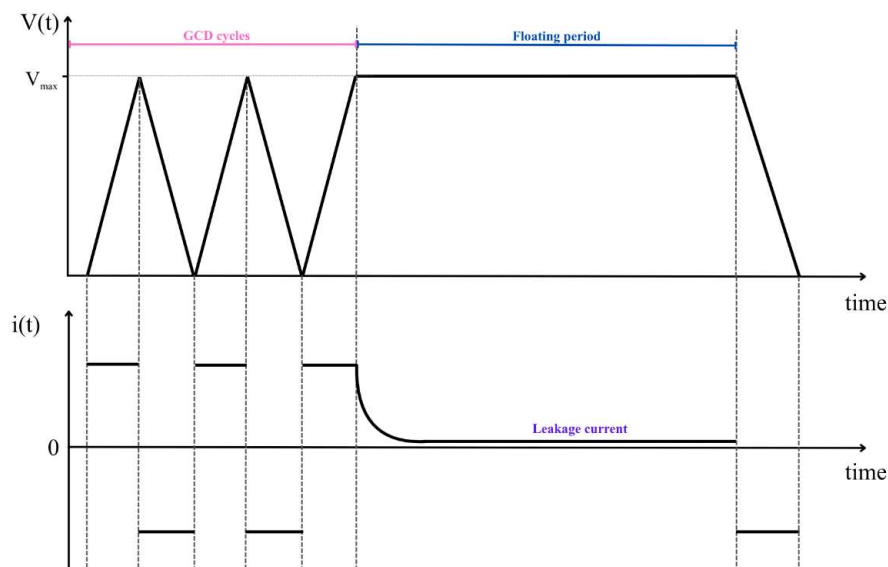


Figure 3.8. Schematic representation of the voltage float test protocol. The upper profile illustrates the evolution of potential, V , as a function of time, displaying the initial galvanostatic charge-discharge (GCD) cycles followed by a floating period where the voltage is held strictly constant at its maximum operational value (V_{max}). The lower profile displays the corresponding alternation between positive and negative constant currents during the GCD stage, followed by a leakage current recorded during the floating period. This leakage current is the current necessary to exactly off-set the self-discharge of the supercapacitor, which encompasses currents flowing due to parasitic faradaic reactions and the movement of charge through the material.

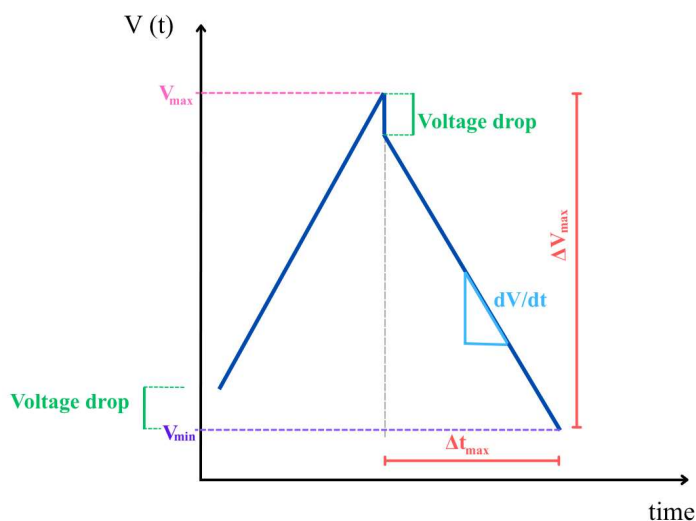


Figure 3.9. Schematic representation of a typical galvanostatic charge-discharge (GCD) profile for a supercapacitor. The curve illustrates the voltage-time response to alternating positive and negative constant currents. Key parameters for electrochemical characterisation are highlighted, including the operating voltage window (from V_{max} to V_{min}) the total discharge time (Δt_{max}) and the discharge slope (dV/dt). The abrupt initial voltage drop at the onset of the charge and discharge phases are also indicated (Adapted from [51]).

The ESR represents the cumulative ohmic resistance of the cell's internal components, encompassing the active materials, electrolyte, separators, current collectors, and wiring. Numerically, it can be calculated using *Equation 3.8* [51].

$$ESR(\Omega) = \frac{V_{\text{drop}}}{2I}$$

Equation 3.8

Where V_{drop} is the potential drop (V) at the onset of the discharge phase and I (A) is the absolute value of the applied constant current during the galvanostatic cycle. The denominator is denoted as $2I$ because the system undergoes a complete current reversal from charge (+I) to discharge (-I) at the turning point, resulting in a total current step of $2I$.

Following this initial drop, the discharge profile of an ideal electrical double-layer capacitor assumes a nearly linear, triangular shape. From this linear segment, the capacitance (C) of the system is quantified using the charge-to-voltage ratio as in *Equation 3.9*.

$$C(F) = \frac{Q_D}{V} = \frac{I_D \cdot \Delta t}{\Delta V}$$

Equation 3.9

Where Q_D is the amount of charge that can be extracted from a charged device in the applied voltage window ΔV . This charge represents the discharge current (I_D) multiplied by the elapsed time Δt .

The capacity retention, calculated using *Equation 3.10*, is a useful metric to assess the long-term electrochemical stability and cycle life of the device under continuous operational conditions.

$$\text{Capacity retention (\%)} = \frac{Q_D}{Q_{D0}} \times 100$$

Equation 3.10

Where Q_D is the discharge capacity at a specific cycle or time during the floating test and Q_{D0} is the initial discharge capacity recorded at the beginning of the test, both typically expressed in mAh.

Furthermore, the Coulombic efficiency (η_c), defined by *Equation 3.11*, evaluates the reversibility of the charge-transfer processes within the supercapacitor. Values close to 100% imply that almost all the electrons injected during the charging phase are successfully recovered during discharge, indicating a minimal presence of irreversible parasitic reactions or micro-short circuits.

$$\eta_c (\%) = \frac{Q_D}{Q_C} \times 100$$

Equation 3.11

Where Q_D and Q_C (mAh) are the total charge capacity delivered during the discharge and the charge phase, respectively.

While Coulombic efficiency measures the conservation of charge, Energy efficiency (η_E) determines the practical energy losses during the device's operation, which are primarily driven by the ESR and dissipated as heat (IR drop). This metric, calculated using *Equation 3.12*, is crucial for determining the practical viability of the energy storage device, as it depends also on the cell voltage at which the charge is transferred.

$$\eta_E (\%) = \frac{E_D}{E_C} \times 100 \quad \text{Equation 3.12}$$

Where E_D is the energy released during the discharge process and E_C is the total energy accumulated during the charging of the device, both in Wh.

Analysis of the current profile during the floating period provides direct insight into the mechanisms driving the capacitor's self-discharge. The float current, illustrated in *Figure 3.8*, is the result of the compensatory current that must be applied to off-set all internal self-discharge processes. These losses are mainly attributed to three factors: internal leakage currents, parasitic faradaic reactions, and internal charge redistribution. Initially, the required current is relatively high as it charges the immediately accessible external surfaces and low resistance macropores. It then exhibits a progressive decay as the charge slowly diffuses deeper into the porous matrix of the electrodes and across the separator, ensuring the electrochemical capacitor is fully charged. Ultimately, the current stabilises at a steady-state value, which is assumed to correspond exclusively to the faradaic contribution to self-discharge. Consequently, the time required for the leakage current to decay serves as a reliable quantitative indicator of the extent of charge redistribution within the system [51,55].

The electrochemical characterisation of the CA membranes for use as **supercapacitor separators** followed the sequence outlined below:

1. Three-electrode configuration cell:

The cell was initially allowed to rest at open-circuit conditions for 1 hour to allow the proper wetting of the cellulose acetate membrane and the electrodes by the electrolyte, ensuring the thermodynamic equilibrium of the system before applying any electrical perturbation. Following this, an initial EIS was performed to evaluate the initial ESR and charge transfer kinetics. The impedance spectra were recorded at the OCV applying a sinusoidal amplitude of 5mV, within a frequency range from 1 MHz down to 10 mHz, collecting 10 points per decade at logarithmic spacing. To determine the practical electrochemical stability window (ESW) of the system, a step-wise CV approach was adopted. Scans were initiated from the open circuit potential (E_{OC}) at a constant scan rate of 5 mV s⁻¹, with the potential window systematically and iteratively expanded in both the anodic and cathodic directions. The operational limits were procedurally defined by monitoring the onset of sharp, irreversible faradaic currents, which signify electrolyte decomposition. Immediately after voltammetry cycles, a second EIS measurement

was conducted using the exact same parameters as the initial EIS. This step was crucial to investigate any impedance changes induced by the electrochemical cycling, such as variations in ionic diffusion resistance within the CA membrane or changes at the electrode-electrolyte interface.

2. Two-electrode configuration cell:

Initially, OCV and EIS were performed utilizing the same parameters as for the three-electrode configuration. Subsequently, a step-wise, multi-scan rate CV approach was adopted. Scans were performed within a fixed potential window from 0.0 V to 0.8 V. The scan rate was systemically increased across ten sequential stages: 1, 2, 5, 10, 20, 50, 100, 200, 500, and 1000 mV s⁻¹. At each specific scan rate, 30 continuous cycles were recorded to ensure a steady-state capacitive response and to rigorously assess the kinetic stability of the system under shifting current demands.

Furthermore, a long-term voltage float test was conducted to evaluate the electrochemical stability, leakage current evolution, and structural robustness of the CA separator under continuous operational stress. Initially, the cell was subjected to a prolonged open-circuit rest period of 3 hours to establish a highly stable thermodynamic baseline prior to the ageing process. Subsequently, an iterative loop was executed 10 times, accumulating a total of around 120 hours of voltage float test. Each iteration in this sequence consisted of three consecutive stages. Firstly, an EIS measurement (from 1 MHz to 10 mHz, with a 5 mV sinusoidal amplitude) was performed to systematically monitor any drift in the equivalent series resistance (ESR) and charge transfer kinetics. Secondly, a standard galvanostatic charge-discharge (GCD) cycle was applied at ± 1.0 mA between 0.0 V and 0.8 V to assess capacity retention before prolonged stress. Finally, during the voltage float step, the cell was charged to the maximum operational voltage of 0.8 V at 1.0 mA and held strictly at this potential for 10 hours to measure the leakage current and evaluate internal parasitic reactions. Upon completion of the float period, the cell was discharged back to 0.0 V at -1.0 mA and subsequently held at 0.0 V for 30 minutes. This final resting phase facilitated ionic relaxation and thermodynamic re-equilibration before the commencement of the next iteration.

The electrochemical characterisation of CA membranes for use as a **coating on LMO-based metal oxide electrodes** was carried out according to the following procedure:

Initially, the assembled cells were subjected to rest at open-circuit conditions for 1 hour to establish a stable OCV. Following this rest period, an initial EIS measurement was performed at the established OCV to evaluate the baseline internal resistance of the device. The EIS analysis was carried out by applying an alternating current (AC) perturbation with an amplitude of 5 mV, sweeping the frequency logarithmically from 1 MHz down to 10 mHz. Subsequently, to assess the capacitive behaviour and long-term cycling stability of the system, CV was employed. The potential was swept continuously between 0.0 V and 1.2 V vs. E_{OC} at a constant scan rate of 0.5 mV s⁻¹. This procedure was repeated for a total of 150 cycles. Immediately after, a second EIS analysis was conducted utilising the exact same parameters as the initial measurement. This final step is crucial for identifying variations at the electrode-membrane interface induced by prolonged electrochemical stress.

3.4.8. Electrochemical characterization for salinity gradient power generation

To further investigate the selective transport properties and the Salinity Gradient Power (SGP) potential of the selected membranes, an H-cell configuration was employed. The setup consisted of two separate compartments divided by the membrane under investigation. To establish a concentration gradient, one half-cell was filled with a 0.1 M KCl solution, while the other contained a 0.01M KCl solution.

Electrochemical characterization was initiated with a brief 1-minute OCV measurement to verify initial system stability. This was immediately followed by an EIS. The initial impedance spectra were recorded at the open-circuit potential using a sinusoidal voltage amplitude of 5 mV and frequency ranging from 1 MHz down to 10 mHz. To evaluate the long-term stability and ion transport behaviour of the membrane under the established concentration gradient, an automated monitoring loop was subsequently implemented. This sequence alternated a 12-hour OCV measurement with an EIS scan, repeating ten times to enable a comprehensive assessment of the membrane's electrochemical response over an extended period of more than 100 hours.

The apparent perm selectivity (α_{app}) of the membrane was determined by *Equation 3.13*, from the initial OCV data [39,56]. It is defined as the ratio of the measured membrane potential ($E_{measured}$) to the theoretical potential of a perfectly (100%) selective membrane ($E_{theoretical}$) [57]:

$$\alpha_{app} = \frac{E_{measured}}{E_{theoretical}} \quad \text{Equation 3.13}$$

The theoretical potential was calculated according to the Nernst equation (*Equation 3.14*):

$$E_{theoretical} = \frac{RT}{zF} \ln \left(\frac{a_c}{a_d} \right) \quad \text{Equation 3.14}$$

Where R is the universal gas constant ($J \text{ mol}^{-1} \text{ K}^{-1}$), T is the absolute temperature (298.15 K), z is the ion valency, F is the Faraday constant ($C \text{ mol}^{-1}$), and a_c and a_d represent the chemical activities (mol L^{-1}) of the diluted KCl solutions, respectively [56,58]. Chemical activities are expressed as the product of the molar concentration and the mean ionic activity coefficient (γ). Using standard literature values for KCl at 25 °C ($\gamma = 0.77$ for 0.1 M and $\gamma = 0.9$ for 0.01 M), the respectively activities are $a_c = 0.077$ and $a_d = 0.009$, yielding a theoretical maximum potential of 55.1 mV [59].

Chapter 4

Results and Discussion

4.1. Thermodynamic Evaluation and Solvent Selection (RED)

Before membrane fabrication, thermodynamic compatibility of the polymer (P)-solvent (S) solutions was investigated by the theoretical determination of the solvents and non-solvent (NS) R_a and the RED values. Results are resumed on *Table 4.1*.

Table 4.1. Hansen solubility parameters (HSP), interaction distance (R_a), and relative energy difference (RED) between cellulose acetate and the investigated solvents (DMSO and GVL) and non-solvent (H_2O).

Materials	solubility parameters (MPa ^{1/2})			$R_{a\ P-S}$	$R_{a\ P-NS}$	$R_{a\ S-NS}$	RED _{P-S}	RED _{P-NS}
	δ_D	δ_P	δ_H					
CA ($R_0=7.4$)	18.6	12.7	11.0	-				
H_2O	15.5	16.0	42.3		32.1			4.3
DMSO	18.4	16.4	10.2	3.8		32.6	0.5	
GVL	15.5	4.7	6.6	11.0		37.5	1.5	

The RED value obtained for GVL, which is three times higher than that of DMSO, indicates a significantly lower dissolution capacity for the polymer compared to the latter. In fact, greater experimental difficulties were encountered in obtaining uniform membranes when using GVL as the solvent. Furthermore, the affinity for water is higher in the case of DMSO, which translates into a faster phase inversion process.

4.2. Rheological and kinetic behaviour of the polymer precursor solutions

The rheological properties of the polymer precursor solutions were initially investigated, as they govern both the casting processability via the doctor blade technique and the subsequent phase separation kinetics. The resulting profiles for the diverse biopolymer concentrations in both GVL and DMSO solvent systems at 20 °C are presented in *Figure 4.1*.

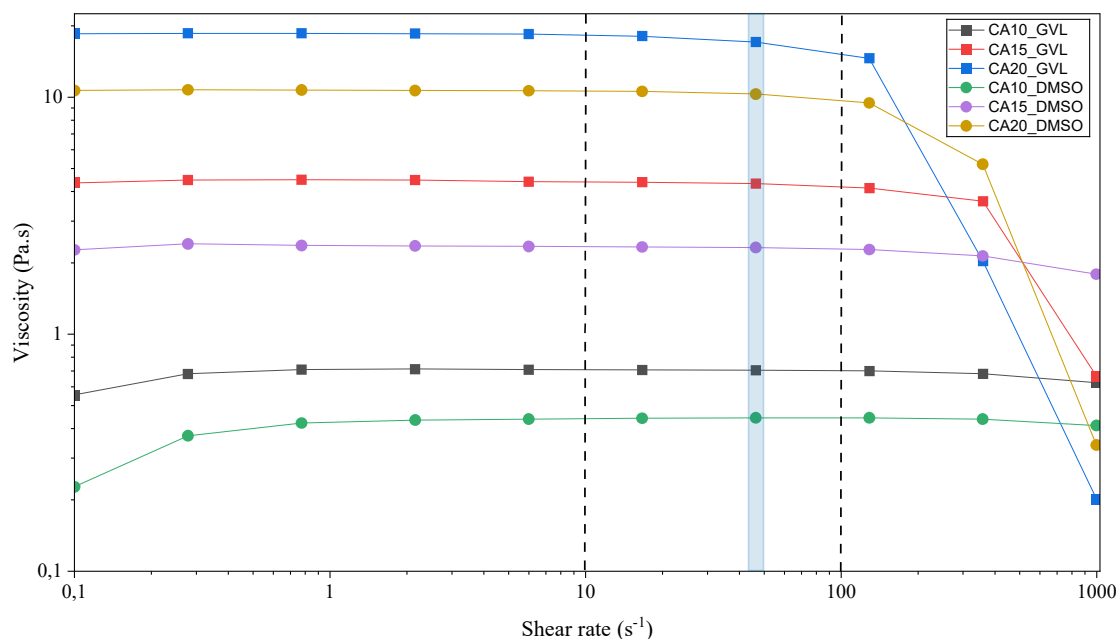


Figure 4.1. Rheological profiles of CA precursor solutions at 20°C. The shear rate window from 10 to 100 s^{-1} , demarcated by the dashed lines, represents the typical processing range associated with the doctor blade technique. The points highlighted in blue correspond to a shear rate of 46.42 s^{-1} , which was selected as a representative value of shear conditions experienced during the casting process.

All evaluated formulations displayed a classic non-Newtonian pseudoplastic (shear-thinning) profile, characterised by a well-defined horizontal region at lower shear rates before experiencing a distinct drop in dynamic viscosity (η) under elevated shear conditions. The horizontal regime represents the zero-shear viscosity (η_0) plateau, where the solution remains in a state of structural equilibrium; at these low shear conditions, the rate of spontaneous macromolecular entanglement formation matches the rate of disruption. As the shear rate accelerates, the mechanical forces surpass this equilibrium threshold, forcing the CA chains to disentangle and progressively align along the shear field. This latter behaviour induces a significant reduction in viscosity due to the minimised resistance to flow. The shear rate at which the solution passes from Newtonian to non-Newtonian is known as the critical shear rate [60].

By analysing the typical processing range associated with the doctor blade technique – delimited by the dashed lines in *Figure 4.1* – it is apparent that most of the formulations operate predominantly within their Newtonian region, with the notable exception of the 20 wt% CA dopes – especially in GVL – which already experience non-Newtonian shear-thinning before reaching a shear rate of 100 s^{-1} . This

implies that the critical shear rate was systematically lower for higher polymer concentrations and for solutions involving GVL in comparison with the ones in DMSO.

For a deeper understanding of the specific behaviour under the mechanical forces imposed during the casting process, the dynamic viscosity was extracted at a representative shear rate of 46.42 s^{-1} for each formulation, as this value closely estimates the real operational shear rate applied in the laboratory. The resulting correlation between this processing viscosity and the biopolymer concentration for each precursor solution is illustrated in *Figure 4.2*.

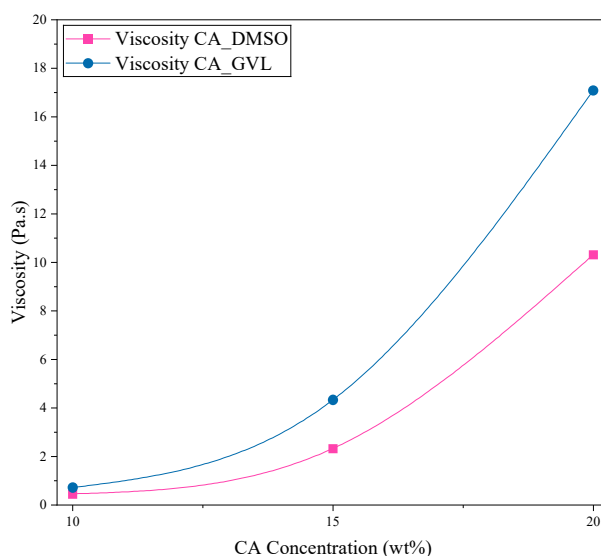


Figure 4.2. Viscosity values for 10, 15 and 20 wt% CA in DMSO and GVL solutions at a shear rate of 42.46 s^{-1} and 20°C .

It is evident that the absolute magnitude of η_0 of the casting dopes exhibited a critical dependence on both the polymer concentration and the nature of the selected solvent, the latter determining the thermodynamic interactions between the CA polymer chains and the solvent molecules. When conducting a comparative evaluation of the profiles at matched mass fractions (10, 15 and 20 wt% CA), the formulations dissolved in GVL systematically positioned themselves along higher η_0 values relative to the DMSO configurations. These results reinforce the previously calculated RED values for the dope solutions, highlighting the restricted affinity of GVL for the CA polymer, as the higher η_0 values indicate a favoured polymer-polymer contact over polymer-solvent interaction.

When performing phase inversion, for a low polymer content of 10 wt% CA, the remarkably low viscosities facilitated an instantaneous and violent liquid-liquid de-mixing rate upon the immersion in the aqueous coagulation bath. Consequently, as shown in *Figure 4.3*, the 10 wt% CA in GVL solutions failed to produce viable structure due to a loss of macro-structural integrity during de-mixing. In the case of 10 wt% CA in DMSO dopes, phase inversion was formally achieved, but the lack of structural reinforcement yielded highly heterogeneous and fragile matrices (*Figure 4.4a*).



Figure 4.3. Immediate structural integrity loss of CA10_GVL membranes when immersed in the water bath due to instantaneous and violent liquid-liquid de-mixing rate.

In contrast, the higher viscosities of the 20 wt% CA formulations acted as a transport barrier, critically retarding the diffusion coefficient at the solvent/non-solvent interface. An increase in polymer concentration is widely reported to retard non-solvent influx and suppress the formation of macro voids, yielding a homogeneous structure [9,22]. While this was true for the alternative formulations, the 20 wt% CA solutions prepared in GVL systematically failed to produce homogeneous matrices, instead displaying prominent macro voids (*Figure 4.4b*). This could be attributed to the lower affinity of GVL with both CA polymer and water, that when coupled with the significantly elevated viscosity of the dope solution, this thermodynamic hindrance led to a delayed de-mixing mechanism where localized solvent-rich pockets became trapped, subsequently giving rise to the observed macro voids.

For the rest of membrane formulations (*Figure 4.4c-e*) doctor blade casting and subsequent phase inversion processes were successfully executed without further inconvenience.

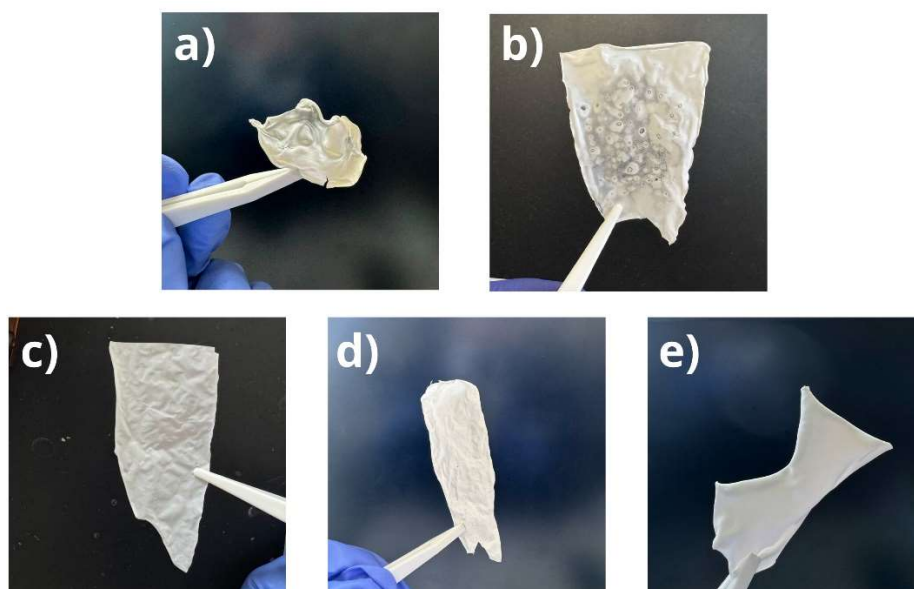


Figure 4.4. Macroscopic appearances of the CA membranes synthesised via the NIPS procedure. Images correspond to: (a) CA10_DMSO and (b) CA20_GVL, both discarded for electrochemical analysis due to a critical fragility and macrostructural heterogeneity, respectively; (c) CA15_DMSO, (d) CA15_GVL, and (e) CA20_DMSO, which exhibited continuous matrices, were selected for subsequent electrochemical characterization. Membranes formulated with 15 wt% CA containing citric acid as an additive displayed a comparable visual morphology to their respective additive-free counterparts.

4.3. Membrane morphology

When evaluating the cross-sectional morphology of the matrices, a primary and definitive structural divergence was observed depending on the solvent system utilised. As shown in *Figure 4.5*, the membranes prepared with pure GVL transitioned into a continuous, cellular sponge-like structure. Conversely, the formulations manufactured using DMSO, represented in *Figure 4.6*, exhibited a classic asymmetric architecture characterised by elongated, well-defined finger-like macro voids. This morphologic contrast strongly correlates with the distinct precipitation kinetics governing the immersion precipitation stage (see Section 2.2.1). Although phase separation occurred within a timeframe of seconds for both systems, the DMSO-based dopes experienced a significantly more rapid, instantaneous de-mixing process upon contact with the aqueous non-solvent.

Furthermore, cross-sectional analysis across the membranes prepared with GVL revealed a dense skin layer at the top surface (the interface with the coagulation bath) followed by a sponge-like substructure, typical of delayed de-mixing. Although this feature was common to all GVL-based formulations, the dense skin layer became increasingly pronounced at higher CA concentrations. In contrast, membranes prepared with DMSO exhibited a porous skin and large, finger-like macro voids at the sub-layer, which is characteristic of instantaneous de-mixing.

When comparing the cross-sections of the pristine 15 wt% CA formulations with their citric acid (CAc) modified counterparts in GVL, the overall macrostructure of the modified membranes appeared distinctly denser, even though precise changes in pore dimensions were difficult to quantify visually. Moreover, the top-surface micrograph of CA15_GVL_CAc revealed no pores that are readily discernible at first glance, whereas pores were clearly identified for the pristine 15 wt% CA formulation. Conversely, for the membranes prepared in DMSO, the incorporation of CAc did not result in any noticeable morphological changes under SEM observation.

An analysis of the surface micrographs corroborated these structural differences. A dense skin layer with limited visible porosity was observed at the non-solvent interface (top surface) across all membranes, whereas the bottom surfaces (in contact with glass) evidence the different resulting surface characteristics due to the diverse de-mixing process for the two solvents.

It is noteworthy that, although the specific CA20_GVL sample selected for SEM analysis appeared visually homogeneous, the micrograph of its top surface exhibits markedly larger pores compared to the other formulations. This microscopic feature directly corroborates the macroscopic inhomogeneity previously discussed for these specific membranes.

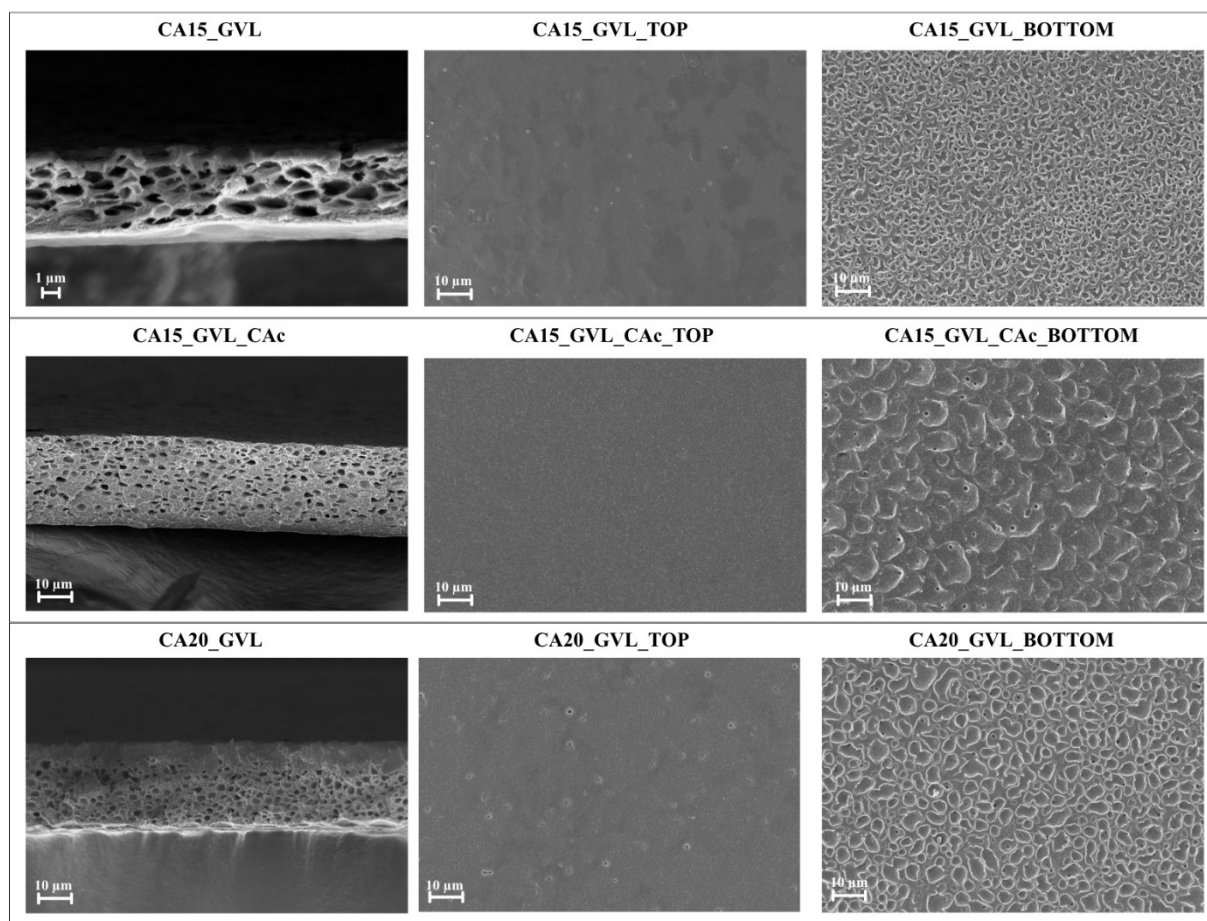


Figure 4.5. Cross-sectional and surface (top and bottom) SEM images of CA membranes obtained via phase inversion from GVL dope solutions.

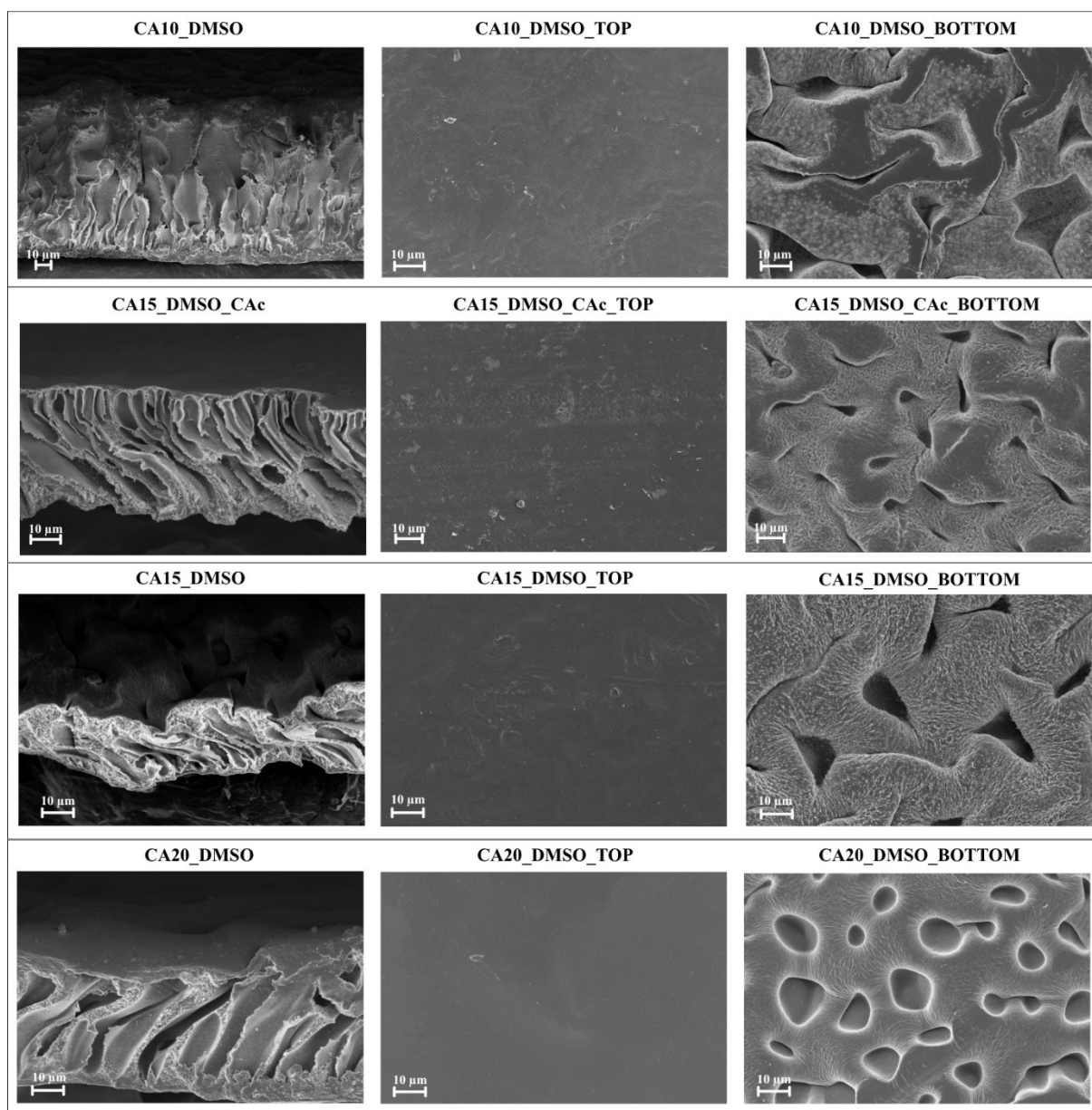


Figure 4.6. Cross-sectional and surface (top and bottom) SEM images of CA membranes obtained via phase inversion from DMSO dope solutions.

4.4. Pore size distribution

Given that all membranes fabricated using GVL as a solvent exhibited a sponge-like structure, their statistical pore size distributions were initially evaluated by analysing cross-sectional SEM micrographs via ImageJ. The mean and median pore sizes (μm), along with the standard deviation for each sample, are detailed in *Table 4.2*.

Table 4.2. Pore size distribution statistical results (in μm), calculated from cross-section SEM images of membranes synthesised using GVL as solvent.

Membrane ID	Mean	Median	Standard Deviation
CA15_GVL	4.648	0.811	8.783
CA15_GVL_CAc	1.107	0.793	5.427
CA20_GVL	1.549	0.793	8.277

A high degree of structural heterogeneity within the membrane structure is evident, as all samples exhibit a high standard deviation. This is particularly notable for the CA15_GVL formulation, which exhibits a substantial standard deviation (8.783) and a mean pore size diameter (4.648 μm) markedly greater than its median (0.811 μm). This significant positive skewness (Mean > Median) for all formulations indicates that membranes are dominated numerically by smaller pores (reflected by the lower median), but the presence of occasional larger pores shifts the arithmetic mean and increases the standard deviation. Consequently, the median value may serve as a more representative value for the description of the resulting pore size of the structural matrix.

Notably, the median value remains practically invariant across all evaluated membranes, stabilising at approximately 0.8 μm . The primary discrepancy lies in the variation of the mean and standard deviation: the incorporation of citric acid into the 15 wt% CA dope solution (CA15_GVL_CAc) drastically reduces the standard deviation to 5.427 and the mean to 1.107 μm . This suggests that the additive acts as a structure-homogenising agent by effectively suppressing the formation of extreme large pores. Conversely, while increasing the polymer concentration to 20 wt% (CA20_GVL) also reduces the mean pore size, the standard deviation remains high (8.277), suggesting that augmenting the polymer concentration alone does not refine the structural heterogeneity as effectively as the CAc additive.

However, it is important to note that calculated values derive from a small area of the total membrane, as they are based on SEM cross-sectional micrographs. While the image analysis algorithm provides a quantification of the visible pores, with $N \geq 300$ pores per sample, the localized nature of SEM imaging means these results represent a specific section of the membrane. Given the polydispersity of the membrane, incorporating multi-area sampling from random locations of the membrane would be useful to validate the global pore size distribution. Furthermore, another common limitation of this method relays on the difficulty to precisely identify the porosity of the cross section, based on the image contrast, due to the three-dimensional nature of the sample and the interference of the porous network within the depth of the micrographs.

To further quantify the through-pore architecture, initial characterisation was attempted via capillary flow porometry. However, this technique lower detection limit of approximately 100 nm failed to yield results for either both analysed CA15_GVL (with and without CAc) and CA15_DMSO membranes. This finding strongly suggested that the active pore dimensions of these materials were significantly smaller than the instrument's operational range. Interestingly, this test incidentally demonstrated the

mechanical robustness of the materials, as the membranes successfully withstood applied pressures of approximately 6 bar without structural failure.

Therefore, to properly resolve this fine structural feature, CO₂ adsorption was employed to target the microporosity. The results obtained from these measurements are illustrated in *Figure 4.7*.

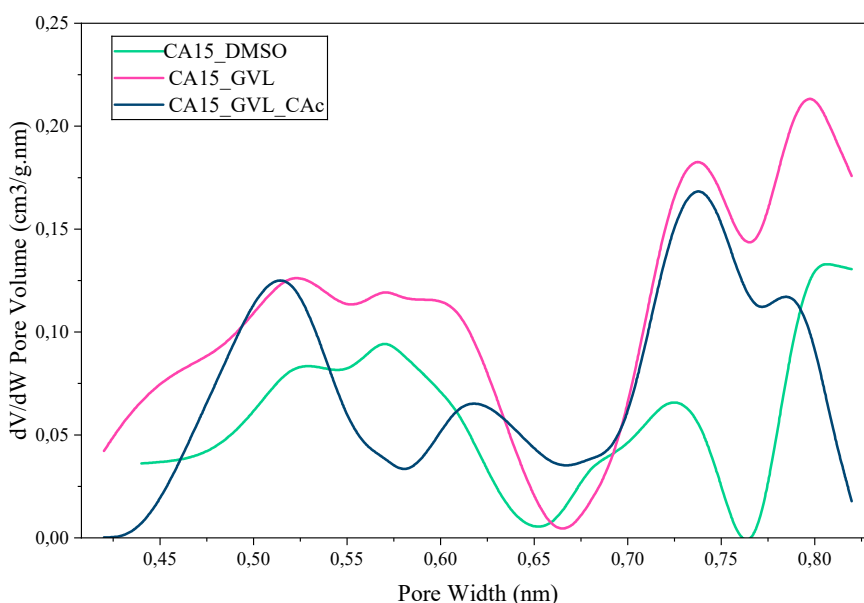


Figure 4.7. Pore Size Distribution (PSD) obtained via CO₂ porosimetry, calculated using a Density Functional Theory (DFT) model with a regularization parameter of 0.01. The presented data have been corrected by subtracting the blank measurement (empty sample tube).

When evaluating these results, it is crucial to contextualise the ultramicroporosity within the broader macroscopic architecture of the membranes. As observed in the SEM micrographs, the CA15_DMSO membranes exhibit a pronounced finger-like morphology, with a relative thin skin layer. Consequently, the CO₂ adsorption data does not represent the global porosity of the membrane, which is dominated by these large macrovoids, but rather characterises the intrinsic microporosity of the dense polymer matrix itself (i.e., the walls separating the macro voids and the skin layer). Contrary, for the CA15_GVL - with and without CAC – the results can also include pores of the total architecture of the membrane, due to the denser polymer matrix characteristic of its sponge-like structure.

The CA15_DMSO sample displays a broad, heterogeneous pore size distribution lacking a markedly dominant pore size. In contrast, the utilisation of GVL promotes the formation of a sharply defined dominant peak at 0.80 nm. Furthermore, the incorporation of citric acid as an additive (CA15_GVL_CAc) demonstrably alters the resulting porous architecture. As observed in the Pore Size Distribution (PSD) profile, the addition of citric acid shifts the distribution towards narrower and more defined peaks at lower pore widths compared to the pristine GVL membrane. This structural refinement aligns with current literature[12]; when added at low concentrations, citric acid disperses uniformly within the polymer network, subtly modifying the solvent/non-solvent exchange kinetics during the

phase inversion process. This modulated thermodynamic pathway ultimately yields a denser polymer matrix characterised by smaller, well-defined ultramicropores.

Moreover, image analysis of the cross-sectional micrographs for the CA15_GVL samples reveals internal pore dimensions that significantly exceed the microporous scale, falling within a range that would have been readily detected by the initial capillary flow porometry. The absence of measurable flow in those initial tests demonstrates that the effective through-pore architecture is governed by much narrower channels than those observed within the bulk internal structure. This phenomenon is primarily attributed to the dense skin layer at the membrane interface, which dictates the overall permeability by acting as a structural bottleneck.

The ATR-FTIR of DMSO-based and GVL-based membranes are shown in *Figure 4.8* and *Figure 4.9*, respectively. All samples exhibited the characteristic absorption bands of CA, confirming that the polymer backbone remained stable throughout the synthesis. The spectrum contains the three saturated ester characteristic peaks, with the C=O stretching group from the acetate's carbonyl group at ~ 1750 cm^{-1} , the special acetate ester C—C—O stretching peak at ~ 1240 cm^{-1} and the C—O—C stretch of the pyranose ring at 1051 cm^{-1} . Absorption peaks at 1370 cm^{-1} and ~ 2915 cm^{-1} correspond to C—H bending and C—H stretching, respectively. The wide stretching band at ~ 3450 cm^{-1} can be attributed to its hydroxyl groups [61–63].

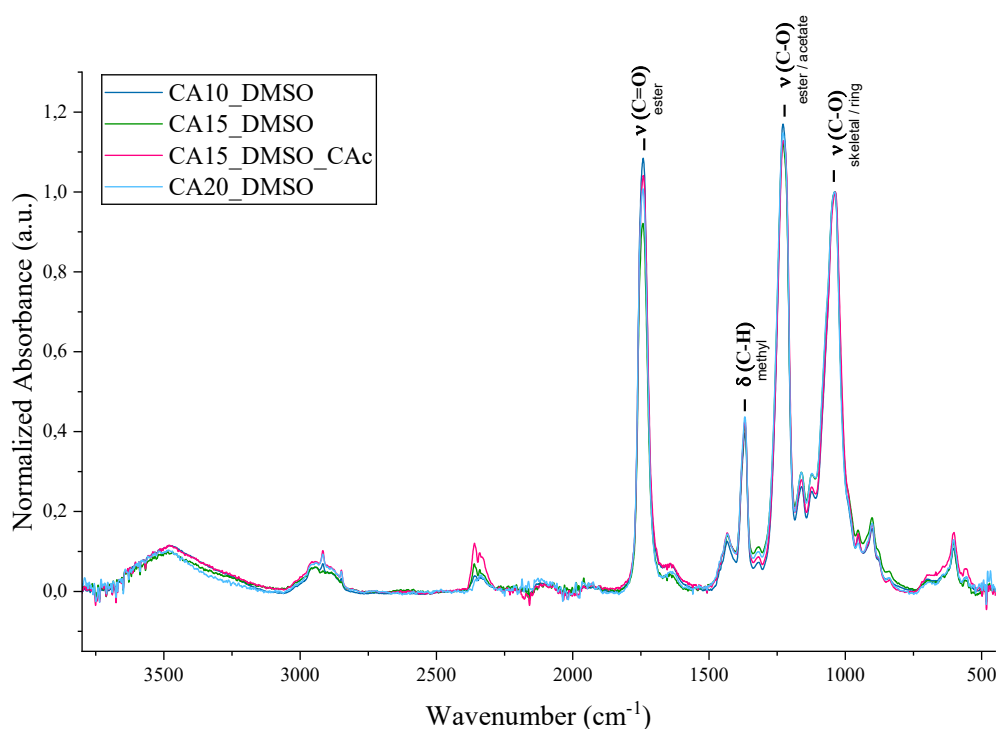


Figure 4.8. ATR-FTIR spectra of the CA membranes prepared using DMSO. Each spectrum has been normalized relative to the pyranose ring stretching band at ~ 1051 cm^{-1} .

An analysis of formulations containing CAC shows different results for the two solvents. In *Figure 4.8* it is evident that the addition of CAC to DMSO-based formulations did not result in chemical structure changes. This phenomenon may be governed by the combination of two synergic factors. On one hand, DMSO exhibits a high affinity for water (the non-solvent), which triggers an instantaneous de-mixing mechanism upon immersion in the coagulation bath. On the other hand, CAC is highly hydrophilic and soluble in water. Due to the fast exchange rate between DMSO and water, the CAC molecules lack the necessary residence time to establish stable intermolecular interactions with the cellulose acetate chains. Consequently, the additive is preferentially drafted into the aqueous phase and leached out of the polymer matrix before the complete formation of the membrane, leaving the final chemical structure virtually identical to that of the neat CA formulation.

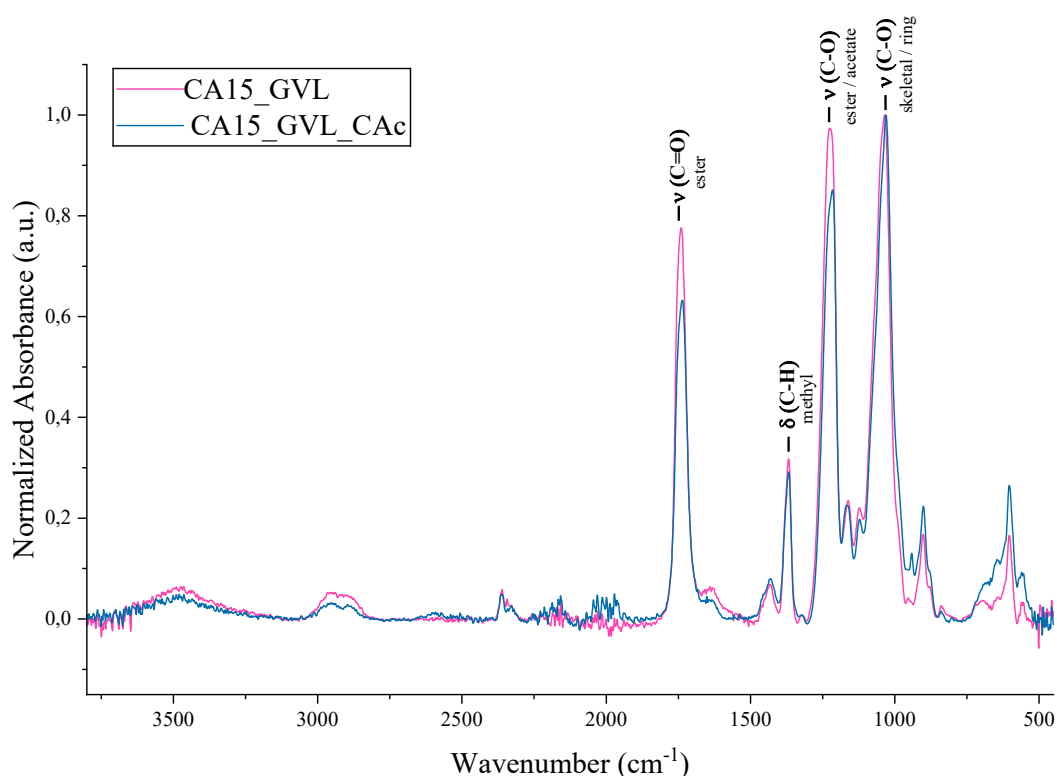


Figure 4.9. ATR-FTIR spectra of the CA membranes prepared using GVL. Each spectrum has been normalized relative to the pyranose ring stretching band at $\sim 1051\text{ cm}^{-1}$.

Conversely, as presented in *Figure 4.9*, the GVL-based system exhibits clear evidence of effective chemical modification upon CAC addition. In this case, a distinct shift of the carbonyl $\text{C}=\text{O}$ stretching band to lower wavenumbers is observed. This redshift, accompanied by a noticeable decrease in the relative peak intensity, is indicative of the presence of intermolecular interactions. Furthermore, this behaviour is consistently mirrored in the ester fingerprint region, where the characteristic acetate ester $\text{C}-\text{C}-\text{O}$ stretching peak at approximately 1240 cm^{-1} undergoes a substantial attenuation in relative intensity for the CA15_GVL_CAc formulation. This distinct difference was attributed to the slower demixing process of the GVL-based formulations, which allows a fraction of the CAC molecules to remain entrapped within the polymer matrix and form strong intermolecular hydrogen bonds with the

carbonyl groups of cellulose acetate. Because this interaction correlates with a reduced pore size distribution compared to the neat CA membrane, based on recent investigations [12], it suggests that the citric acid concentration is sufficiently low to induce crosslinking among the CA polymer chains rather than plasticization, ultimately yielding a more compact structure.

4.5. Electrochemical Characterization

Initial stability testing of the CA membranes across a range of pH conditions revealed their unsuitability for use in alkaline environments. Specifically, the membranes suffered a complete loss of structural integrity after one hour of immersion in 1 M NaOH. Consequently, the preliminary electrochemical testing was conducted exclusively performed in acidic (0.5 M H₂SO₄) and neutral (0.5 M Na₂SO₄) media.

It is worth saying that, when performing the electrochemical characterisations for all samples, it was observed that the resistance measured immediately after immersing the membrane in the electrolyte solution was lower after the one measured after an approximate time of three hours, which was consequently the time of “hydration” of the membrane on the aqueous electrolyte established before performing the following discussed electrochemical characterisations. This effect was attributed to a progressive physical swelling dynamics of the cellulose acetate matrix rather than chemical interactions with the specific electrolyte.

Upon initial contact, the aqueous solution rapidly permeates the larger pores of the dry membrane, providing a temporary, low-resistance pathway for ionic transport. Over time, as the membrane remains immersed, the hydrophilic functional groups of the cellulose acetate chains absorb the solvent, causing the polymer matrix to swell. This volumetric expansion of the polymer network physically constricts the internal porous channels, reducing the effective pore size and increasing the tortuosity of the membrane. This structural constriction inherently hinders ionic mobility, leading to the observed increase in electrical resistance. After the established hydration period, the swelling reaches a thermodynamic and structural equilibrium. At this point, the membrane achieves a fully swollen, stable state, thereby explaining the constant and steady resistance recorded in all subsequent measurement loops and highlighting its dimensional stability under continuous operation [5,64,65].

Table 4.3 summarises the ionic conductivity values (mS cm⁻¹) obtained during the preliminary electrochemical screening of the investigated membranes. These conductivities were derived according to *Equation 3.5*, utilising the membrane resistances extracted from the EIS measurements.

Table 4.3. Ionic conductivities (mS cm^{-1}) calculated from the bulk membrane resistances (R_m) extracted via EIS measurements in an H-cell configuration, using 0.5 M H_2SO_4 and 0.5M Na_2SO_4 aqueous electrolytes.

Sample	H_2SO_4 0.5 M	Na_2SO_4 0.5 M
pCA15_GVL	1,99E-02	1,09E-03
pCA15_GVL_CAc	7,94E-03	1,05E-04
pCA15_DMSO	2,05	2,63E-02
pCA20_DMSO	1,38	5,17E-02

The ionic conductivity values obtained for all fabricated membranes are at least one order of magnitude greater in 0.5 M H_2SO_4 than when tested in 0.5 M Na_2SO_4 . When evaluating the influence of the casting solvents, a clear superiority was observed for the DMSO-based membranes, which yielded significantly higher ionic conductivities. Regarding the CA membranes prepared using GVL, the formulation incorporating citric acid demonstrated the highest electrical resistance. This elevated resistance was attributed to its dense morphology, corroborated by SEM imaging. Both the thicker dense skin layer and the more compact sponge-like sub-layer contribute to a highly tortuous pore network, which restricts ion mobility and increases the overall transport resistance across the separator.

Following this comprehensive screening, the subsequent research framework was divided to explore specific applications for the most notable formulations. Exhibiting the lowest overall resistance, the CA15_DMSO membranes were tested as separators in supercapacitors using a 0.5 M H_2SO_4 electrolyte. Meanwhile, the CA20_DMSO formulation was subjected to preliminary testing as polymeric coating for LMO-based electrodes. Finally, the CA15_GVL_CAc membrane was selected for a preliminary proof-of-concept evaluation regarding its potential for reverse electrodialysis applications.

4.6. Proof-of-Concept Applications

4.6.1. Supercapacitor performance of CA15_DMSO separators

To determine the electrochemical stability window (ESW), cyclic voltammetry scans were initiated from the open circuit potential at a constant scan rate of 5 mV s^{-1} . This slow sweep rate was selected to ensure the system completed all possible reactions at the electrode/electrolyte interface. The resulting curves are presented in *Figure 4.10(a)*. The sharp increase in cathodic current observed when approaching -0.5 V is indicative of the hydrogen evolution reaction (HER), while the anodic current surge at $+0.8 \text{ V}$ corresponds to the oxygen evolution reaction (OER). To avoid these parasitic decomposition reactions, the safe operational voltage window for the system was established between -0.2 V and $+0.6 \text{ V}$.

The Nyquist plots for the EIS measurements exhibit a distinct semicircle in the high-frequency region. This feature can be attributed both to charge-transfer processes associated with redox reactions occurring at the surface of the carbon material in aqueous electrolytes and to the resistance arising from the contact

between AC–AC/AC–CB particles and the active material with the current collector, which contributes to the overall cell resistance [46]. As presented in *Figure 4.10(b)*, the initial and post-cycling impedance spectra exhibit practically the same behaviour. This stability demonstrates that the charge-discharge cycles induced no significant changes in ionic diffusion resistance within the CA membrane or at the electrode-electrolyte interface.

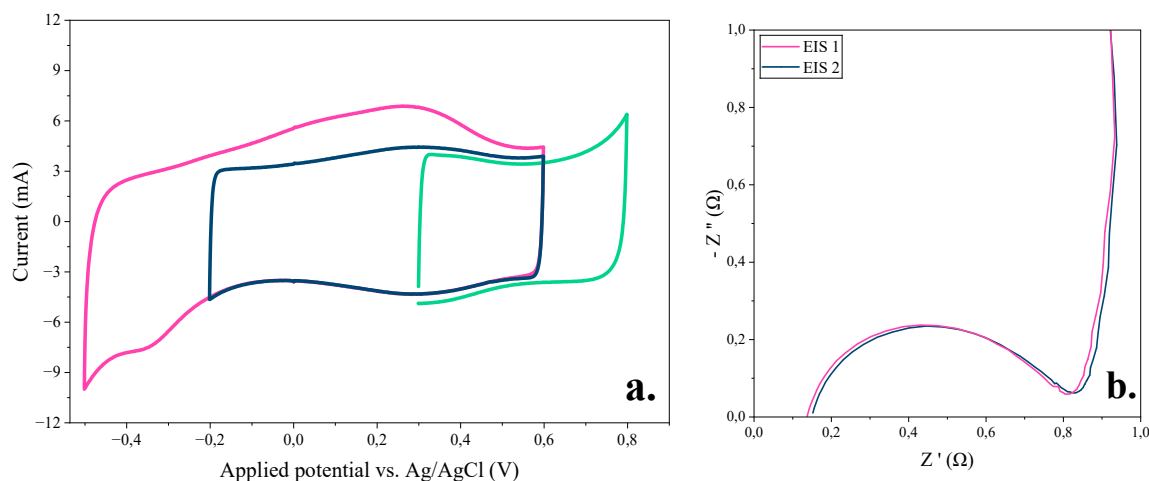


Figure 4.10. Electrochemical characterization of the CA15_DMSO membrane in a three-electrode configuration in 0.5 M H_2SO_4 aqueous electrolyte. (a) Cyclic voltammograms recorded at a scan rate of 5 mV s^{-1} at different potential windows. (b) Nyquist plots before (pink curve) and after (blue curve) cycling

To assess the comprehensive performance of the device, a two-electrode configuration was employed to carry out EIS, CV and float test measurements. The symmetrical supercapacitor setup consisted of two identical AC/HPC@Ti, with 0.5 M H_2SO_4 serving as the aqueous electrolyte.

The Nyquist plot derived from the EIS measurements, presented in *Figure 4.11* reveals a high-frequency intercept of 0.58Ω , which strictly corresponds to the bulk resistance (R_s). Conversely, the medium-frequency intercept, which accounts for the additional charge transfer and contact resistance (R_{ct}) introduced by the porous carbon electrodes, reaches 10.51Ω . This mid-frequency value is remarkably high compared to the results obtained in the preliminary three-electrode configuration, which yielded an R_s of 0.14Ω and a mid-frequency intercept of 0.80Ω . Although a moderate increase is expected in a symmetrical two-electrode system—as the resistive contributions of both electrodes are combined—an increase of this magnitude was primarily attributed to a poorer interfacial contact between the titanium current collector and the composite electrode within this specific test cell, rather than inherent limitations of the membrane or the active material.

The cyclic voltammograms recorded for the symmetric supercapacitor assembled with the CA15_DMSO separator are shown in *Figure 4.12*. The applied scan rates varied from 1 mV s^{-1} to 1000 mV s^{-1} , with all measurements conducted within the previously established voltage window of 0.0 to 0.8 V. It can be noted that at slower scan rates, the curves exhibit a near-rectangular shape, indicating typical capacitive behaviour. However, this profile begins to deviate noticeably starting at 50 mV s^{-1} . Increasing

the scan rate leads to a slower current response at the voltage reversal points, resulting in curves with a “modified ellipse” shape. This deformation becomes increasingly pronounced as the sweep rate rises, ultimately exhibiting a fully resistive response at 500 and 1000 mV s^{-1} . This transition occurs because, at fast sweep rates, ions do not have enough time to access the deeper pores of the electrode material before current reversal.

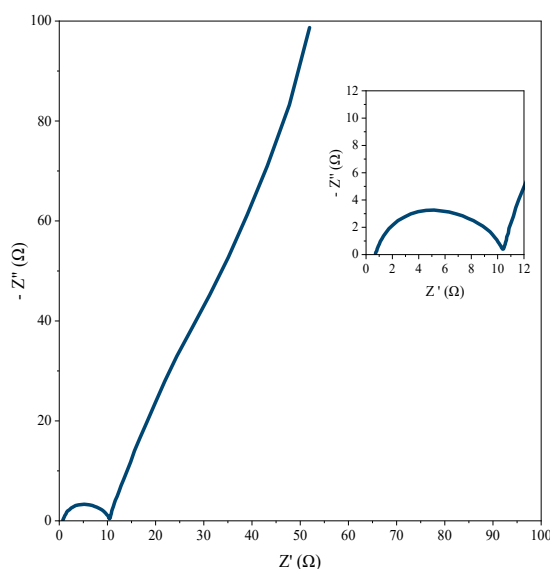


Figure 4.11. Nyquist plots of the CA15_DMSO membrane in a symmetric two-electrode configuration using AC/HPC@Ti as electrodes and a 0.5 M H_2SO_4 aqueous electrolyte. The inset shows an enlarged view of the high-frequency region.

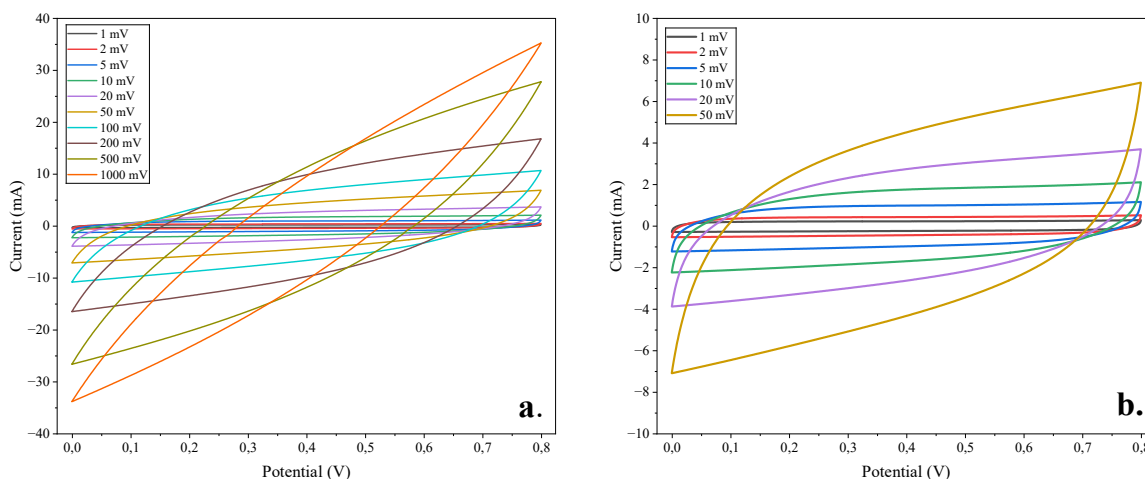


Figure 4.12. (a) Cyclic voltammograms of a symmetric supercapacitor incorporating the CA15_DMSO separator at scan rates from 1 to 1000 mV s^{-1} in 0.5 M H_2SO_4 . (b) Magnified view of the CV curves at lower scan rates (1 to 50 mV s^{-1}).

The stability of the symmetric supercapacitor under continuous operational conditions was evaluated through a continuous voltage floating test over approximately 120 hours. As shown in the capacity retention profile (Figure 4.13a), the system experienced minor initial fluctuations before stabilizing at a plateau of approximately 105%. This increase beyond the initial baseline could be a phenomenon

associated with surface conditioning of the electrodes. The reversibility of the system remained remarkably robust, evidenced by a Coulombic efficiency (Figure 4.13b) that stayed nearly constant around 96% throughout the entire test. This high stability indicates a minimal occurrence of irreversible parasitic reactions. Furthermore, the energy efficiency (Figure 4.13c) consistently maintained around 70-71%. Moreover, the ESR (Figure 4.13d) maintained a low baseline, starting at a minimum of 1.47 Ω , but experienced a temporary peak of 2.24 Ω at an intermediate cycle. This transient spike in internal resistance - likely related to minor interfacial rearrangements or transient pore blockage - perfectly coincides with the singular drop in energy efficiency to 67%. Finally, the leakage current profile (Figure 4.13e) confirms the structural integrity of the CA15_DMSO membrane. The current required to maintain the maximum holding voltage started at negligible values and, although it progressively increased through the aging process, it reached a plateau around 0.013 mA cm⁻². This value may be attributed to corrosion occurring at the negative electrode in these conditions. However, it is an exceptionally low value, representing a leakage current requirement of only 1.5% of the initial current.

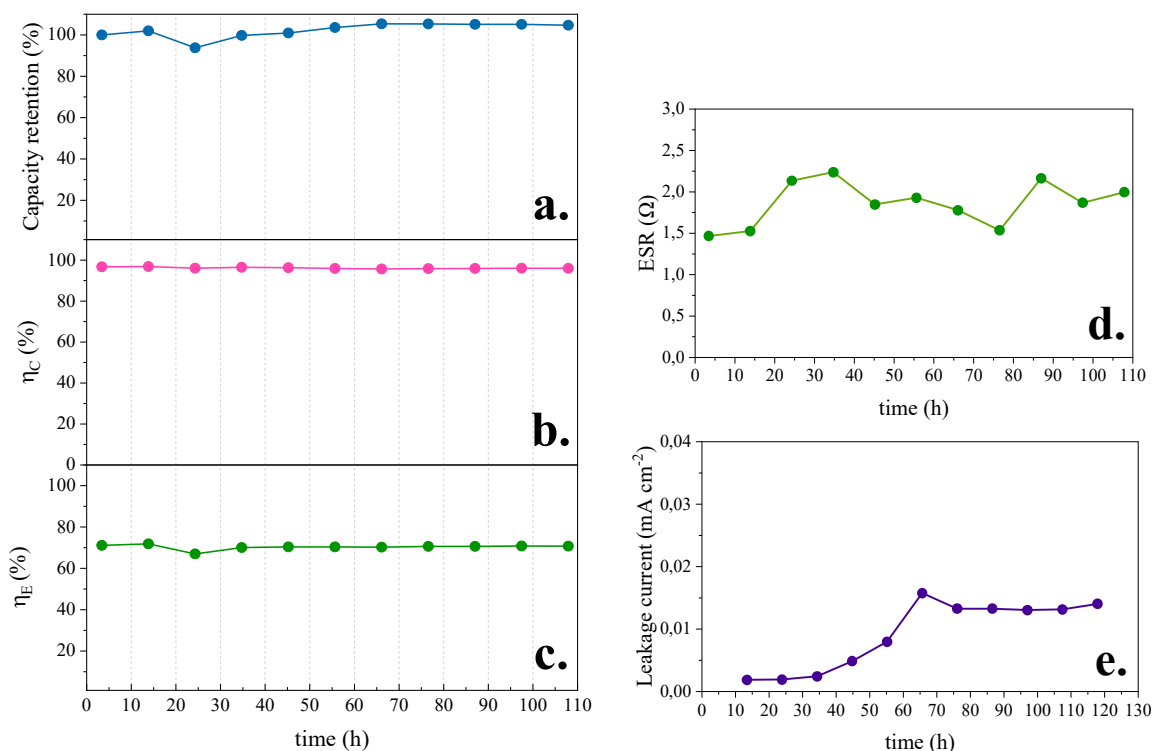


Figure 4.13. Performance metrics of the symmetric supercapacitor assembled with the CA15_DMSO separator during the continuous voltage floating test in 0.5 M H₂SO₄: (a) Capacity retention (Q/Q_0), (b) Coulombic efficiency (η_c), (c) Energy efficiency (η_E), (d) Equivalent series resistance (ESR), and (e) Leakage current density profile. Note that the time axis for the leakage current profile (e) reflects the measurement points at the end of each floating stage, distinct from the cycling periods shown in panels (a–d).

4.6.2. Coating assessment of CA20_DMSO for LMO-based electrodes

The coated LMO electrodes, obtained as described in *Section 3.2*, could be successfully characterised since, upon visual inspection, the membrane appeared to adhere effectively to the electrode surface. To evaluate the protective efficacy, electrochemical stability and interfacial kinetic behaviour of the synthesised DMSO-based membranes, a three-electrode Swagelok cell was assembled using the coated LMO electrode as WE and 2 M Li_2SO_4 as aqueous electrolyte.

Figure 4.14 presents the Nyquist plots of the symmetric cell, recorded prior to the voltametric sweeping and immediately after the completion of 150 continuous CV cycles. Notably, the bulk resistance (R_s) at the high-frequency intercept on the real axis remains practically unaltered before and after cycling. This indicates that the CA20_DMSO coating is electrochemically robust and chemically stable in the tested medium, and that it does not delaminate from the LMO surface into the electrolyte, thereby preserving the bulk transport pathways of the cell.

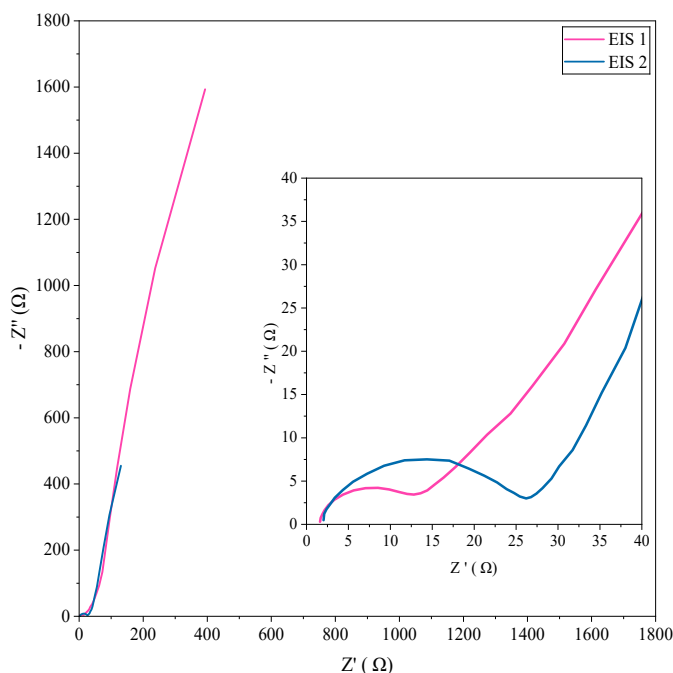


Figure 4.14. Nyquist plots before (pink curve) and after (blue curve) cycling of the three-electrode Swagelok cell with a CA20_DMSO-coated LMO working electrode in a solution of 2 M Li_2SO_4 as aqueous electrolyte.

The R_{ct} at the mid-frequency region, reflected by the diameter of the semicircle, represents the resistance at the electrode-coating-electrolyte interface. Prior to cycling, the modified electrode exhibits an initial R_{ct} of 13 Ω . After 150 cycles, the R_{ct} increases to 25.5 Ω . This increase may be attributed to two possible factors: the inherent dynamic evolution of the cathode–electrolyte interphase (CEI) in aqueous systems, and/or the degradation of the active material. Typically, CEI evolution is driven by the progressive formation and stabilisation of a surface layer, coupled with minor mechanical stresses induced by Jahn–Teller lattice distortions during lithium insertion [66–68]. However, it remains unclear whether a true

CEI layer actually forms under these specific conditions, given that the CA coating prevents direct contact between the active electrode material and the electrolyte. Crucially, although this leads to a measurable increase in charge transfer resistance, the final R_{ct} value still confirms that the protective CA20_DMSO matrix successfully maintains electrode integrity throughout the cycling regime.

The cyclic voltammograms, presented in *Figure 4.15*, corroborate the steady electrochemical performance enabled by the CA20_DMSO coating. The curves display the characteristic faradaic redox peaks associated with the lithium extraction and insertion processes within the LMO spinel framework[67], indicating that the coating did not impede the transport of lithium ions. This functional feature was maintained over 150 cycles, with no significant alterations observed in the anodic (delithiation) and cathodic (lithiation) profiles across all sweeps.

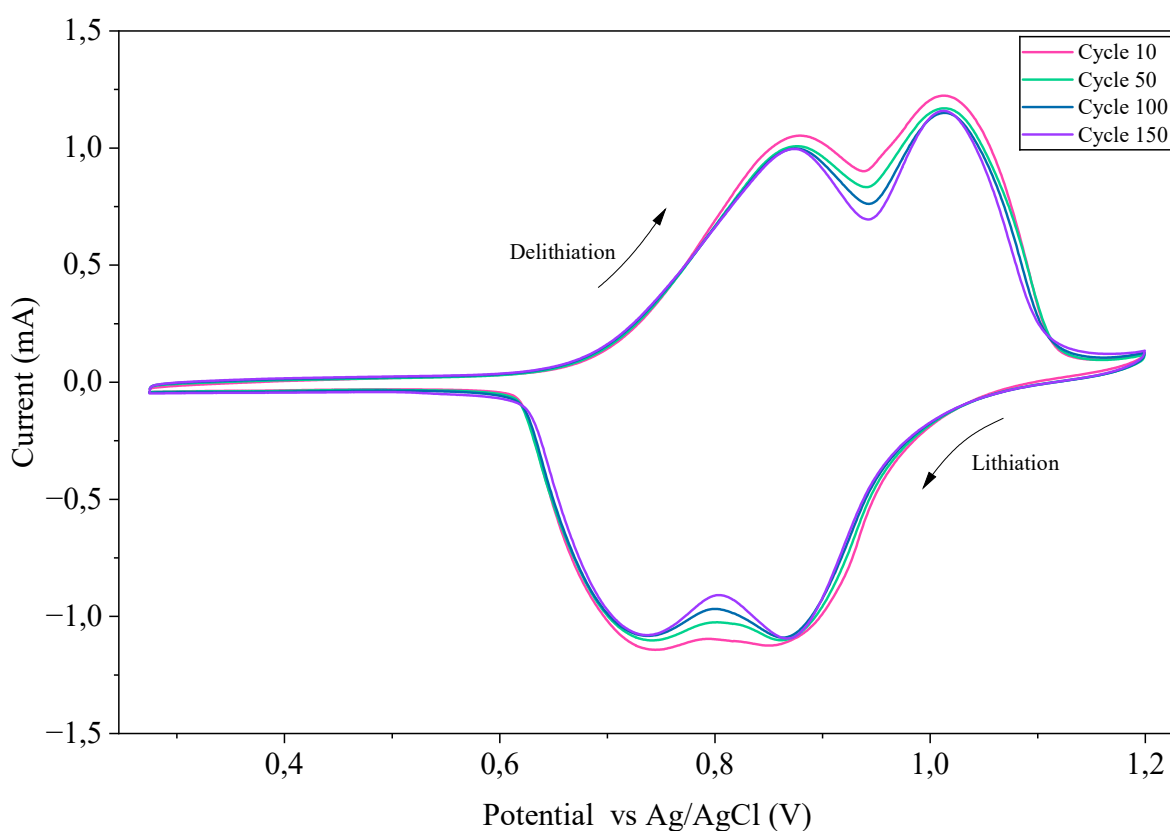


Figure 4.15. Cyclic voltammograms of a symmetric supercapacitor incorporating the CA20_DMSO coating to LMO-based electrodes at a scan rate of 0.5 mV s^{-1} in $2 \text{ M Li}_2\text{SO}_4$. The distinct peaks observed correspond to the faradaic bulk intercalation processes characteristic of these metallic oxide electrodes, specifically representing the anodic (delithiation) and cathodic (lithiation) profiles.

To further quantify the stability of the system, the areal capacity, alongside the coulombic and energy efficiencies of the CA20_DMSO-coated LMO electrode, were evaluated by integrating the areas under the corresponding cyclic voltammetry curves. The resulting values are shown in *Figure 4.16*.

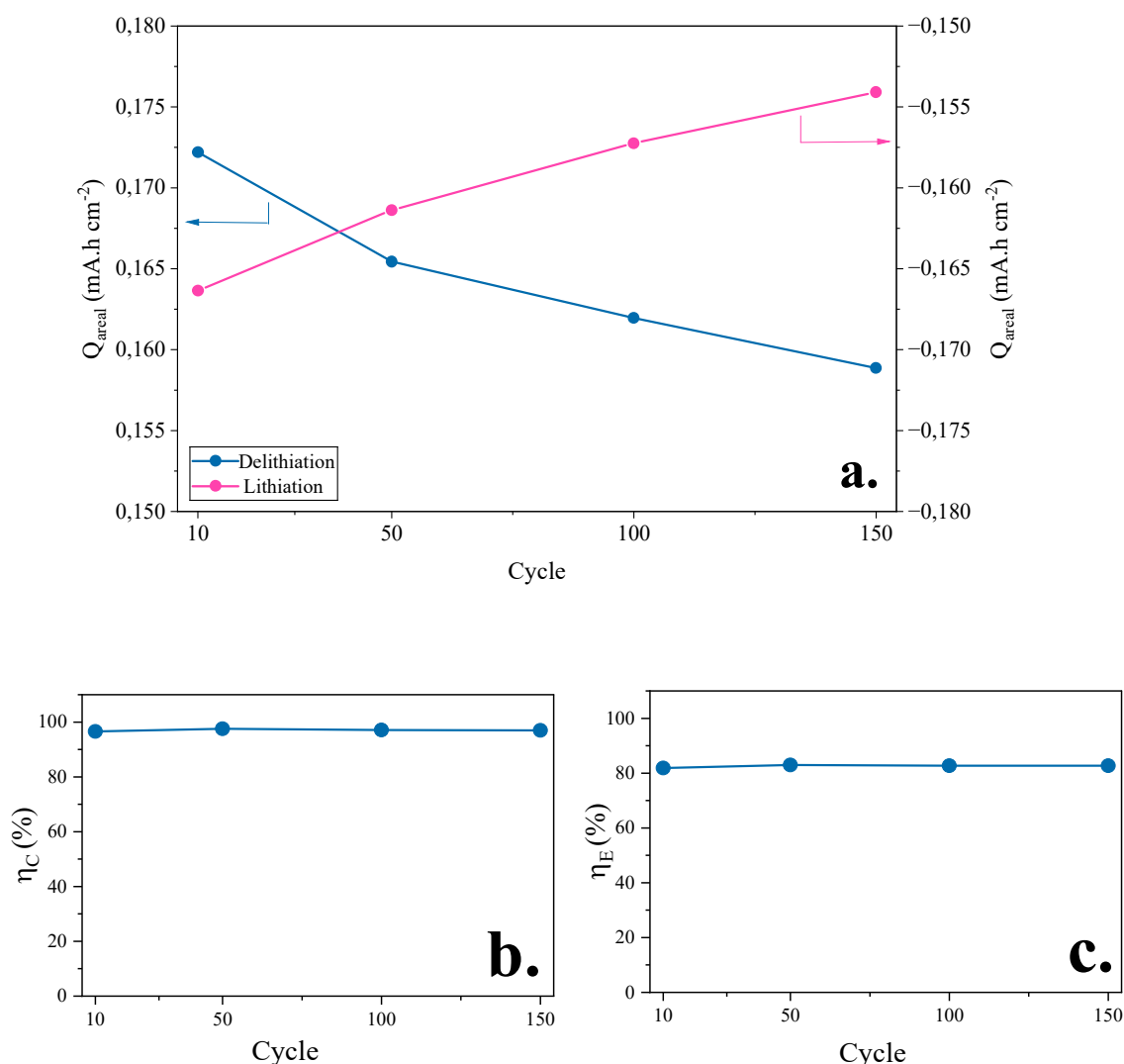


Figure 4.16. (a) Areal capacity of the CA20_DMSO-coated LMO electrode calculated from cyclic voltammograms performed at a scan rate of 0.5 mV s^{-1} in $2 \text{ M Li}_2\text{SO}_4$. The blue line corresponds to the delithiation (anodic process) and the pink line to the lithiation (cathodic process). (b) Coulombic efficiency, and (c) Energy efficiency extracted from the recorded CV data.

At the 10th cycle, the electrode exhibited an anodic areal capacity of $0.172 \text{ mA.h cm}^{-2}$ and a cathodic areal capacity of $0.166 \text{ mA.h cm}^{-2}$. After 150 cycles, the areal capacity experienced a decrease of only 7.75% and 7.34% for the anodic and cathodic sweeps, respectively. These results suggest that the CA20_DMSO coating not only allows the lithium-ion transport but also provides a stable interfacial environment that suppresses side reaction between the electrode and the electrolyte. Furthermore, the energy efficiency remained highly stable at approximately 83% throughout the cycling process. This is a further corroboration that the ionic transport pathways within the membrane remain unobstructed and stable.

Following electrochemical testing, the electrode was analysed via SEM imaging (Figure 4.17). The top-view micrographs of the CA20_DMSO coating revealed a uniform membrane deposition with

occasional superficial pinholes. Furthermore, a pattern of parallel striations is evident on the membrane surface. This topographical feature is a direct consequence of the mechanical compression of the glass fibre separator against the membrane in the Swagelok cell configuration. Additionally, the cylindrical structures observed across the surface correspond to remnants of the glass fibres that remained adhered to the membrane upon dismantling the cell after the electrochemical tests. A closer inspection within these pinholes reveals the presence of some LMO electrode particles deposited onto the internal surface of the membrane macro voids (*Figure 4.17c*). This observation is further corroborated by cross-sectional imaging, which additionally demonstrates relatively good adhesion of the membrane to the electrode.

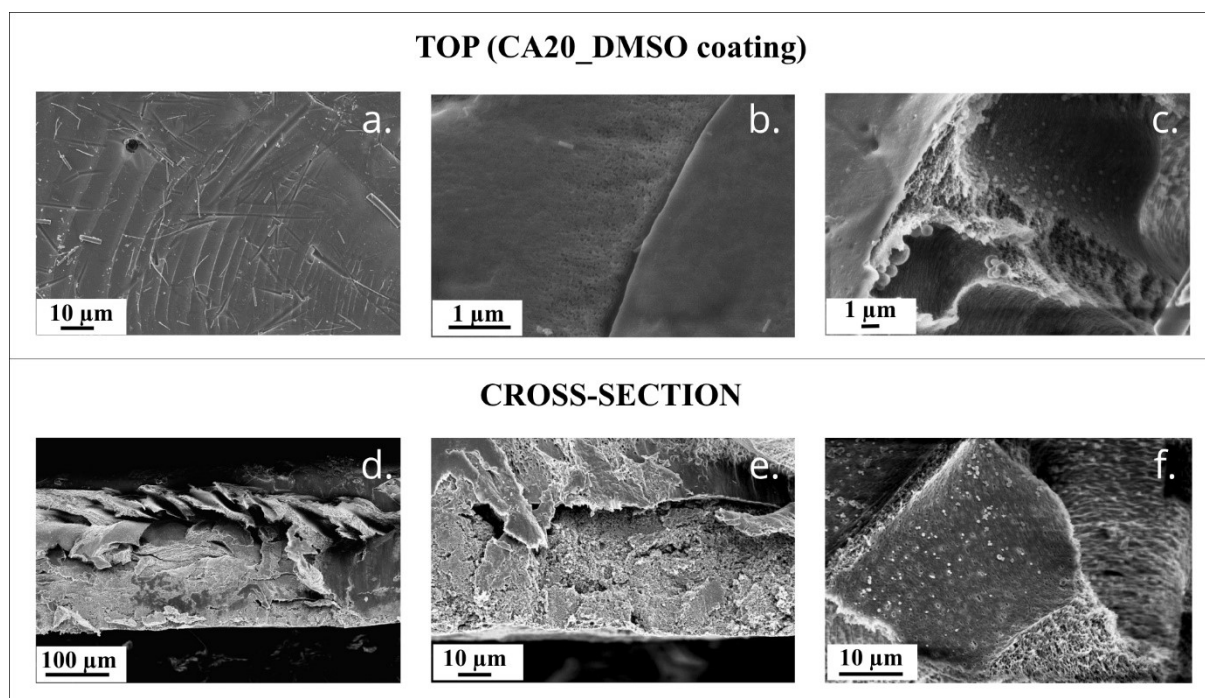


Figure 4.17. Scanning electron microscopy (SEM) images of the CA20_DMSO-coated LMO electrode at various magnifications. (a–c) Top-view micrographs of the CA20_DMSO coating surface. (d–f) Cross-sectional views detailing the internal structure and the interface between the membrane and the underlying electrode.

4.6.3. Salinity Gradient Power potential of CA15_GVL_CAc

To evaluate the Salinity Gradient Power (SGP) potential of the CA15_GVL_CAc membrane, inspired by reverse electrodialysis principles, the Open Circuit Voltage (OCV), alternated with periodical EIS, was continuously monitored across the established concentration gradient over a total of 134 hours.

The Nyquist plot illustrating the resistive behaviour of the CA15_GVL_CAc membranes, assembled in an H-cell configuration with each half-cell containing different KCl concentration, is depicted in *Figure 4.18*. For the EIS measurement performed one minute after the start of the OCV test (First EIS), the Nyquist plot exhibited a lower resistance at the mid frequency intercept. However, the resistance immediately shifted to a higher, stable value, indicating a good membrane stability. Given that the membrane was not pre-immersed in the electrolyte prior to the test, this initial behaviour may be

attributed to the progressive physical swelling dynamics of the cellulose acetate matrix, as comprehensively detailed in *Section 4.5*.

Nevertheless, it must be emphasised that the overall resistances observed are exceedingly high. Although the first intercept at high frequencies remains at relatively low values (approximately $50\ \Omega$), the mid-frequency intercept, which incorporates the intrinsic membrane resistance (R_m), must be factored into the performance analysis. These elevated values can be directly attributed to the extremely dense skin layer of the membrane and the high tortuosity of the pathways that migrating ions must traverse. Furthermore, this restricted ionic mobility strongly suggests that a significant proportion of the micropores previously detected via CO_2 porosimetry are likely 'dead-end' pores, thereby contributing to the total pore volume without facilitating through-plane ion transport.

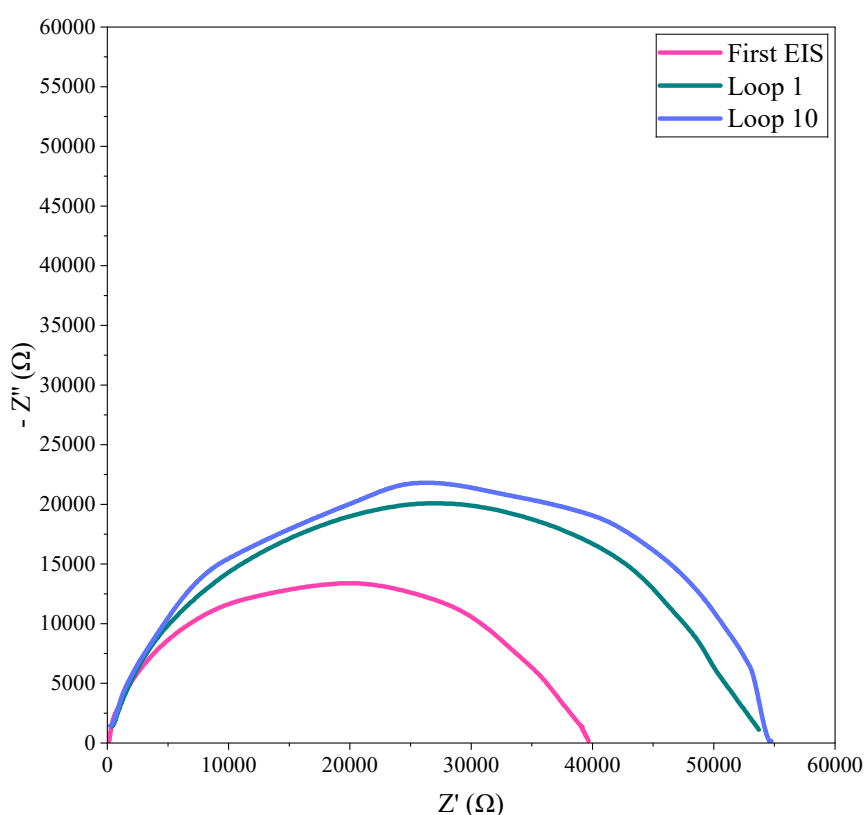


Figure 4.18. Nyquist plot of the H-cell configuration, comprising two half-cells containing $0.1\ \text{M KCl}$ and $0.01\ \text{M KCl}$ solutions respectively, separated by a CA15_GVL_CAc membrane.

Results of the OCV are shown in *Figure 4.19*. During the initial 1-minute stabilization phase, a membrane potential of $-0.04236\ \text{V}$ was recorded. This measurable voltage, generated by the concentration difference between the two half-cells separated by the membrane, represents the initial membrane potential and, consequently, demonstrates the membrane's fundamental capacity to harness energy from a salinity gradient.

It is noteworthy that a more pronounced decay in the OCV magnitude occurred during the first few hours. This rapid decline is directly attributed to the initially high electrochemical potential gradient, which provides the maximum driving force for ion transport. After just two hours, the recorded membrane potential had dropped to -0.019 V, representing a 55% decrease from the initial voltage.

Over the subsequent hours, as the concentration gradient and the associated driving force gradually diminished, the magnitude of the OCV exhibited a slower, continuous decay, ultimately reaching -0.00225 V at the end of the test. However, it is crucial to contextualise this decay within the operational dynamics of a practical reverse electrodialysis stack. In a full-scale reverse electrodialysis system, the membrane operates under a continuous crossflow of both concentrated and diluted feed solutions. Consequently, the residence time of the electrolytes at the membrane interface is significantly shorter than in the static batch configuration investigated here, which effectively prevents bulk concentration depletion. Considering these hydrodynamic factors, the initial OCV results are highly promising; the fact that the potential did not exhibit an instantaneous drop to zero confirms that the membrane offers sufficient initial resistance to unhindered co-ion crossover, maintaining a viable electromotive force during the critical initial contact period.

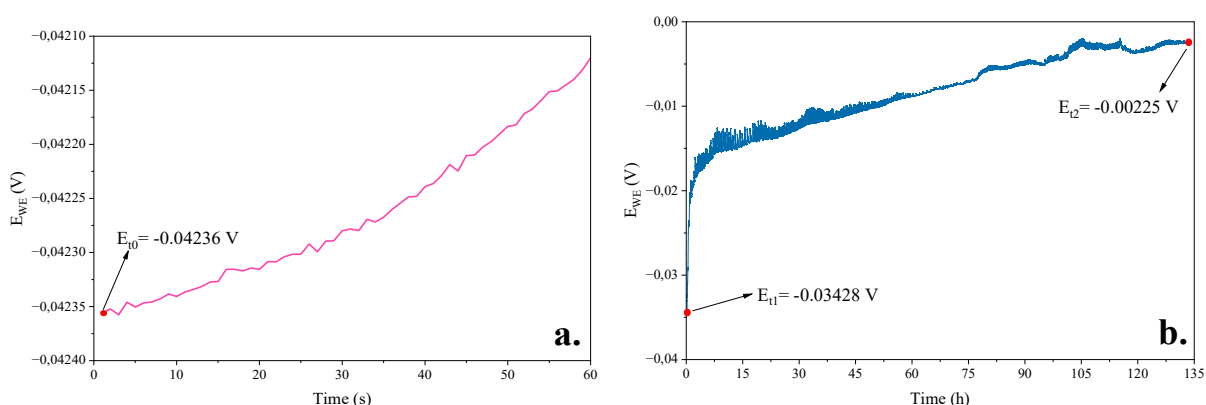


Figure 4.19. Open Circuit Voltage (OCV) across the H-cell configuration (0.1 M KCl | CA15_GVL_CAc membrane | 0.01 M KCl). (a) Initial 1-minute measurement (time in seconds) used to extract the apparent membrane potential ≈ 0 . (b) Extended measurement illustrating the membrane potential decay over 134 hours.

As an initial assessment of the membrane's viability for this application, the apparent perm selectivity (α_{app}) of the CA15_GVL_CAc membrane was determined by the Equation 3.13, using the OCV recorded immediately after cell assembly ($t=1$ s). This approach was adopted to account for the experimental constraints of the static batch configuration, where the Open Circuit Voltage (OCV) recorded at $t \approx 0$ represents the maximum apparent membrane potential. At this initial transient stage, the interfacial electrolyte concentrations most closely approximate the known bulk concentrations, effectively mitigating the underestimation artefacts caused by subsequent concentration polarisation.

The estimated apparent perm selectivity was calculated to be 76.8%. Although this value falls below the strict perm selectivity threshold typically exhibited by commercial Cation Exchange Membranes

(CEMs) [58], it is a highly promising preliminary result for a bio-based, porous separator. This intermediate value physically demonstrates that the polar functional groups within the cellulose acetate backbone, alongside with the possible unreacted carboxyl groups from the citric acid, confer a moderate ion-selective character to the membrane matrix. Consequently, these chemical features successfully establish an initial electromotive force, validating the material's responsiveness to salinity gradients.

However, the exceptionally high R_m observed would severely limit the maximum achievable power density, as the two parameters are inversely proportional. This currently restricts the membrane's practical viability for this specific application. Furthermore, the lower permselectivity compared to conventional CEMs can primarily be attributed to the significantly lower intrinsic fixed charge density of this bio-based matrix relative to densely functionalised commercial alternatives.

Therefore, while static batch measurements verify a fundamental electromotive response, the EIS data dictate that the fabrication process requires further optimisation to be in line with the requirements of this technological application. Specifically, developing membranes with an interconnected, more open porosity is essential to substantially reduce ionic resistance.

Chapter 5

Conclusions and Future Prospects

This research successfully demonstrated the feasibility of fabricating sustainable, bio-based cellulose acetate (CA) membranes using green solvents via the non-solvent induced phase separation (NIPS) method. The replacement of highly toxic traditional solvents with eco-friendly alternatives, namely dimethyl sulfoxide (DMSO) and γ -valerolactone (GVL), yielded distinct morphological and structural properties heavily dependent on the thermodynamic interactions of the specific solvent system. Furthermore, the polymer concentration proved to be a critical parameter for both the necessary structural integrity and appropriate phase inversion kinetics.

The thermodynamic affinity between the solvent and the non-solvent dictated the final membrane architecture, which directly influenced their technological applications. DMSO induced an instantaneous de-mixing, resulting in an asymmetric structure with finger-like macro voids. Within this solvent system, both the 15 wt% and 20 wt% CA formulations yielded successful, robust membranes. When evaluated as separators in two-electrode supercapacitor configurations, the CA15_DMSO membranes exhibited excellent performance, with long-term float tests demonstrating outstanding electrochemical stability. Meanwhile, the CA20_DMSO formulation as a protective barrier layer on LMO electrodes represents a highly innovative coating strategy proposed in this thesis, which yielded promising preliminary results in preventing the dissolution of active materials. Notably, attempts to functionalise these membranes with citric acid (CAc) were unsuccessful in the DMSO system, as the additive was lost to the coagulation bath during the rapid phase inversion process.

Conversely, the use of GVL induced a delayed de-mixing process, generating a sponge-like structure with a dense skin layer. For this specific solvent, the formulation at 15 wt% CA emerged as the optimal formulation. This concentration provided the necessary structural integrity and phase inversion kinetics, successfully avoiding the critical defects observed at lower (10 wt%) and higher (20 wt%) concentrations. In contrast to the DMSO system, the incorporation of citric acid into the CA15_GVL membranes resulted in the additive being successfully retained within the polymeric matrix. These modified CA15_GVL_CAc membranes were evaluated as functional barriers for energy harvesting in

reverse electrodialysis. The membranes successfully maintained their integrity and functionality in static H-cell configurations for salinity gradient power generation over more than 130 hours but failed in obtaining acceptable ionic resistances for this technological application.

While this thesis establishes a solid foundation for the deployment of sustainable cellulose acetate membranes, several avenues for future research remain to fully optimise their technological integration.

With respect to energy storage technologies, the long-term float tests have already validated the exceptional electrochemical stability of the CA15_DMSO separators. Therefore, future efforts should be directed towards the upscaling of the membrane fabrication process for commercial-sized supercapacitor cells. Furthermore, evaluating the compatibility of these bio-based separators with deep eutectic electrolytes would represent a significant step towards the development of entirely green energy storage devices. While initial cyclic voltammetry evaluations (up to 150 cycles) demonstrated promising electrochemical stability, further validation of the novel LMO coating strategy introduced in this work requires extended investigation. Comprehensive long-term galvanostatic charge-discharge cycling (e.g., exceeding 1,000 cycles), potentially under elevated temperature conditions, should be explored. This will fully assess the coating's protective capabilities against severe manganese dissolution over prolonged operational lifespans.

Moreover, to comprehensively validate the environmental profile of the developed CA membranes, a quantitative Life Cycle Assessment (LCA) constitutes an imperative avenue for future research. While the substitution of fossil-derived polyolefins with bio-based polymers and the elimination of REACH-restricted solvents qualitatively suggest a lowered ecological impact, a rigorous cradle-to-grave or cradle-to-gate analysis is required to quantify net trade-offs. Future investigations should define a functional unit based on membrane area (e.g., 1 m^2) or device performance (per Wh of energy storage capacity). This framework would model the compounding burdens of green solvent synthesis — such as the cumulative energy demand of manufacturing dimethyl sulfoxide (DMSO) or γ -valerolactone (GVL)— against the end-of-life benefits of a fully biodegradable separator. Utilising software architectures like SimaPro coupled with the Ecoinvent database, will allow the calculation of key environmental indicators, including Global Warming Potential (GWP) and human toxicity, thereby establishing a benchmark for the industrial scalability of sustainable energy storage systems.

Regarding energy harvesting applications, future research should focus on optimising the fabrication parameters of the modified CA15_GVL_CAc membranes. Specifically, alternative methodologies must be explored to minimise the prominent, dense skin layer and reduce internal tortuosity, thereby substantially lowering the ionic resistance. Furthermore, open-circuit voltage (OCV) measurements should be conducted under conditions that closely resemble practical reverse electrodialysis systems.

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