



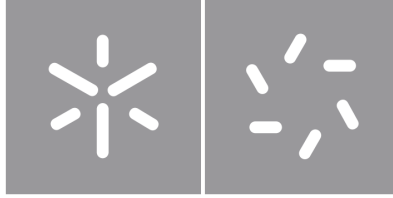
University of Minho
School of Sciences

Sara Alves de Sousa

**Development of Innovative
Components for the New Generation
of Batteries**

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Generation of Batteries

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Development of Innovative Components for the New Generation of Batteries

Master Thesis

MSc. in Chemical Analysis and Characterisation Techniques

Work done under the supervision of:

Dr Rui Francisco Gonçalves Pinto Fernandes Pereira

Professor Maria Manuela da Silva Pires da Silva

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STATEMENT OF INTEGRITY

I hereby declare having conducted this academic work with integrity. I confirm that I have not used plagiarism or any form of undue use of information or falsification of results along the process leading to its elaboration.

I further declare that I have fully acknowledged the Code of Ethical Conduct of the University of Minho.

ABSTRACT

Development of Innovative Components for the New Generation of Batteries

The growing demand for renewable energy systems and high-energy-density applications has intensified the need for advanced and more efficient energy storage technologies. Lithium-ion batteries, though historically valued for their versatility, efficiency and energy density, are approaching their theoretical limits. Their reliance on liquid electrolytes continues to raise concerns regarding interfacial stability, longevity, and safety. Solid-state electrolytes, particularly solid polymer electrolytes (SPEs), have emerged as safer and more stable alternatives, compatible with alkali metal anodes. Simultaneously, embedded sensors enable *in situ* operation monitoring and improve battery safety and performance.

This dissertation, developed within an FCT-funded project on smart battery components, focused on synthesising SPEs based on sodium carboxymethyl cellulose (NaCMC), doped with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and plasticised with glycerol. A systematic set of compositions was prepared by varying dopant concentrations to identify optimal formulations for solid-state batteries. Membranes were characterised for optical, chemical, structural, thermal, mechanical, electrochemical, and surface properties using techniques such as ultraviolet-visible spectroscopy, attenuated total reflectance Fourier transform infrared spectroscopy, electrochemical impedance spectroscopy (EIS), X-ray diffraction, polarised optical microscopy, scanning electron microscopy, thermogravimetric analysis, tensile testing, and contact angle measurements. The highest ionic conductivity (4.40×10^{-4} S/cm) was achieved for the NaCMC-based membrane with 150% LiTFSI and a 1:2 NaCMC-to-glycerol ratio, although mechanical fragility limited applicability. The 1:1 formulation with 50% LiTFSI offered a better compromise, with conductivity of 2.62×10^{-5} S/cm, $F_{\max} = 3.0 \pm 1.4$ N, and $\epsilon_b = 58 \pm 15\%$. All membranes exhibited thermal stability of at least 160 °C. Additionally, exploratory experiments assessed membrane interactions with loop antenna-based sensors. Electrical characterisation revealed signal shifts upon membrane application, supporting sensor sensitivity and SPE integration. Preliminary lithium-metal half-cells were also assembled and characterised via cyclic voltammetry, galvanostatic charge and discharge, and EIS, establishing protocols for future integration of the synthesised SPEs.

Overall, this study provides a comprehensive assessment of biopolymer-based SPEs as multifunctional battery components, contributing to the development of safer, more sustainable, and smart next-generation batteries.

Keywords: solid polymer electrolytes, solid-state batteries, embedded sensors.

RESUMO

Desenvolvimento de Componentes Inovadores para a Nova Geração de Baterias

A transição para sistemas energéticos renováveis e aplicações de elevada densidade energética exige tecnologias de armazenamento mais avançadas e eficientes. As baterias de íão de lítio, embora versáteis e eficientes, aproximam-se dos seus limites teóricos. Além disso, a utilização de eletrólitos líquidos levanta desafios de estabilidade, durabilidade e segurança. Os eletrólitos sólidos, em particular os eletrólitos sólidos poliméricos (SPEs), surgem como alternativas mais seguras e estáveis, compatíveis com ânodos de metais alcalinos. Simultaneamente, sensores embebidos nos componentes das baterias permite a monitorização *in situ* e *in operando*, reforçando a segurança e a performance.

Esta dissertação, inserida num projeto financiado pela FCT sobre componentes inteligentes para baterias, focou-se na síntese de SPEs à base de carboximetilcelulose de sódio (NaCMC), dopados com bis(trifluorometanossulfonil)imida de lítio (LiTFSI) e plastificados com glicerol. Foi preparada uma série sistemática de composições, variando as concentrações dos dopantes para identificar formulações ótimas aplicáveis a baterias de estado sólido. As membranas foram caracterizadas quanto às propriedades óticas, químicas, estruturais, térmicas, mecânicas, eletroquímicas e de superfície, através de técnicas como espectroscopia ultravioleta-visível, infravermelho por refletância total atenuada, impedância eletroquímica (EIS), difração de raios-X, microscopia ótica polarizada, eletrónica de varrimento, análise termogravimétrica, testes de tração e medições de ângulo de contacto. A maior condutividade iónica (4.40×10^{-4} S/cm) foi obtida para a membrana com 150% de LiTFSI e uma razão NaCMC:glicerol de 1:2, embora a sua fragilidade mecânica limitasse a aplicabilidade. A formulação com razão 1:1 e 50% de LiTFSI revelou um melhor equilíbrio, com condutividade de 2.62×10^{-5} S/cm, $F_{\max} = 3.0 \pm 1.4$ N e $\varepsilon_b = 58 \pm 15\%$. Todas as membranas apresentaram estabilidade térmica de, pelo menos, 160 °C. A caracterização elétrica de sensores de antena *loop* revelou variações de sinal induzidas pela aplicação das membranas, confirmando a sua sensibilidade e potencial integração em SPEs. *Half-cells* de lítio metálico foram também montadas e caracterizadas preliminarmente por voltametria cíclica, carga–descarga galvanostática e EIS, estabelecendo protocolos para futura aplicação dos SPEs.

De modo geral, este trabalho fornece uma avaliação abrangente de SPEs à base de biopolímeros enquanto componentes multifuncionais para baterias, contribuindo para o desenvolvimento de sistemas de armazenamento de energia de nova geração mais seguros, sustentáveis e inteligentes.

Palavras-chave: eletrólitos sólidos poliméricos, baterias de estado sólido, sensores embebidos.

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LIST OF ABBREVIATIONS AND ACRONYMS

ATR-FTIR	Attenuated total reflectance Fourier transform infrared
CAM	Contact angle measurement
CMC	Carboxymethyl cellulose
CV	Cyclic voltammetry
EIS	Electrochemical impedance spectroscopy
ESS	Energy storage system
GCD	Galvanostatic charge and discharge
IR	Infrared
LFP	Lithium iron phosphate
LIB	Lithium-ion battery
LiTFSI	Lithium bis(trifluoromethanesulfonyl)imide
NaCMC	Sodium carboxymethyl cellulose
POM	Polarised optical microscopy
SEI	Solid electrolyte interphase
SEM	Scanning electron microscopy
SPE	Solid polymer electrolyte
SOC	State of charge
SSB	Solid-state battery
SSE	Solid-state electrolyte
TGA	Thermogravimetric analysis
UV-Vis	Ultraviolet-visible
VTF	Vogel-Tamman-Fulcher
XRD	X-ray diffraction

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CHAPTER 1 – INTRODUCTION

1.1. Motivation and Scientific Relevance of this Master's Thesis

The growing demand for safe, high-performance energy storage systems (ESSs) is closely linked to the global transition towards sustainable energy and the increasing reliance on electric mobility.¹⁻³ As these technologies depend heavily on batteries to manage fluctuations in energy supply and maintain grid stability, lithium-ion batteries (LIBs) have played a central role in enabling this shift, owing to their high energy density and efficiency.³⁻⁵ However, challenges related to safety, lifespan, and thermal stability persist—particularly in applications requiring compact design and high-rate discharge capabilities.⁶⁻⁹ As energy storage becomes more critical in both stationary and portable systems, the development of next-generation batteries that are more stable, reliable, safer and capable of delivering higher energy densities is imperative.⁸ In this context, *in situ* and *in operando* sensing technologies have emerged as powerful tools for monitoring internal battery parameters in real time, allowing for early failure detection, degradation tracking, and performance optimisation.⁷

A key limitation of current LIBs lies in the use of liquid electrolytes, which are prone to leakage, flammability, and instability at high voltages.^{8,10} These drawbacks have motivated extensive research into solid-state alternatives, particularly solid polymer electrolytes (SPEs), which offer improved safety, flexibility in design, and potential to suppress lithium dendrite growth.^{10,11} They constitute the electrolyte component within the broader concept of solid-state batteries (SSBs), which also enable higher energy densities and the use of lithium metal (Li) as the anode.^{8,10} Among the various polymer systems under investigation, biopolymer-based matrices such as sodium carboxymethyl cellulose (NaCMC) have shown promise due to their processability, environmental compatibility, and ability to host salts in gelled or plasticised forms.¹² The use of SPEs may also be compatible with the integration of embedded sensors, providing a multifunctional platform for battery development.

This Master's thesis was conducted within the scope of an FCT-funded project aimed at designing smart battery components, incorporating sensors, for *in situ* and *in operando* monitoring. The development of these sensors is being carried out by the Materials for Electronics, Optoelectronics and Nanotechnologies (MEON) research team at the Center of Excellence in Microelectronics Optoelectronics and Processes (CEMOP), NOVA University Lisbon, to which the project's principal investigator is affiliated. The integration

of such sensors within battery components, such as the electrolyte, enables real-time monitoring of internal conditions, thus providing a critical tool for advancing battery safety and performance.

The research carried out in this study primarily focused on the synthesis and comprehensive characterisation of SPEs based on NaCMC, incorporating systematically varied contents of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and glycerol as salt and plasticiser, respectively. The aim was to identify the most promising formulations in terms of physicochemical, electrochemical, thermal, mechanical, and interfacial properties, with a view to their potential integration into battery systems.

In parallel, preliminary work was carried out on the assembly and optimisation of lithium half-cells using commercial components, in an effort to establish a reproducible testing platform for future electrolyte evaluation.

Additionally, the interaction between the synthesised SPEs and the novel loop antennas was investigated through electrical characterization. Although full integration of the sensors into coin cells was not achieved within the timeframe of this work, these initial experiments were conducted to assess their sensitivity to the biopolymer membranes' composition in isolation.

Taken together, the results presented in this dissertation provide a comprehensive overview of the material development, characterisation, and sensing interface strategies required to support the integration of functional sensors in SSBs.

1.2. Document Structure

This dissertation is organised into five main chapters, each addressing a specific phase of the research. Following the introductory chapter, Chapter 2 provides the theoretical background required to contextualise the work, covering the evolution and challenges of lithium-based batteries, the development of solid-state electrolytes (SSEs), the integration of embedded sensors in batteries, and an overview of the characterisation techniques employed.

In Chapter 3, the experimental methodologies are described, including the materials, synthesis protocols, and analytical procedures used for the development and characterisation of SPEs, the evaluation of their interaction with loop antenna sensors, and the preliminary assembly and testing of lithium-metal coin cells.

The results obtained are presented and discussed in Chapter 4, structured according to the major experimental areas: the physicochemical, thermal, mechanical, optical, and electrochemical

characterisation of the SPEs; the electrical characterisation of the sensor–SPE interactions; and the electrochemical evaluation of the coin cells performance.

Finally, Chapter 5 summarises the main conclusions drawn from the study and proposes future perspectives for the further development and integration of SPEs and embedded sensing systems in next-generation battery architectures.

CHAPTER 2 – THEORETICAL BACKGROUND

2.1. State of the Art

2.1.1. Evolution and Challenges of Lithium-Based Batteries

A battery is an electrochemical device that converts the chemical energy stored in active materials into electrical energy through reduction–oxidation (redox) reactions. In rechargeable systems, this process is reversible, enabling multiple charge–discharge cycles to occur over time.^{13,14} It is fundamentally composed of one or more electrochemical cells, which may be connected in series or in parallel to meet the voltage and current requirements of the intended application. When integrated into an external circuit, the battery enables a continuous and controlled flow of electric charge.¹³

The historical evolution of battery technologies can be traced back to the voltaic pile, developed by Alessandro Volta in 1799, which marked the first demonstration of a continuous source of electric current.¹⁵ This breakthrough laid the foundation for electrochemical energy storage. Throughout the 19th and 20th centuries, numerous primary battery systems, such as zinc–carbon and alkaline batteries, were developed to address the growing demand for portable power.¹⁶ Subsequent innovations led to the advent of rechargeable batteries, including lead–acid, nickel–cadmium, and metal hydride chemistries, which progressively shaped the modern energy storage landscape. This technological trajectory culminated in the emergence of lithium-based rechargeable batteries, notably lithium-ion, which offered significant improvements in energy density and cycle life.¹⁴

The development of LIBs technology began in the 1970s with Whittingham’s pioneering work on lithium intercalation compounds, followed by Goodenough’s fundamental contributions to cathode materials and Yoshino’s innovations in cell safety and manufacturability.¹⁷⁻¹⁹ Their combined efforts provided the scientific and technological basis for the commercialisation of LIBs, which were introduced by Sony in the early 1990s and rapidly revolutionised the field of portable electronics.^{18,19} Since then, LIBs have become indispensable in modern ESSs owing to their high energy density, long cycle life, and reliability.^{20,21}

A typical LIB cell is composed of two electrodes—an anode and a cathode—each consisting of a metallic current collector coated with active materials.^{22,23} The cathode generally comprises a lithium-containing transition metal oxide, such as lithium cobalt oxide (LCO), LiCoO_2 , lithium iron phosphate (LFP), LiFePO_4 , or nickel manganese cobalt (NMC), LiNiMnCoO_2 , while the anode is typically composed of graphite.^{20,22,24,25}

The electrodes are separated by a microporous polymer membrane—separator—and immersed in an organic liquid electrolyte containing a lithium salt, which facilitates ionic conduction during operation.^{20,23,26}

The separator usually consists of a polyethylene (PE), polypropylene (PP), or combinations of both, such as PE/PP (bilayer) and PP/PE/PP (trilayer) membranes.²⁷ Among the various salts, lithium hexafluorophosphate (LiPF_6) remains the most commonly used, typically dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC).²⁸

The working principle of LIBs is based on redox reactions involving the reversible intercalation and deintercalation of lithium ions (Li^+) between the electrodes.^{18,19,25} During charging, Li^+ are extracted from the cathode and migrate to the anode, where they are reduced and stored within the graphite structure via intercalation. Upon discharge, lithium atoms in the anode undergo oxidation to Li^+ and are deintercalated from the graphite, subsequently moving back to the cathode, where they are reinserted into the host lattice.^{22,26} Meanwhile, the electrons released during the oxidation process at the anode travel through the external circuit and are accepted by redox-active species in the cathode material, which undergo reduction to maintain electrochemical balance.^{20,21,29,30} This electron flow through the external circuit constitutes the electrical energy delivered to the connected device. The coordinated transport of Li^+ through the electrolyte and electrons through the external circuit ensures a continuous and efficient energy output.¹³

Despite their numerous advantages, LIBs present several intrinsic limitations. One of them is the restricted energy storage capacity, as these systems are approaching the upper limit of their theoretical energy density.^{21,31} This is mainly due to the use of graphite anodes which, despite their stability and low cost, deliver limited specific capacity ($\approx 372 \text{ mAh/g}$) and undergo irreversible lithium loss during initial SEI formation, resulting in low initial coulombic efficiency (typically $<90\%$).^{21,22,31} Additionally, excessive and recurrent SEI formation leads to the continuous consumption of lithium and electrolyte, increasing interfacial resistance and accelerating capacity fade and cell ageing.²¹

These issues are further exacerbated under adverse operating conditions. For instance, during fast charging or low-temperature operation, lithium plating may occur on the anode surface.²⁶ This phenomenon promotes the formation of uneven surfaces and concentrated electric fields ("hotspots"), which favour dendritic growth.^{26,32} Dendrites can ultimately penetrate the separator, potentially triggering internal short circuits, thermal runaway, and, in extreme cases, fire or explosion hazards—raising critical safety concerns.^{21,26}

In addition, LIBs display significant temperature sensitivity. Their optimal performance is generally restricted to the $20\text{ }^\circ\text{C}$ to $40\text{ }^\circ\text{C}$ range, outside of which performance degrades significantly, impacting

cycle life and internal resistance.²⁰ At elevated temperatures, the volatility of organic liquid electrolytes becomes a major safety hazard: thermal decomposition can generate flammable gaseous by-products, resulting in increased internal pressure and potential cell swelling in sealed configurations. In severe cases, this leads to thermal runaway events capable of igniting fires or causing explosions due to the flammability of the liquid electrolyte components.^{14,26}

The increasing requirements of electric vehicles and renewable ESSs has fuelled a surge in research aimed at suppressing these limitations by improving energy density, mitigating degradation mechanisms, and enhancing operational safety.^{20,21,32,33}

There is a growing interest in next-generation materials that can overcome the energy ceiling of current systems.³² Among these, lithium metal has emerged as a particularly promising alternative. With the highest theoretical specific capacity (3860 mAh/g), low density, and the most negative redox potential of any element, lithium metal enables plating/stripping mechanisms that surpass the energy density of intercalation-based systems by at least 18%.^{21,32} Life cycle assessment studies further indicate that replacing graphite with lithium metal could reduce the environmental impact of batteries.²¹ However, the implementation of lithium-metal anodes remains limited by major challenges, including dendrite formation, interfacial instability, and mechanical degradation.^{20,21,32} Even with advances in electrolyte formulation and artificial SEI engineering, no existing solution has yet demonstrated the performance, safety, and scalability required for commercialization.^{21,32}

In addition, the widespread implementation of lithium metal anodes should be critically reconsidered. The surging global demand for lithium—driven largely by the rapid expansion of electric vehicles and portable electronics—has critically strained supply chains, which in turn has led to a threefold increase in lithium prices since the early 2000s. In this context, the increased reliance on metallic lithium could exacerbate resource scarcity and economic volatility, ultimately undermining the sustainability of next-generation battery technologies.³⁴⁻³⁶ In response, alternative chemistries are being actively explored. Sodium, in particular, has gained momentum as a viable substitute for lithium in large-scale applications. Chemically similar to lithium and abundantly available in both seawater and the Earth's crust, sodium offers significant advantages in terms of cost and resource sustainability. As a result, sodium-ion batteries (NIBs) have emerged as a promising and feasible alternative for future energy storage.³⁴⁻³⁶

In parallel, there is growing interest in SSB technologies, which promise to offer improved energy density, fast charging, longevity, and safety. By replacing liquid electrolytes with solid-state counterparts, SSBs mitigate key safety concerns such as thermal runaway, electrolyte leakage, and flammability.^{14,21,36} These systems also enable the safe operation of highly reactive metal anodes—such as sodium—while

suppressing dendritic formation and enhancing interfacial stability. Furthermore, solid electrolytes offer superior mechanical strength and thermal stability, allowing for wider operating temperature windows and improved long-term reliability.³⁴

This shift towards safer, smarter and more sustainable battery technologies underscore the urgent need for alternative SSE systems, which are explored in greater detail in the following chapter. These innovations mark a critical transition point in the development of next-generation electrochemical storage devices.

2.1.2. Electrolytes in Batteries: From Liquid to Solid-State

The electrolyte is a fundamental component in batteries, serving as the medium for ionic conduction between the electrodes while maintaining electronic insulation.^{29,37} By enabling the transport of ions during charge and discharge, it sustains the electrochemical reactions that occur at the electrode interfaces.¹³ The efficiency of this transport is governed by the electrolyte's ionic conductivity, which is influenced by factors such as ion mobility, ion dissociation, and temperature.³⁸ Moreover, the electrolyte plays a critical role in the formation of the solid electrolyte interphase (SEI) on the surface of the anode. Originated through reductive decomposition of electrolyte components, it acts as an electronically insulating yet ionically conductive passivation layer, protecting the anode while enabling selective Li^+ transport and suppressing further electrolyte degradation.^{21,26,32} Its properties strongly impact battery performance, affecting cycle life, capacity retention, and safety.^{21,22,31} In addition to facilitating ion transport and SEI formation, an ideal electrolyte should combine a wide electrochemical stability window and chemical inertness towards electrode materials to ensure the safe and efficient operation of the battery throughout its lifespan.^{8,39}

Despite their widespread use in commercial LIBs, liquid electrolytes present several well-known limitations. These limitations are further explored below.

Liquid electrolytes are commonly composed of organic solvents that are highly flammable and volatile, significantly increasing the risk of thermal runaway in the event of internal short circuits.^{21,26,39} Their low boiling point and susceptibility to leakage also pose considerable safety hazards during operation and storage.⁸

Additionally, liquid electrolytes operate effectively only within a limited temperature range, which limits their applicability under extreme temperature conditions.⁴⁰ At temperatures below 0 °C, electrolyte freezing leads to a marked drop in ionic conductivity, which hinders charge-transfer kinetics and results

in increased internal resistance and slower electrochemical reactions. These effects contribute significantly to the degradation of LIB performance.²⁰ At elevated temperatures, the thermal decomposition of liquid electrolytes exacerbates their safety risks by generating flammable gases, leading to increased internal pressure, cell swelling, and, in severe cases, thermal runaway and fire or explosion hazards.^{14,26}

Moreover, these systems also suffer from a narrow electrochemical window; when the cell voltage exceeds this range, the electrolyte undergoes decomposition, which restricts the selection of electrode materials and imposes operational voltage limitations, ultimately compromising the energy density and long-term performance of the battery.⁸

Another critical issue is their chemical instability.³⁹ Poor compatibility between electrolyte components and electrode materials often results in surface degradation phenomena, such as corrosion and side reactions.^{8,40} This interfacial instability is particularly problematic at lithium metal anodes but has also been reported in graphite-based systems, particularly under abusive conditions like those mentioned above. In such circumstances, repeated cycling can lead to the non-uniform deposition of metallic lithium and the growth of dendritic structures. These needle-like formations may penetrate the separator, initiating internal short circuits that can cause localised high-current discharge and rapid heat generation. If left unchecked, this thermal build-up may trigger thermal runaway, potentially resulting in fire or explosion.^{21,26} In addition, dendrite accumulation contributes to the formation of inactive – or “dead” – lithium, ultimately resulting in higher internal resistance and gradual capacity fade.³² Dendrite growth is thus considered one of the main degradation pathways in liquid electrolyte-based batteries and is often cited as a cause of early cell failure.⁴⁰ Similar degradation processes have also been reported in sodium-based systems.^{37,41}

From a practical standpoint, liquid electrolytes require hermetically sealed battery architectures to prevent leakage, which can lead to cell contamination and performance degradation. However, ensuring long-term sealing integrity presents a considerable engineering challenge.⁴⁰

Finally, from an environmental perspective, the organic solvents used in liquid electrolytes are often toxic and hazardous.³⁴ These substances pose risks not only in the event of leakage but also during end-of-life battery recycling. Furthermore, the industrial production of lithium salts and solvent components contributes to a significant environmental footprint, particularly due to high energy consumption and the use of non-renewable chemical precursors.^{42,43}

Taken together, these limitations not only compromise the safety and electrochemical performance of batteries, but also restrict their applicability in extreme environments, reduce their operational lifespan,

and hinder the development of more sustainable and advanced ESSs. These drawbacks have driven increasing interest in alternative electrolyte solutions, particularly those based on solid-state materials. SSEs are attracting growing interest due to their potential to improve the safety, energy density, and cycle life of rechargeable batteries.⁴⁴ Their technological relevance emerged in 1967, following the discovery of two systems— Mag_4I_5 ($\text{M} = \text{Rb}, \text{K}, \text{NH}_4^+$) and Na- β -alumina—which exhibited exceptional ionic conductivities for Ag^+ and Na^+ , respectively. Since then, a wide variety of solid electrolytes has been reported, incorporating mobile ions such as H^+ , Ag^+ , Li^+ , Na^+ , K^+ , Mg^{2+} , F^- , and O^{2-} , and spanning several structural categories.⁴⁰

When compared to their liquid counterparts, solid electrolytes offer several critical advantages. By simultaneously functioning as both electrolyte and separator, they prevent direct contact between the electrodes, significantly lowering the risk of internal short circuits.³⁹ Additionally, the absence of organic solvents eliminates leakage risks and enhances thermal stability, while also contributing to their non-flammable and non-volatile nature. These characteristics not only minimise the likelihood of fire or explosion, but also enable a more compact and inherently safer cell design.^{39,45} Moreover, solid electrolytes exhibit favourable electrochemical stability, which helps suppress dendrite formation. This, in turn, results in higher power output and improved cyclability when compared to LIBs.³⁹ These combined properties make SSEs excellent candidates not only for LIBs but also for sodium-based systems, where similar benefits can be achieved.⁴⁵

SSEs can be broadly categorised into two main classes: inorganic and SPEs. Inorganic SSEs comprise both crystalline ceramics and amorphous glasses and are predominantly metal-based. While they often exhibit high ionic conductivities, these materials are typically brittle and expensive to process. In contrast, SPEs are polymer-based systems incorporating heteroatoms such as oxygen or nitrogen, which facilitate the solvation and transport of metal ions.⁴⁵ Their properties vary widely depending on the polymer backbone, functional groups, and molecular architecture.⁴⁶

2.1.3. Solid Polymer Electrolytes

SPEs have gained increasing prominence in SSB research due to a combination of structural, practical, and economic advantages over their inorganic counterparts. Their flexible architecture allows for effective interfacial contact with the electrodes, which is essential to minimise interfacial resistance and enhance overall cell performance.³⁷ Moreover, their mechanical resilience enables them to accommodate volume changes in the electrodes and suppress dendrite formation, thus prolonging the operational life of the

battery. Additionally, SPEs preparation often involves mild temperatures, air-stable conditions, and compatibility with roll-to-roll processing, facilitating their production.⁴⁵ Finally, the intrinsic tunability of polymer chemistry—through the selection of monomers, functional groups, or copolymerisation strategies—provides a broad design platform to tailor the physical, chemical and electrochemical behaviour of these materials.⁴⁶ These characteristics make them particularly attractive for scalable, low-cost production of next-generation batteries.⁴⁵

The interest in polymer-based electrolytes dates back to the pioneering proposal by Armand for their use in lithium batteries. Since then, significant developments have been achieved globally. Notably, in the 1990s, the Japanese company Yuasa commercialised primary lithium polymer batteries and, by 1998, introduced ultrathin rechargeable versions for compact electronic devices. However, the systems marketed under this name generally relied on semi-solid electrolytes, rather than fully solid-state formulations.⁹ As such, the commercialisation of true SSBs remains an ongoing challenge.

SPEs can be classified into five main types, based on their composition and method of preparation: dry SPEs, plasticised SPEs, gel polymer electrolytes (GPEs), rubbery polymer electrolytes, and composite polymer electrolytes (CPEs).⁴⁰ Dry SPEs, also known as polymer–salt complexes, are typically formed by dissolving lithium salts into polar polymer matrices and processed via solution casting or hot-pressing.^{40,47} These systems offer good mechanical stability but suffer from low ionic conductivity at ambient temperature.⁴⁰ Plasticised SPEs are obtained by introducing liquid plasticisers into dry SPEs to enhance their ionic transport; however, this results in diminished mechanical integrity and increased chemical reactivity with the electrodes.^{40,45,48} GPEs contain larger amounts of organic solvents or plasticisers dispersed within a polymer network.^{40,45} While they exhibit high ionic conductivity, they share similar drawbacks to plasticised systems.⁴⁹ Moreover, their high solvent content reintroduces issues such as volatility, flammability, and the risk of leakage.⁵⁰ In rubbery electrolytes—also referred to as “polymer-in-salt” systems—the high salt content relative to polymer leads to rubbery behaviour at room temperature and improved conductivity, but these systems are often limited by salt crystallisation during storage or cycling.^{40,51,52} Finally, CPEs are developed by incorporating micro- or nanoscale inorganic fillers, such as ceramic particles, into a polymer–salt matrix.⁴⁰ These fillers can enhance ionic conductivity, mechanical robustness, and electrode–electrolyte interfacial stability, depending on their dispersion, surface chemistry, and interaction with the polymer phase.^{40,53}

Having outlined the main types of polymer-based electrolytes, it is important to understand the fundamental ion transport mechanisms that govern their performance. At the macroscopic level, ionic conduction within polymer matrices can encompass multiple phases, involving both intra and inter-chain

ion migration mechanisms and polymer-segmental movement. Fundamentally, however, ionic transport in SPEs is governed by the ion-hopping mechanism, wherein conductive ions migrate between coordination sites in monomer units within individual polymer chains or across adjacent chains through successive coordination exchanges.^{39,54,55}

The efficiency of this ion transport mechanism, nonetheless, strongly depends on the morphological characteristics of the polymer matrix. Polymers typically consist of both crystalline and amorphous phases and are therefore classified as semicrystalline materials. Initially, it was believed that the ionic conductivity of these systems is predominantly influenced by the properties of the amorphous phase. Upon heating, polymers in the amorphous state undergo a transition from a rigid, glassy phase to a more flexible, rubbery phase. This transformation occurs at the glass transition temperature (T_g), a critical property in the context of SPEs. Below T_g , amorphous chains remain relatively immobile, resulting in negligible ionic conductivity; above T_g , increased segmental mobility significantly enhances ion transport. By contrast, crystalline domains instead experience melting transitions and their presence typically suppresses ionic conduction, which has motivated extensive research efforts towards maximising the amorphous content in SPEs to enhance their ionic conductivity.⁴⁵ However, this traditional viewpoint has since been re-evaluated.^{40,56} The experimental work by Gadjourova and co-workers challenged this assumption by demonstrating that static, ordered crystalline domains are also capable of sustaining efficient ionic conduction, thereby redefining the established understanding of ion transport mechanisms in SPEs.^{40,57}

Further clarification regarding the nature of ionic conduction has been provided by temperature-dependent conductivity studies. These investigations revealed two predominant conduction behaviours, allowing SPEs to be classified into two distinct groups. The first group is characterised by a non-linear dependence of conductivity on the reciprocal of temperature, described by the Vogel–Tamman–Fulcher (VTF) relationship, indicative of an ionic hopping mechanism coupled to the segmental relaxation and breathing motions of polymer chains. Conversely, the second group exhibits a linear Arrhenius-type dependence, suggesting a simpler hopping mechanism that operates independently of polymer chain segmental dynamics.⁴⁰

The exploration of polymer matrices for SPEs began in 1975, when Wright reported the ionic conductivity of poly(ethylene oxide) (PEO) complexed with a sodium salt.⁵⁸ Since then, in addition to PEO, various synthetic polymers such as polyvinylidene fluoride (PVDF), polymethyl methacrylate (PMMA), and polyacrylonitrile (PAN) have been investigated.³⁹ Among these, PEO has distinguished itself due to its remarkable ability to dissolve lithium salts and coordinate cations through its ether oxygen atoms.²⁹

However, synthetic polymer electrolytes are expensive, derived from non-renewable petroleum sources, and insoluble in water, which limits their sustainability and ease of processing.⁵⁹

In response to these limitations and in light of growing concerns about environmental impact, research in recent decades has increasingly shifted towards natural, biodegradable alternatives. Biopolymers sourced from renewable feedstocks—such as polysaccharides and proteins—have garnered interest due to their abundance, low cost, non-toxicity, and reduced environmental footprint during both production and disposal.⁶⁰ These macromolecules can be broadly categorised based on their origin into: (i) polymers extracted directly from biomass (e.g. starch, cellulose, chitosan), (ii) polymers synthesised by microorganisms (e.g. bacterial cellulose), and (iii) polymers chemically modified from natural monomers (e.g. polylactic acid).⁶¹

Several biomass-derived polymers, including chitosan and alginate, have been investigated as polymer hosts; however each exhibits limitations that restrict their standalone use in SPE systems. For instance, chitosan-based electrolytes often require harsh demineralisation treatments with acids and complex crosslinking strategies to improve their solubility and mechanical integrity, while still exhibiting relatively low ionic conductivities in the order of 10^{-6} to 10^{-5} S/cm.⁶⁰⁻⁶² Alginate-based membranes, despite their excellent film-forming capacity and biocompatibility, tend to be mechanically weak and highly water-sensitive, leading to instability in humid environments.⁶³

To overcome these shortcomings, cellulose and its derivatives have emerged as particularly promising candidates for SPE design.⁶¹ Cellulose ($C_6H_{10}O_5$)_n is the most abundant biopolymer on Earth.⁶⁴ It is widely found in nature, being present in a variety of living organisms such as fungi, bacteria, algae, and some marine animals, and constitutes a major structural component of the plant cell wall.⁶⁵ Structurally, cellulose is a linear and unbranched homopolysaccharide of β -D-glucose units linked by $\beta(1\rightarrow4)$ glycosidic bonds.⁶⁵⁻⁶⁷ In its native form, cellulose is insoluble in water and common organic solvents, which limits its direct applicability. However, its chemical modification has led to a variety of water-soluble and film-forming derivatives with film-forming ability, including ethyl cellulose, methyl cellulose, hydroxypropyl cellulose, hydroxyethyl cellulose, hydroxypropyl methyl cellulose, and carboxymethyl cellulose (CMC).⁶⁴ Cellulose general chemical structure is illustrated in Figure 1, and each of the aforementioned derivatives features a different functional group (R) depending on the synthetic route employed, as depicted in Table 1.⁶⁸ Among them, CMC is an anionic, cellulose ether that stands out due to the presence of functional groups capable of effectively interacting with ionic species, a feature that offers a significant advantage in electrolyte design.⁶⁴

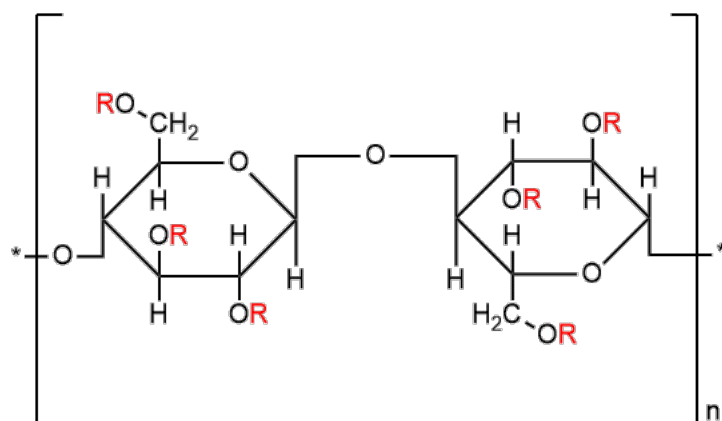


Figure 1. General chemical structure of cellulose and its derivatives.

Table 1. Cellulose and its derivatives with corresponding functional groups (R).

Natural Polymer	R group
Cellulose	H
Cellulose Derivatives	R group
Cellulose acetate	H / CH ₃ CO
Cellulose sulphate	H / SO ₃ H
Cellulose nitrate	H / NO ₂
Ethyl cellulose	H / CH ₂ CH ₃
Methyl cellulose	H / CH ₃
Hydroxypropyl cellulose	H / CH ₂ CH(OH)CH ₃
Hydroxyethyl cellulose	H / CH ₂ CH ₂ OH
Hydroxypropyl methylcellulose	H / CH ₃ / CH ₂ CH(OH)CH ₃
Carboxymethyl cellulose	H / CH ₂ CO ₂ H

NaCMC is derived from cellulose through a two-step synthesis process involving an initial alkaline activation of the cellulose, followed by etherification via carboxymethylation with an etherifying agent (Figure 2).^{66,67,69}

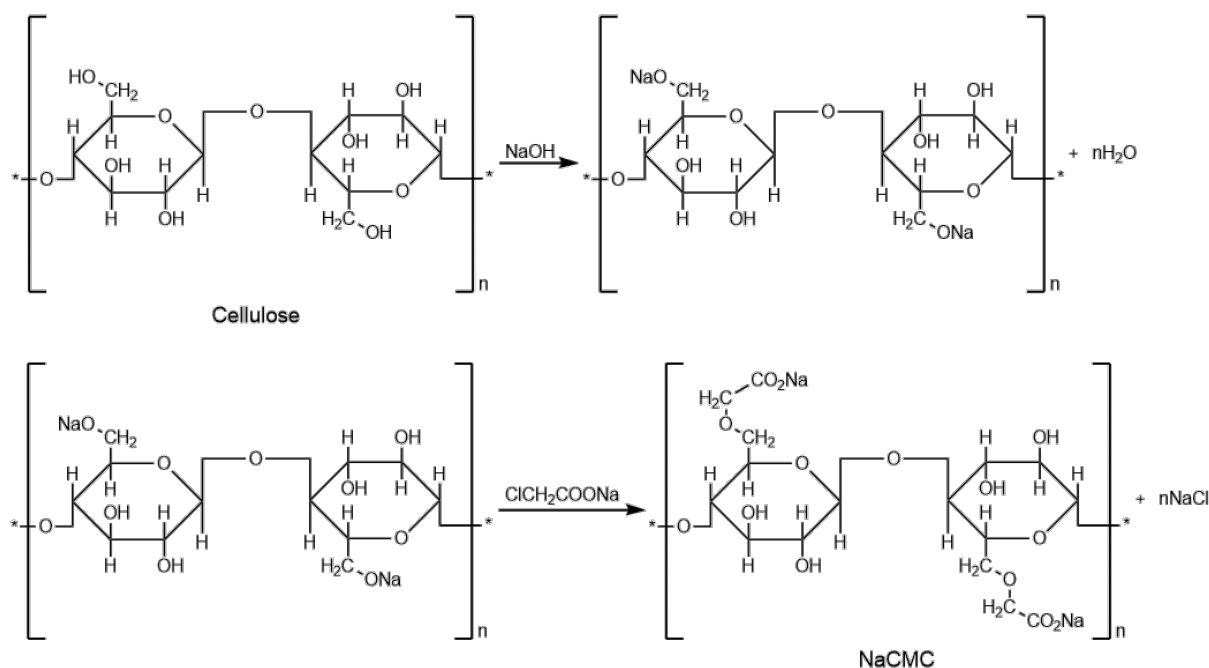


Figure 2. Two-step synthesis of NaCMC from cellulose.

Compared to other biopolymer candidates, NaCMC-based systems generally exhibit lower energy demands and reduced toxic emissions during production,⁶¹ while also providing excellent mechanical integrity and ionic transport properties when used alone or in combination with other polymers or plasticisers.^{61,70,71}

NaCMC requires only mild chemical processing, aligning with the principles of sustainable material development.⁷⁰ Its chemical structure combines the reactivity of carboxylate groups with the rheological versatility of polysaccharides, enabling the formation of flexible and robust membranes without the need for strong acidic conditions or extensive chemical modification.^{64,66} Furthermore, the polyelectrolytic nature of NaCMC facilitates the incorporation of ionic dopants, while its sensitivity to pH and ionic strength enhances its ionic conductivity and adaptability to various operating environments. The ability to form homogeneous and transparent films reinforces its role as a processable matrix for SPEs.⁷²

Overall, the incorporation of NaCMC into SPEs offers a balanced combination of electrochemical performance, mechanical robustness, and environmental sustainability—making it a key candidate in the development of next-generation energy storage materials.

As previously mentioned, the primary function of the electrolyte in an electrochemical device is to enable ionic conduction between the two electrodes. To achieve this, salts must be incorporated into the polymer matrices in order to increase the number of charge carriers within the system, thereby enhancing its ionic conductivity.⁷³ The choice of salt is therefore critical for efficient ion transport. Ideally, it should exhibit low

dissociation energy to promote the formation of free ions, a small cation size to ensure high mobility, and a large anion size to minimise ion–polymer interactions and favour salt dissociation.²⁹

Out of the different candidates, LiTFSI is a suitable choice due to its low lattice energy, large anion size, and high dissociation degree, which facilitate ion transport in the polymer matrix.²⁹ The compatibility of LiTFSI with natural polymers, including CMC-based systems, has been demonstrated in multiple studies, showing improved electrochemical performance and potential for application in SSBs.⁶¹

In these cases, the Li⁺ cations interact preferentially with the oxygen-rich sites of NaCMC, particularly the carboxylate (–COO[–]) and hydroxyl (–OH) groups, forming transient coordination complexes that enhance charge carrier mobility.^{70,74} FTIR analysis supports this, revealing shifts in characteristic bands upon salt doping, which indicates strong polymer–salt interactions and reduced crystallinity.^{60,70} These interactions contribute to the disruption of the hydrogen bonding network between polymer chains, favouring an increase in the amorphous regions — the primary domains for ionic conduction in SPEs.⁷⁴

Despite their environmental and processing advantages, most SPEs suffer from intrinsically low ionic conductivity, especially at room temperature, due to their semi-crystalline nature and limited chain mobility.^{32,40,75} To mitigate these effects, plasticisers are commonly incorporated into the polymer matrix.²⁹ These additives are typically non-volatile, low molecular weight liquids with high boiling points.¹¹ Their inclusion reduces the number of active centres in the polymer structure and weakens inter- and intramolecular interactions, thereby increasing the free volume and enhancing chain mobility—factors that directly promote ion transport.^{11,76,77} Beyond this, plasticisers also disrupt van der Waals forces and hydrogen bonding between polymer chains, promoting the formation of amorphous regions and lowering the glass transition temperature. This dual effect improves both the segmental dynamics of the polymer and its thermal and mechanical stability.^{11,76,78} Additionally, the reduced transition temperature facilitates the dissociation of lithium salts within the matrix, which can raise the ionic conductivity to values as high as 10^{–3} S/cm at room temperature.³⁹

Among the available plasticisers, glycerol stands out due to its high dielectric constant (42.5), biodegradability, and non-toxicity.⁷⁸ In NaCMC-based systems, it interacts via hydrogen bonding with hydroxyl (–OH) and carboxylate (–COO[–]) groups and this molecular rearrangement enhances the mobility of both the polymer chains and the ionic species.^{79,80}

Spectroscopic and electrochemical analyses confirm that, in NaCMC-based SPEs, glycerol increases the number density and mobility of free ions, as well as the diffusion coefficient. Additionally, dielectric relaxation studies reveal that glycerol reduces the relaxation time and facilitates ion hopping between coordination sites. These combined effects result in a significant improvement in the ionic conductivity of

the system.⁷⁹ Plasticisation also plays a key role in improving interfacial contact between the electrolyte and the electrodes. The increased flexibility conferred by plasticisers enhances electrode–electrolyte adhesion, allowing for more efficient ion transfer across the interface.^{45,81} Finally, plasticised membranes offer notable processing advantages. They are easier to handle, more flexible, and often exhibit high transparency and strong adhesion to substrates such as glass and metal.⁸¹

Despite their potential, SPEs still face important challenges that limit their integration in commercial ESSs. Among the most critical issues are, as previously mentioned, their intrinsically low ionic conductivity (range of 10^{-4} S/cm)—particularly at ambient temperature.^{32,40,75} The low conductivity is often attributed to strong interactions between cations and electronegative sites in the polymer matrix which significantly reduce ion mobility.⁷⁵

In parallel, extensive research has focused on minimising the poor compatibility with electrode materials.⁹ Although SPEs offer promising mechanical flexibility and close interfacial contact, this compatibility issue results in increased interfacial resistance and hampers efficient ion transfer. Consequently, these limitations prevent SPEs from fully meeting the performance standards required for commercialisation, which include high energy density, stable cycling, and reliable operation after prolonged rest periods.^{9,32,75} In light of these constraints, it is essential that SPEs are designed to meet a series of demanding criteria to enable their effective implementation in next-generation solid-state ESSs. First and foremost, they should exhibit an ionic conductivity ideally above 10^{-3} S/cm across a broad temperature range, ensuring sufficient ion transport even under ambient conditions.⁴¹ A high cation transference number, close to unity (≈ 1), is also essential to minimise concentration polarisation during cycling and promote high energy efficiency.^{40,41} In terms of electrochemical stability, a wide voltage window, typically from 0 to 5 V, is required to prevent undesired side reactions with electrode materials, preserve the reversibility of redox processes, and enable the use of high-voltage cathodes in next-generation sodium or LIBs.^{40,41} Additionally, these materials must exhibit high thermal stability, preferably in the range of -40 to 150 °C, to avoid deformation, internal short circuits, and thermal runaway under operational stress.⁴¹ Mechanical robustness is another crucial property, both to maintain structural integrity during handling and to suppress sodium dendrite formation—particularly in the context of sodium-based batteries.^{40,41} Finally, biocompatibility and non-toxicity are desirable features to support the widespread use of these systems, especially in environmentally sustainable energy storage applications.⁴¹

Various recent formulations have been explored to enhance the performance of NaCMC-based SPEs. Among these, the incorporation of salts, with or without plasticisers, into the polymer matrix has received particular attention. A summary of selected recent studies is presented in Table 2.

Table 2. NaCMC-based SPEs reported in the literature since 2021.

Year	Polymer Matrix	Salt	Plasticiser	Salt Content (wt%)	σ (S/cm)	ESL* (V)	Reference
2021	NaCMC	NaClO ₄ ·H ₂ O	—	25	2.00×10^{-4}	—	⁸²
2023	NaCMC	LiCH ₃ COO	—	30	2.47×10^{-5}	3.5	⁸³
2023	NaCMC-Pectin (blend)	NH ₄ Br	Glycerol	25	4.68×10^{-4}	≈2.5	⁸⁴
2024	NaCMC	NaI	—	25	4.68×10^{-4}	≈2.5	⁸⁵

*ESL = Electrochemical Stability Limit (Maximum voltage up to which the electrolyte remains stable without decomposition)

The studies on NaCMC-based SPEs show ionic conductivities between 2.47×10^{-5} S/cm and 4.68×10^{-4} S/cm at room temperature. Higher conductivities were observed in systems doped with NaClO₄, NaI, and NH₄Br, the latter incorporating glycerol as a plasticiser, which likely contributed to enhanced ion mobility. These conductivity values meet the minimum threshold required for basic electrochemical applications (10^{-5} S/cm) and are significantly higher than those of non-doped CMC matrices, which typically display conductivities below 10^{-6} S/cm.^{83,86}

Electrochemical stability limits ranged from approximately 2.5 V to 3.5 V. The LiCH₃COO/NaCMC membrane exhibited the highest value at 3.5 V, while the NaClO₄-, NaI- and NH₄Br-based systems, including the plasticised membrane, presented slightly lower values (≈2.5 V).

Mechanical properties were only reported for the LiCH₃COO/NaCMC membrane, with a tensile strength of 12.84 MPa and elongation at break of 30.94%.⁸³ As this information was available in only one out of the four articles reviewed, it was not included in the comparative table. This highlights the need for more comprehensive mechanical characterisation in future studies.

In light of the stringent requirements for SPEs in solid-state ESSs previously presented, the formulations analysed here still present considerable limitations. Although the ionic conductivities achieved are sufficient for proof-of-concept studies, they fall short of the ideal targets for high-performance battery applications. Similarly, the electrochemical stability limits observed (≈2.5–3.5 V) are lower than the ≈5 V window required for compatibility with high-voltage cathode materials. These observations highlight the need for further optimisation. Nevertheless, the results confirm the potential of NaCMC-based SPEs as flexible and tunable materials, with the choice of salt and the possible incorporation of plasticisers playing critical roles in defining key electrolytes properties.

Accordingly, based on the present comparative analysis and considering the promising characteristics of LiTFSI discussed earlier, the combination of NaCMC, LiTFSI and glycerol emerges as a bio-based and experimentally valid strategy for enhancing SPE performance, which, to the best of our knowledge, has not yet been systematically explored.

2.1.4. Embedded Sensors in Batteries: Enabling Real-Time Monitoring

One recent innovation in battery technology is the integration of embedded sensing platforms within the cell architecture. In recent years, the pursuit of safer, smarter and more durable batteries has intensified the development of real-time monitoring strategies that can provide direct insight into internal physicochemical processes of the system.^{7,87}

Traditional battery management systems (BMSs), which rely primarily on external measurements of voltage, current, and surface temperature, remain fundamentally limited in their ability to assess the internal electrochemical state of cells. Such approaches struggle to accurately estimate key indicators such as state of charge (SOC) and state of health (SOH), or to anticipate failure mechanisms, especially in next-generation high-density cell architectures where significant internal gradients may go undetected.^{7,87}

The integration of *in situ* and *in operando* monitoring solutions addresses these limitations by enabling the collection of localised data from within the cell during operation.^{88,89} These data include, among others, internal temperature gradients, pressure evolution, strain development, ionic conductivity, and changes in dielectric properties.^{88,90-92} Such parameters are essential to detect early signs of degradation, non-uniform lithium plating, electrolyte decomposition, and the formation of gas pockets or dendrites.^{7,87,90} The ability to continuously track these internal changes not only enhances safety by allowing prompt intervention in case of anomalies, but also improves performance optimisation and extends battery lifetime through adaptive control strategies.^{89,90}

To fulfil these needs, different sensor technologies have been investigated as candidates for seamless integration within lithium battery architectures.^{7,93} Among the most prominent are fibre-optic sensors, such as fibre Bragg gratings (FBGs), and electromagnetic sensors, including passive LC circuits and antenna-based structures.^{88,93} Fibre-optic sensors are valued for their miniaturisation, chemical inertness, and multiplexing capabilities, and have been widely applied for temperature and strain monitoring.^{88,89} Meanwhile, passive electromagnetic sensors are capable of detecting shifts in the local dielectric

environment, impedance, or pressure, making them especially promising for electrolyte-sensitive applications.^{94,96}

Loop antennas, a specific class of LC sensors, operate through electromagnetic coupling and are highly sensitive to variations in the surrounding dielectric environment.^{87,97} Their resonant frequency shifts according to changes in the real part of the permittivity, making them particularly suited for detecting processes that alter the dielectric properties of electrode–electrolyte interfaces.⁹⁷ In addition, they are traditionally designed for wireless operation, enabling integration in battery architectures.^{87,97} When embedded within battery systems, loop antennas can serve as non-invasive probes to track physicochemical changes related to SOC or electrolyte ageing, as long as they are properly coupled to the surrounding matrix.^{87,98} This sensing strategy may complement optical and thermal approaches by providing an alternative electromagnetic readout pathway.^{87,97}

Despite their promise, several challenges hinder the practical implementation of embedded sensors.⁹⁹ Foremost among them is the requirement that the sensor be integrated without compromising the structural integrity, sealing, or electrochemical performance of the battery. The internal environment of lithium batteries is chemically aggressive, mechanically constrained, and highly sensitive to material interfaces. Sensors must therefore exhibit minimal invasiveness, chemical stability, and reliable signal transmission under operational conditions.⁸⁸

A critical parameter in this integration is the selection of a suitable host material. SPEs represent an ideal matrix in this context, owing to their favourable combination of dielectric properties, adhesive behaviour, mechanical flexibility and processability.¹⁰⁰ SPEs can accommodate conformal contact with sensor surfaces, stabilise the sensor environment, and in some cases enhance signal quality by suppressing parasitic conduction or electromagnetic interference.^{7,88,90} Additionally, their viscoelastic nature allows for mechanical compliance, essential for maintaining sensor integrity during battery cycling.¹⁰⁰

In summary, embedded sensors constitute a key enabling technology for next-generation batteries, offering real-time access to critical internal parameters that are otherwise inaccessible.⁷ Their integration into solid-state systems, particularly in combination with SPEs, paves the way for advanced diagnostic and control strategies aimed at maximising battery performance, safety and lifetime.^{7,90}

2.2. Analysis and Characterisation Techniques

The following analysis and characterisation techniques were selected for their relevance in assessing the physicochemical properties of SPEs and the electrochemical behaviour of Li-metal half-cells. Their fundamental principles are briefly outlined below.

2.2.1. Ultraviolet-Visible Spectroscopy

Ultraviolet-visible (UV-Vis) spectroscopy is a technique that studies the promotion of electrons within molecules, atoms, or ions to higher energy states upon the absorption of electromagnetic radiation in the ultraviolet (UV) or visible (Vis) regions. This phenomenon occurs exclusively when the energy of the incident radiation corresponds precisely to the energy required for electronic transitions between quantised states, resulting in the absorption of radiation at that specific energy.¹⁰¹

The instrument employed for UV-Vis spectroscopy, known as a spectrophotometer, is designed to scan across a broad range of wavelengths to generate absorption or transmission spectra. These devices typically comprise a continuous radiation source, a monochromator for isolating specific wavelengths, a sample holder, a radiation detector, and a current meter for processing the detected signal. Spectrophotometers are available in two principal configurations: single-beam and double-beam systems, as illustrated in Figure 3. In most routine laboratory applications, the UV range covers wavelengths from 200 to 350 nm, while the Vis region extends from 350 to 700 nm.¹⁰²

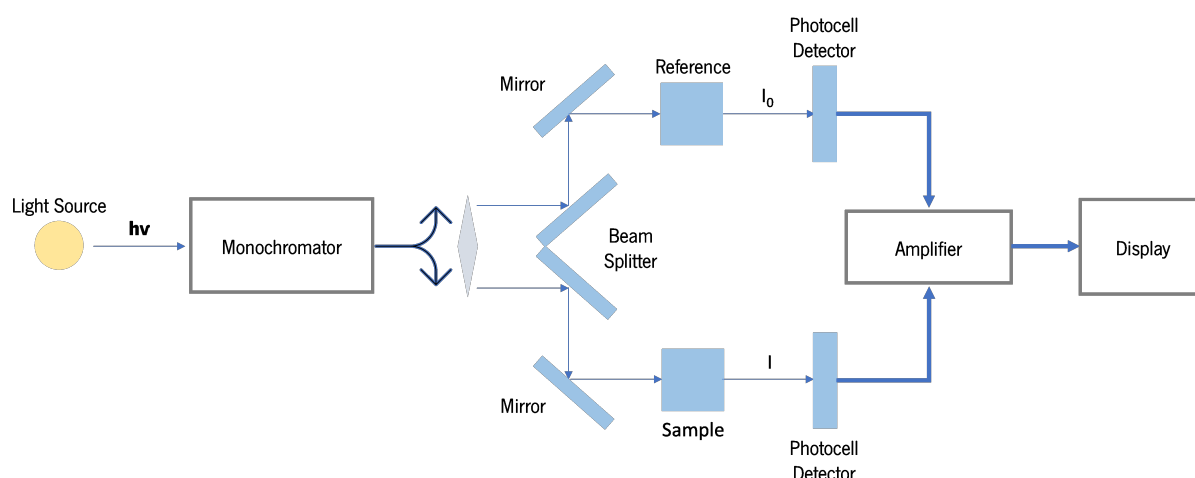


Figure 3. Schematic representation of a double-beam UV-Vis spectrophotometer configuration.

As a beam of electromagnetic radiation traverses an absorbing material, its intensity diminishes from an initial value (I_0) to a final value (I) on the opposite side. This reduction is caused by the absorption of photons by the sample's absorbing species.¹⁰² The ratio of these intensities, known as transmittance (T), is calculated experimentally using Equation 1 and may also be expressed as a percentage, Equation 2. Transmittance ranges from zero ($I = 0$) in fully absorbing media to unity ($I = I_0$) in completely transparent media.¹⁰¹

$$T = \frac{I}{I_0} \quad \text{Equation 1}$$

$$\%T = \frac{I}{I_0} \times 100 \quad \text{Equation 2}$$

For qualitative analysis, transmittance alone often provides sufficient information. However, absorbance (A) is generally preferred for quantitative assessments, as it not only describes the relationship between I and I_0 but also exhibits linear proportionality with the concentration of the absorbing species under appropriate conditions. This enables the determination of an analyte's concentration. Absorbance is mathematically defined in terms of transmittance, as demonstrated in Equation 3.^{101,102}

$$A = \log_{10} \left(\frac{I_0}{I} \right) = -\log_{10} T \quad \text{Equation 3}$$

2.2.2. Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy

Infrared (IR) spectroscopy is a highly regarded absorption technique used to examine the vibrational and rotational movements of atoms within molecules in the IR region of the electromagnetic spectrum. For a molecule to absorb IR radiation, it must exhibit a variable electric dipole moment during its motion, resulting in interactions between radiation and matter that cause atomic vibrations and rotations.¹⁰³

An IR spectrum is obtained by passing radiation through a sample and measuring the fraction of incident radiation absorbed at specific energy levels. The position of any peak or band in the spectrum corresponds to the characteristic frequency of a molecular vibration within the sample.¹⁰³

Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) Spectroscopy is particularly advantageous compared to conventional IR spectroscopy. It allows for the direct analysis of a wide range

of samples, including liquids, solids, powders, and pastes, with minimal preparation. Additionally, its rapid data acquisition process, typically within seconds, adds to its versatility and efficiency.^{104,105}

ATR-FTIR is based on the principle of attenuated total reflectance. In this method, the sample is brought into direct contact with an internal reflection element (IRE), through which the IR beam is directed at an angle (θ) exceeding the critical angle (θ_c). This process results in total internal reflection, as depicted in Figure 4, and generates an evanescent wave at the points of reflection. The wave penetrates the sample's surface, facilitating absorption.¹⁰⁶ After several internal reflections, the beam exits the IRE and reaches the detector.¹⁰⁵

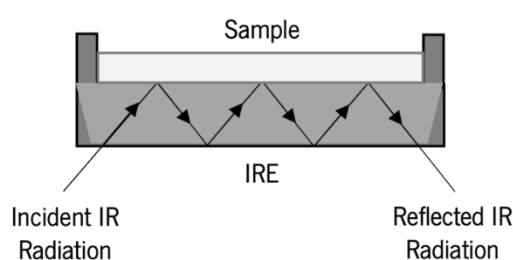


Figure 4. Schematic representation illustrating the ATR principle.

The IREs are typically designed as horizontal crystals that provide optimal contact between the sample and the solid surface, ensuring accurate measurements. They are often made of zinc selenide (ZnSe), diamond, and germanium (Ge).¹⁰⁵

This technique proves to be a valuable tool for investigating ionic association in SPEs, as ion coordination induces characteristic shifts in spectral bands, including band splitting and variations in intensity, offering crucial insights into their structural dynamics.¹⁰⁷

2.2.3. Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is a widely recognised and extensively employed method for characterising the electrical behaviour of the electrode/electrolyte interface. This steady-state technique is particularly suited to electrochemical systems that remain temporally stable, offering valuable insights into the overall dynamics of these systems, where multiple interrelated processes occur simultaneously at different rates. Furthermore, EIS facilitates the evaluation of the individual contributions from both the electrode and the electrolyte to these dynamics.^{108,109}

The technique is grounded on the principle that the electrode/electrolyte interface can be represented as a network of passive circuit elements, including resistors, capacitors, and inductors, and it operates within the frequency domain.¹⁰⁸ During measurements, an alternating signal with a small amplitude (typically 5 to 20 mV) is applied to the electrode in contact with the electrolyte to minimise the non-linearities in the system response obtained at large amplitudes.^{108,109} By analysing the resulting response across a broad frequency spectrum and at different applied potentials, it becomes possible to distinguish between processes characterised by different timescales.¹⁰⁸

In contemporary research, EIS has become an essential tool for studying various electrochemical processes, including those in LIBs, photovoltaic devices, and corrosion systems.¹⁰⁸

2.2.4. X-Ray Diffraction

X-ray diffraction (XRD) is a fundamental analytical technique employed to investigate the structural properties of crystalline materials at the atomic level.¹¹⁰ The versatility of XRD lies in its ability to determine fundamental structural parameters such as lattice constants, crystallite size, microstrain, and phase composition.¹¹¹

The method is grounded on the elastic scattering of X-rays by electrons in a periodic lattice, resulting in constructive interference when the Bragg condition is fulfilled. This occurs when the path difference between rays reflected from adjacent crystallographic planes equals an integer multiple of the incident wavelength, as defined by the Bragg equation (Equation 4).¹¹²

$$n \lambda = 2 d \sin \theta \quad \textbf{Equation 4}$$

where n is an integer, λ is the X-ray wavelength, d is the interplanar spacing, and θ is the angle of incidence.

Depending on the arrangement of atoms within the unit cell, the diffracted intensities vary, enabling the determination of crystal symmetry and preferred orientations.¹¹¹

Instrumentation for XRD, represented in Figure 5, typically comprises an X-ray source (often a copper anode generating Cu $K\alpha$ radiation), a monochromator to ensure wavelength specificity, a goniometer for precise angular control, and a detector to measure diffracted intensities.¹¹⁰ Modern diffractometers are often equipped with computerised control for efficient data acquisition and analysis, including Rietveld refinement transform approaches for full structural resolution.^{110,113}

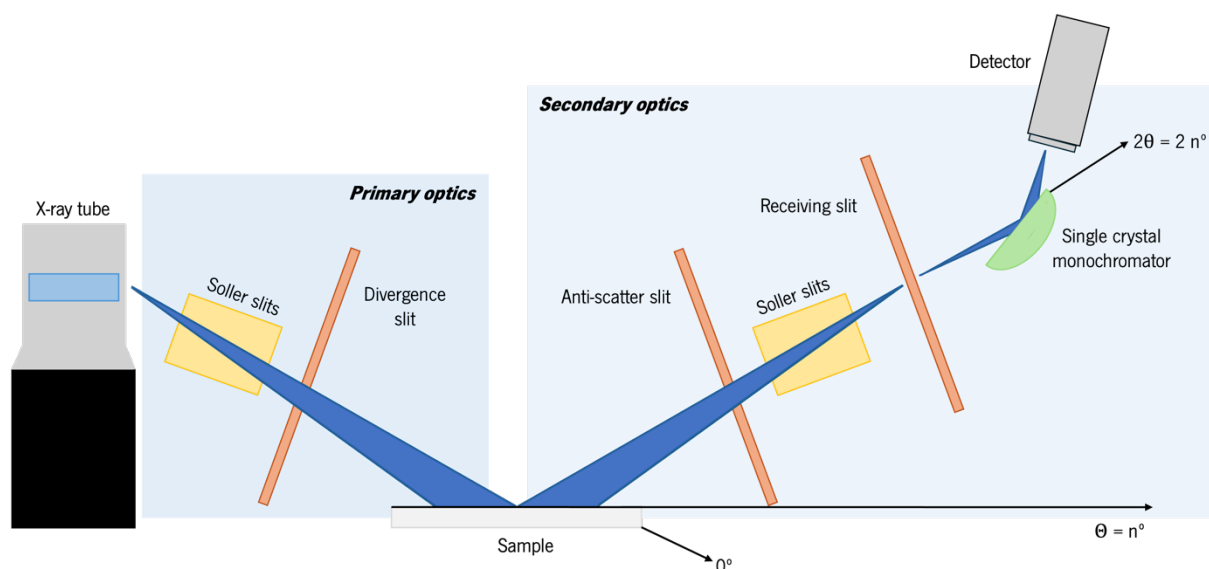


Figure 5. Schematic representation of the instrumentation used for XRD analysis.

Powder XRD is particularly valuable for polycrystalline samples, generating characteristic diffraction patterns that function as material fingerprints.¹¹⁰ Alternatively, single-crystal and grazing incidence techniques allow for more detailed surface and thin film analysis.¹¹⁴ Advanced XRD techniques, such as surface X-ray diffraction (SXRD), extend the method's capabilities to the atomic-scale characterisation of surfaces and interfaces, proving useful in the study of thin films and epitaxial layers.¹¹⁴ Overall, this technique remains an indispensable tool in material science, offering non-destructive, quantitative insight into structural characteristics with high accuracy and resolution.¹¹⁰

2.2.5. Polarised Optical Microscopy

Polarised optical microscopy (POM) is an imaging technique used to investigate optically anisotropic materials by analysing their interaction with plane-polarised light. This approach enables the visualisation of structural, physical, and, in some cases, chemical features that are not discernible through conventional brightfield microscopy.¹¹⁵

When a birefringent specimen is illuminated by plane-polarised light, differences in its refractive indices cause the incident beam to split into two orthogonally polarised components that propagate at different velocities. The resulting phase shift between these components gives rise to interference effects, which are observed as characteristic contrast and colour variations in the transmitted light.^{116,117}

A standard POM setup consists of a transmitted light microscope equipped with a polariser below the sample, a rotatable stage for adjusting the sample's orientation, and an analyser positioned above the

sample, oriented perpendicular to the polariser to enable cross-polarised observation. This optical configuration is illustrated in Figure 6.^{115,117} Under crossed polars, isotropic specimens such as amorphous polymers or glasses, or regions devoid of birefringent features, appear dark. Conversely, anisotropic materials – including crystalline polymers, fibres, and deformed amorphous phases – produce bright and often vividly coloured images due to their directional optical behaviour.¹¹⁷

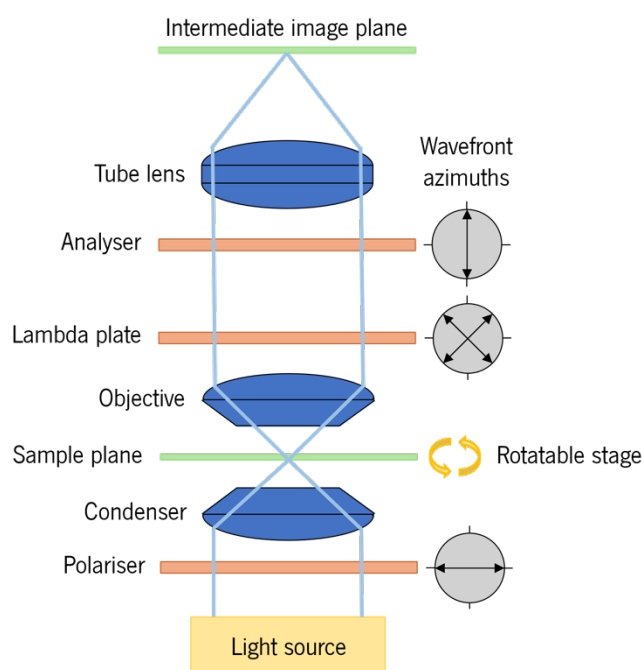


Figure 6. Schematic representation of a typical POM setup.

This technique is particularly advantageous for the study of polymeric materials, especially those exhibiting semi-crystalline morphology. By enabling the direct observation of features such as spherulites, fibrillar structures, and liquid crystalline domains, this technique provides valuable qualitative insights into molecular orientation and processing-induced anisotropy. When examined under crossed polars, these anisotropic regions often display distinctive extinction patterns and vivid interference colours, which serve as optical signatures of internal structural organization.^{115,117}

Due to its versatility, minimal sample preparation requirements, and compatibility with thermal stages and compensators, POM has found extensive application in both academic research and industrial polymer analysis. It has been successfully employed to examine heterogeneous polymer blends, oriented films, and composites.^{115,117}

2.2.6. Scanning Electron Microscopy

Scanning electron microscopy (SEM) is an indispensable technique for the high-resolution imaging of material surfaces, offering structural, morphological and, when coupled with additional detectors, even compositional and crystallographic information.¹¹⁸ The technique operates on the principle of electron–matter interactions: a focused beam of accelerated electrons is directed onto the sample surface, where it interacts with the atoms in the specimen and produces a range of signals that carry information about the texture, shape, size, and spatial distribution of surface features.^{118,119}

The SEM instrument, illustrated in Figure 7, consists of an electron-optical system composed by a column and a control console.¹¹⁸ The electron beam is typically generated using one of three types of electron sources—thermionic, Schottky, or field emission guns—which differ in their brightness, energy spread, and vacuum requirements. Once emitted, the electrons are accelerated and the beam is subsequently focused into a nanometric probe using a series of electromagnetic lenses and apertures. The probe is then raster-scanned across the surface of the sample, and various detectors collect the emitted or scattered electrons, most notably secondary electrons (SEs) and backscattered electrons (BSEs), these are then converted into electrical signals to generate a detailed image of the surface morphology.^{118,120}

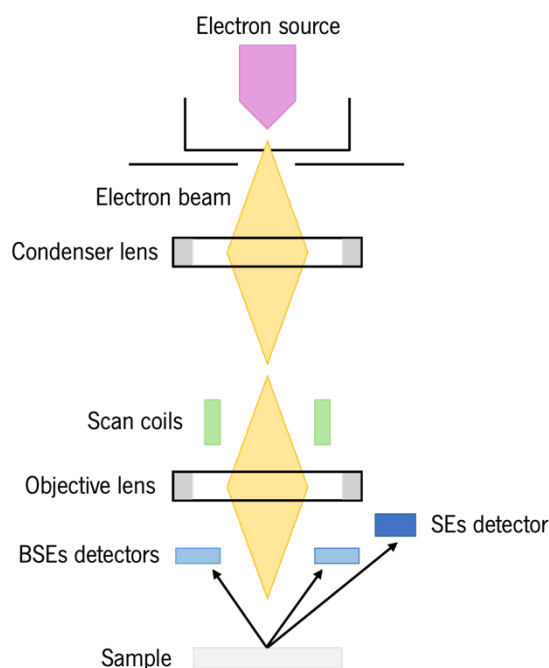


Figure 7. Schematic representation of a SEM instrument.

In SEs emerge predominantly from the top few nanometres of the sample, making them ideal for revealing surface morphology and fine topographic features. BSEs, on the other hand, originate from deeper regions and their yield increases with atomic number, providing useful compositional contrast.^{118,121} Additional signals such as characteristic X-rays, Auger electrons, and cathodoluminescence can also be detected when appropriate detectors are integrated into the system, thereby extending the technique's analytical capabilities.^{118,120,122}

One of the key advantages of SEM is its large depth of field, which produces images with a pronounced three-dimensional appearance.¹¹⁸ However, the resolution ultimately depends on the diameter of the electron probe at the sample surface, which is influenced by instrumental factors such as the electron source brightness, beam current, accelerating voltage, lens aberrations, and working distance.¹²³

Recent developments in electron optics, vacuum technology and detector design have significantly improved SEM performance.¹²² High-resolution imaging is now routinely achieved with field emission sources, and low-voltage SEM has gained popularity for surface-sensitive imaging with reduced charging and beam damage.^{120,122}

2.2.7. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is a well-established thermal technique that quantifies changes in a sample's mass as a function of temperature or time under a controlled atmosphere. By continuously monitoring mass variations during a programmed temperature regime, TGA enables the investigation of thermal stability, compositional features, degradation behaviour, and kinetic parameters of physical and chemical processes involving volatilisation, decomposition, or oxidation.¹²⁴

A standard TGA apparatus comprises a precision microbalance integrated within a temperature-programmed furnace, as shown in Figure 8. The sample is typically placed in an inert crucible and subjected to a linear or isothermal thermal profile under an inert or reactive gas flow. The design may vary across instruments, with top-, bottom-, or side-loading configurations and, in more advanced systems, symmetrical furnace assemblies to minimise buoyancy effects and signal artefacts.^{124,125} The resulting thermogram reflects the material's thermal response and can generally be divided into distinct stages, corresponding to moisture loss, the release of volatiles, polymer degradation, and the formation of carbonaceous or inorganic residues.¹²⁵

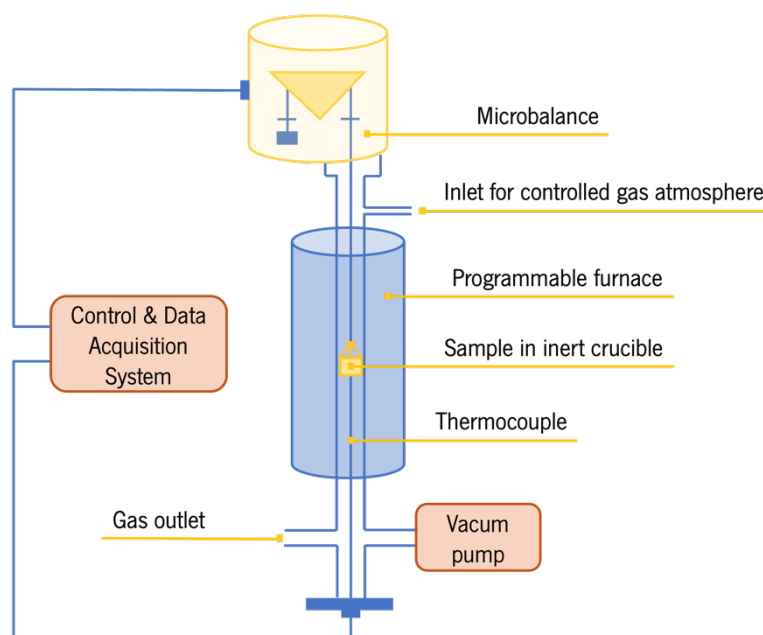


Figure 8. Schematic representation of a standard TGA apparatus.

The shape, resolution, and onset of thermogravimetric events are highly dependent on experimental parameters including sample mass, particle size, gas flow rate, crucible geometry, and the heating rate. Rigorous baseline determination and instrument calibration—specifically adjusted to the selected heating rate and temperature range—are essential to ensure both the reproducibility and interpretability of results, as discrepancies may lead to inaccurate identification of critical temperatures, such as the onset of decomposition or the temperature at which the degradation rate is maximal.¹²⁵⁻¹²⁷

Further analytical detail can be obtained from derivative thermogravimetric (DTG) curves, which are calculated from the first derivative of the mass loss signal. These curves help resolve overlapping decomposition steps and enhance the discrimination between thermal events within multicomponent systems.¹²⁷

In the context of polymeric materials, this technique provides critical insights into thermal degradation mechanisms, the impact of plasticisers or dopants, and the thermal operating limits of the material.^{124,125,127} Additionally, it contributes to assessing the temperature range over which the material maintains thermal stability, supporting decisions regarding its suitability for processing and long-term performance under oxidative or inert atmospheres.^{124,125}

2.2.8. Tensile Testing

Tensile testing is a fundamental mechanical characterisation technique employed to evaluate the behaviour of materials under uniaxial tensile load.¹²⁸ This method provides critical information on properties such as elastic modulus, yield strength, ultimate tensile strength, and elongation at break.^{128,129} These parameters are particularly relevant in the design and optimisation of polymer-based systems, such as SPEs, where mechanical integrity directly influences processing, stability, and application performance.¹³⁰

In a typical tensile test, represented in Figure 9, a specimen with standardised geometry is subjected to a controlled tensile force until failure. The force and elongation are continuously recorded, producing a stress–strain curve from which the mechanical parameters are derived. The initial slope of the stress–strain curve is used to determine the elastic modulus (E), while other key parameters—such as the yield strength (σ_y), ultimate tensile strength (σ_{UTS}), and elongation at break (ϵ_b)—provide insight into the onset of plastic deformation, maximum load-bearing capacity, and material ductility, respectively.^{128,129,131}

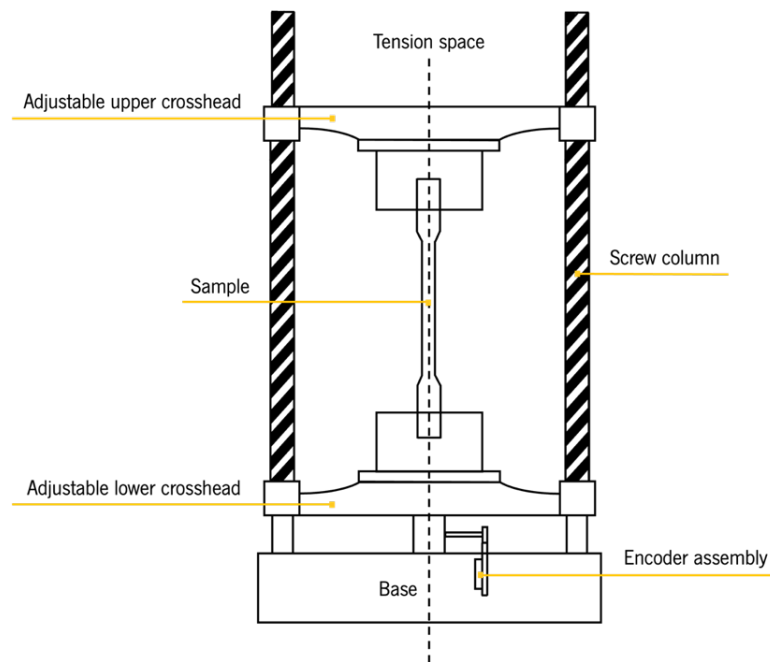


Figure 9. Schematic representation of a tensile test.

The accuracy and reproducibility of tensile strength measurements are significantly influenced by both testing conditions and specimen characteristics. Factors such as strain rate, temperature, gripping method, and specimen geometry play a crucial role in the results obtained.^{129,130,132}

Advanced tensile setups, such as those incorporating digital image correlation (DIC), improve the precision and interpretability of mechanical tests by enabling full-field strain mapping and capturing localised deformation phenomena.¹³¹

Despite its apparent simplicity, tensile testing remains an indispensable tool in materials science. When carefully designed it offers robust and reproducible mechanical data essential for understanding and engineering a broad spectrum of functional materials.^{100,128,131,132}

2.2.9. Contact Angle Measurement

Contact angle measurements (CAMs) are a surface characterisation technique broadly applied to assess the wettability of solid materials, a property intrinsically linked to surface energy.¹³³ The method involves the evaluation of the angle formed at the interface where a liquid droplet contacts a solid surface in the presence of a surrounding gas phase—contact angle (θ_c).^{133,134} This three-phase junction (solid, liquid, and gas) is governed by intermolecular interactions, and the angle observed provides valuable information about the balance between adhesive and cohesive forces at the interface.¹³³ A schematic representation of this equilibrium configuration and the interfacial tensions involved is shown in Figure 10.

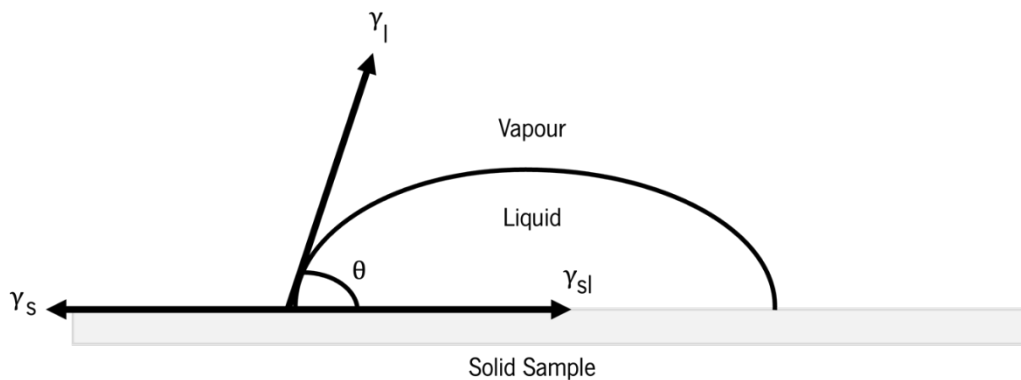


Figure 10. Schematic representation of the contact angle at the solid–liquid–vapour interface.

The foundational principles of contact angle analysis are expressed by the Young equation (Equation 5), which defines the equilibrium contact angle (θ_Y) on an ideal, smooth, chemically homogeneous, and rigid surface.¹³⁵

$$\cos\theta_Y = \frac{\gamma_s - \gamma_{sl}}{\gamma_l} \quad \text{Equation 5}$$

where γ_s is the solid surface energy (N/m), γ_{sl} is the solid-liquid surface tension (N/m) and γ_l is the liquid surface tension (N/m).

However, real surfaces often deviate from these ideal conditions due to factors such as surface roughness or chemical heterogeneity, leading to variations in the measured angles.^{135,136} These effects are accounted for in modified models, such as those proposed by Wenzel (Equation 6) and Cassie–Baxter (Equation 7), which extend the Young equation by incorporating roughness (r) and surface fraction (f), respectively, as shown below:^{134,135}

$$\cos\theta_W = r \cos\theta_Y \quad \text{Equation 6}$$

$$\cos\theta_{CB} = r_1 f_s \cos\theta_Y - (1 - f_s) \quad \text{Equation 7}$$

where r is the roughness ratio of the true surface area of the solid to its projection, r_1 is the roughness ratio of the solid that is wetted, f_s is the fraction of the liquid base in contact with the solid surface and $(1 - f_s)$ is the fraction of the liquid base in contact with air pockets.

In terms of instrumentation, contact angles are usually measured using optical goniometry, in which a side-profile image of a sessile droplet is captured and analysed using image processing algorithms to determine the droplet's base and height.¹³⁷ Common methodological approaches include the sessile drop and captive bubble techniques.¹³⁸ Depending on the measurement protocol, the reported value may correspond to a static, advancing, or receding contact angle.¹³⁶ Recent developments include computerised systems capable of real-time tracking of contact angle evolution, improving precision and enabling the study of dynamic wetting behaviours.^{137,138}

CAMs are also widely employed in soft matter research to qualitatively assess changes in surface chemistry or morphology, and to evaluate hydrophilic and hydrophobic behaviour across a wide range of materials, particularly in polymer-based systems.¹³⁸

2.2.10. Cyclic Voltammetry

Cyclic voltammetry (CV) is one of the most versatile and widely employed electroanalytical techniques for probing the redox properties of electroactive species.¹³⁹ In CV, a linearly varying potential is applied to a working electrode and the resulting current is recorded as a function of time or potential, generating a cyclic voltammogram that reflects the system's redox behaviour.¹⁴⁰

A typical CV experiment involves a three-electrode setup composed of a working electrode (where the redox reactions occur), a reference electrode (which maintains a constant potential), and a counter electrode (to complete the circuit).¹³⁹ The potential is swept at a constant scan rate from an initial value to a set switching potential and then reversed, completing a full potential cycle.¹⁴⁰ The resultant current–potential profile exhibits characteristic peaks associated with oxidation and reduction processes, allowing identification and analysis of electroactive species in the system.¹³⁹

Electrochemical systems are classified as reversible, quasi-reversible, or irreversible depending on the relative rates of electron transfer and mass transport.¹⁴¹ A redox process is considered electrochemically reversible when the electron transfer occurs rapidly enough to ensure that the concentrations of the oxidised and reduced species at the electrode surface remain in equilibrium. At any given potential, this equilibrium ratio is governed by the Nernst equation (Equation 8).¹⁴⁰

$$E = E^{\circ} - \frac{RT}{nF} \ln \left(\frac{[R]}{[O]} \right) \quad \text{Equation 8}$$

where E is the electrode potential (V), E° is the standard electrode potential (V), R is the universal gas constant, T is the absolute temperature (K), n is the number of electrons involved in the redox process, F is the Faraday constant and $[R]$ and $[O]$ are the concentrations of the reduced and oxidised species at the electrode surface, respectively.

In an ideal reversible redox system, the cyclic voltammogram displays well-defined anodic and cathodic peaks with a small potential separation and symmetric peak shapes. The peak positions correspond to the redox potentials of the system.¹⁴⁰ In contrast, quasi-reversible and irreversible systems exhibit broader peak separation and a current–potential response that deviates from ideal Nernstian behaviour.^{139,141}

Furthermore, transient CV experiments—where the scan rate, potential window, or solution composition are varied—have emerged as powerful tools to investigate time-dependent electrochemical systems and to decouple overlapping processes.¹⁴²

Its operational simplicity, combined with its ability to provide comprehensive information on electrochemical processes, makes CV an indispensable tool not only for the characterisation of redox behaviour, but also for the investigation of reaction mechanisms, surface phenomena, adsorption–desorption processes, and charge-transfer kinetics.^{139,141}

2.2.11. Galvanostatic Charge and Discharge

Galvanostatic charge and discharge (GCD) is an extensively adopted electrochemical characterisation technique. This technique enables the differentiation of capacitive, diffusional, and resistive processes occurring at distinct timescales within the electrode and electrolyte system, and proves particularly useful for evaluating the charge storage behaviour of devices such as supercapacitors and rechargeable batteries.^{143,144}

During a GCD experiment, the current is maintained constant throughout both the charging and discharging phases, and the corresponding voltage response is plotted as a potential–time curve.¹⁴³ The features of this curve provide valuable information about the internal processes of the system, including ion transport, electrical resistance, and time-dependent interfacial phenomena often associated with electrode kinetics.^{143,144} For instance, ideal capacitive behaviour results in a linear voltage–time profile, whereas in electrochemical systems deviations from linearity are often associated with resistive losses, ion transport limitations, or delayed electrolyte response under confinement.¹⁴⁴

GCD measurements enable the extraction of several key electrochemical parameters, including the specific capacity of the electrode material, which is determined from the total charge exchanged during discharge and normalised by the mass of the active material.¹⁴⁵ Furthermore, by analysing the evolution of the voltage profiles over consecutive cycles, it is possible to monitor capacity retention, and detect degradation mechanisms.^{145,146}

Owing to its experimental simplicity, reproducibility, and strong correlation with real-world device performance, galvanostatic cycling remains a cornerstone technique in battery research.¹⁴⁶ GCD, commonly used alongside CV and EIS, is increasingly employed not only for performance evaluation but also for mechanistic understanding of electrochemical systems through advanced data analysis.^{143,145}

CHAPTER 3 – EXPERIMENTAL SECTION

3.1. Overview

This chapter details the methodologies and experimental procedures developed during this work, providing a comprehensive description of the materials and equipment used to achieve the research objectives. The content is divided into three major sections, each focusing on a specific aspect of the experimental work: SPEs, sensor-SPE interaction, and coin cells.

The first section describes the reagents and synthesis protocols used for sample preparation, as well as the analytical techniques employed to characterise their properties.

The second section discusses the methodology developed to evaluate the interaction between SPEs and sensors, including the instrumentation setup and the experimental procedures followed to assess the electrical response of the sensors in the presence of the synthesised membranes.

The third section offers a detailed account of the materials and processes involved in assembling lithium-metal coin cells. It also describes the instrumentation and analytical methods used to evaluate the electrochemical performance of these cells.

The experimental work outlined in this chapter was carried out across three institutions. The synthesis and characterisation of SPEs were conducted at the Chemistry Centre of the University of Minho (CQ-UM), which forms the main body of this dissertation. The analysis of sensor-SPE interactions was performed at the CEMOP of the NOVA University Lisbon in the MEON group. Finally, the assembly and electrochemical evaluation of the coin cells were completed at the International Iberian Nanotechnology Laboratory (INL) in the Nanofabrication, Optoelectronics, and Energy Applications (NOA) group.

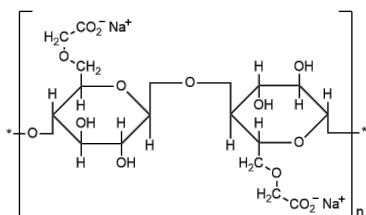
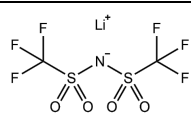
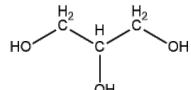
3.2. Solid Polymer Electrolytes

3.2.1. Reagents

The reagents used for the synthesis of the SPEs are listed in Table 3. Sodium carboxymethyl cellulose (NaCMC), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), and glycerol were purchased from Sigma-

Aldrich (Darmstadt, Germany). Pure water was prepared using a Milli-Q EQ 7000 purification system (Darmstadt, Germany) to serve as the common solvent.

Table 3. Identification, molecular weight, and purity of the reagents used in the synthesis of the SPEs.

Designation	Chemical Structure	Molecular weight (g/mol)	Purity and Specifications
Sodium carboxymethyl cellulose		≈90.000	-
Lithium bis(trifluoromethanesulfonyl)imide		287.09	Anhydrous, 99.99% trace metals basis
Glycerol		92.09	≥99.5%

3.2.2. Synthesis of the Samples

In this work, eighteen SPEs were synthesised by using one general polymer matrix, NaCMC, with varying concentrations of salt and plasticiser – LiTFSI and glycerol, respectively.

The fabrication of these samples was conducted via the solvent casting method, divided into three batches. The first batch established a baseline system. An iterative approach was then adopted based on insights from initial ionic conductivity measurements at room temperature, with each subsequent batch refining the system's understanding until a comprehensive dataset was achieved. The first two batches consisted of eight samples each, while the final batch comprised two samples.

An initial bulk solution of 2% (w/v) NaCMC was prepared for each batch by dissolving the required mass of NaCMC in pure water under magnetic stirring at room temperature until complete dissolution. The total volume of the solution is calculated based on the number of SPEs to be synthesised on that day.

For the first batch of samples, the polymer matrix film was prepared directly from the bulk NaCMC solution. Afterwards, glycerol was added to the remaining mixture, creating a working solution that was then employed to prepare the remaining samples, all of which shared the same NaCMC-to-glycerol concentration ratio. This working solution was also used to prepare the film containing only NaCMC and

glycerol. For the other samples, 10 mL aliquots of the working solution were transferred to pre-weighed vials containing predetermined masses of LiTFSI, equivalent to 10, 25, 50, 100, 150, and 200% of the NaCMC mass.

For the second and third batches, a similar procedure was followed; however, only the bulk polymer solution was utilised since glycerol varied across these samples. Vials containing pre-weighed masses of LiTFSI and, where applicable, glycerol were prepared, and 10 mL aliquots of the 2% NaCMC bulk solution were added. In the second batch, four samples containing only LiTFSI were synthesised, with salt concentrations of 10, 50, 100, and 200% relative to the polymer mass. In the remaining samples, glycerol equivalent to half and double the mass of NaCMC was incorporated for two LiTFSI concentrations: 10 and 200%. Finally, for the third batch, two additional samples were prepared using the same glycerol quantities but with a LiTFSI concentration of 150%.

Once the mixtures were prepared, they were stirred thoroughly for 1 hour to ensure complete dissolution and homogeneity. The resulting solutions were then carefully poured onto clean plastic Petri dishes (diameter of 55 mm) and left to dry in a UNB 200 oven (Mettler GmbH + Co. KG, Schwabach, Germany) using a heating ramp of 25 °C for 5 hours, followed by 40 °C for 12 hours, 60 °C for 5 hours, and finally cooled down to 25 °C for 2 hours to ensure complete solvent evaporation. After drying, the membranes were gently removed from the casting surface and visually inspected for uniformity and absence of defects, such as bubbles or cracks.

The synthesised SPEs were stored inside a silica (SiO₂) desiccator with controlled conditions to prevent moisture absorption until further analysis and testing.

To improve the clarity and comprehension of this dissertation, as well as to simplify the presentation of the experimental data, identification (ID) codes were assigned to each sample. These codes will be consistently used throughout this chapter and the following ones, ensuring a streamlined and more efficient reference system.

In Table 4, the quantities of reagents used in the synthesis of the SPEs are highlighted alongside their respective ID codes. Where the subscript for glycerol indicates the mass ratio between NaCMC and glycerol. For example, G_{0.5} corresponds to a mass ratio of 1:0.5 NaCMC-to-glycerol. Similarly, the subscript for LiTFSI denotes the mass percentage of LiTFSI relative to the polymer. For instance, LiTFSI₁₀ indicates that the mass of LiTFSI used in this sample is 10% of the mass of NaCMC.

Table 4. Masses of reagents used in the synthesis of the SPEs, with ID codes indicating glycerol ratios and LiTFSI percentages relative to NaCMC.

Batch	Sample ID	Mass (g)		
		NaCMC	Gly	LiTFSI (± 0.0001)
1	CMC		-	-
	CMC@G ₁			-
	CMC@G ₁ @LiTFSI ₁₀			0.0224
	CMC@G ₁ @LiTFSI ₂₅	0.2023 ± 0.0022		0.0558
	CMC@G ₁ @LiTFSI ₅₀		0.2000 ± 0.0001	0.1003
	CMC@G ₁ @LiTFSI ₁₀₀			0.2004
	CMC@G ₁ @LiTFSI ₁₅₀			0.3196
	CMC@G ₁ @LiTFSI ₂₀₀			0.4116
2	CMC@LiTFSI ₁₀		-	0.0202
	CMC@LiTFSI ₅₀		-	0.1034
	CMC@LiTFSI ₁₀₀		-	0.2009
	CMC@LiTFSI ₂₀₀	0.2003 ± 0.0022	-	0.4009
	CMC@G _{0.5} @LiTFSI ₁₀		0.1111 ± 0.0001	0.0200
	CMC@G ₂ @LiTFSI ₁₀		0.4189 ± 0.0001	0.0278
	CMC@G _{0.5} @LiTFSI ₂₀₀		0.1048 ± 0.0001	0.4108
	CMC@G ₂ @LiTFSI ₂₀₀		0.4133 ± 0.0001	0.4058
3	CMC@G _{0.5} @LiTFSI ₁₅₀	0.2017 ± 0.0009	0.1369 ± 0.0001	0.3100
	CMC@G ₂ @LiTFSI ₁₅₀		0.4089 ± 0.0001	0.3018

3.2.3. Instrumentation and Analysis Procedure

The properties of the SPEs were comprehensively characterised using a variety of advanced techniques, including UV-Vis and ATR-FTIR spectroscopy, EIS, XRD, TGA, SEM, tensile testing, POM, and CAM.

UV-Vis spectroscopy was conducted using a UV-2501PC spectrophotometer (Shimadzu, Kyoto, Japan) fitted with a specialised sample holder for films. Transmittance spectra were collected over the wavelength

range of 200–700 nm at room temperature, with a maximum resolution of 0.1 nm. The spectra were acquired and analysed using UVProbe software.

ATR-FTIR analysis was performed using a Spectrum Two™ spectrometer (PerkinElmer, Waltham, MA, USA) equipped with an ATR accessory featuring a diamond crystal. Data were recorded at room temperature in the range of 4000–400 cm⁻¹ with a resolution of 4 cm⁻¹, averaging 16 scans per sample. The acquisition and analysis of the spectra were carried out using LabSolutions IR software.

EIS measurements were carried out using an Autolab PGSTAT12 potentiostat/galvanostat (Metrohm Autolab, Utrecht, Netherlands). A 1 cm diameter disk, cut from the prepared membranes, was placed between two parallel gold (Au) electrodes (1 cm in diameter and 250 µm thick) within a Macor® support cell. Prior to assembly, the thicknesses of the gold electrodes were measured using a micrometre (Mitutoyo, Kanagawa, Japan). After that, the overall thickness of the stack was determined, allowing the membrane's thickness to be calculated by subtracting the contribution of the electrodes. The setup was then inserted into a TO-51 oven (BÜCHI Labortechnik AG, Flawil, Switzerland) equipped with a thermocouple connected to a Fluke 51 thermometer (Fluke Corporation, Everett, WA, USA) (± 0.01 °C). Then, it was exposed to a controlled temperature range, starting at room temperature and increasing to approximately 100 °C. Stabilisation periods of 30 minutes were maintained following each temperature increment to ensure thermal equilibrium before measurements were taken. A sinusoidal electrical potential of 10 mV (peak-to-peak) was applied at open circuit potential over a frequency range from 0.5 MHz to 0.5 Hz. The acquired data were processed and analysed using NOVA software.

XRD characterisation was conducted at room temperature using a Dmax III/C X-ray diffractometer (Rigaku, Akishima, Japan) operating at 30 kV and 15 mA, employing monochromated CuKα radiation ($\lambda = 1.5418 \text{ \AA}$). The diffraction patterns were obtained over a 2θ range of 10 ° to 70 ° with a scanning rate of 1.2 °/min.

TGA curves were recorded in an STA 449 F3 Jupiter® thermal analyser (NETZSCH, Selb, Germany) under a nitrogen (N₂) atmosphere with a flow rate of 20 cm³/min and a heating rate of 10 °C/min. Before measurements, 5 mg of each sample was transferred to an open alumina (Al₂O₃) crucible. The acquisition and processing of data were performed using the *Proteus*® software.

SEM analysis was conducted using an S-3400N Type II microscope (Hitachi, Tokyo, Japan) equipped with a Bruker XFlash 5010 detector. Micrographs were acquired at an accelerating voltage of 20 kV under high vacuum conditions. Samples were sputter-coated with a thin layer of gold before imaging.

Tensile testing was performed using an AGX-10KN testing machine (Shimadzu, Kyoto, Japan) at room temperature, operating at a strain rate of 50 mm/min. The samples were clamped between the 50 N

stainless steel grips coated with chloroprene rubber, and stress-strain curves were recorded during the tests. Data acquisition and analysis were carried out with the aid of Trapezium™ X software.

POM micrographs were obtained using a B-600 Pol microscope (OPTIKA, Ponteranica, Italy) through an 8 MP Digital Photo camera. Image analysis was subsequently conducted using the Optika Vision Pro software.

CAM were carried out using an OCA 15plus optical goniometer (DataPhysics Instruments, Filderstadt, Germany) at room temperature. A 1 μ L ultrapure water droplet was placed on the sample surface, and the static contact angle was determined using the sessile drop method.

3.3. Instrumentation and Analysis Procedure for Sensor-SPE Interaction

The interaction between the synthesised SPEs and the sensors was analysed to evaluate their electrical response to the membranes and sensitivity to variations in the SPE composition. Since the loop antennas were developed by the MEON research team, their fabrication process lies outside the scope of this experimental work and will therefore not be detailed in the present thesis.

Initially, the resistance of the sensors was measured using a MY64 digital multimeter (Kaise, Barcelona, Spain) to confirm their conductive behaviour. Variations in the fabrication process resulted in differing resistance values among the sensors. To ensure consistent and reproducible results, three sensors with similar resistance values (approximately 30 Ω) were carefully selected for the subsequent measurements. These loop antennas are depicted in Figure 11 and going forward they will be identified by the codes assigned to them in this same figure.

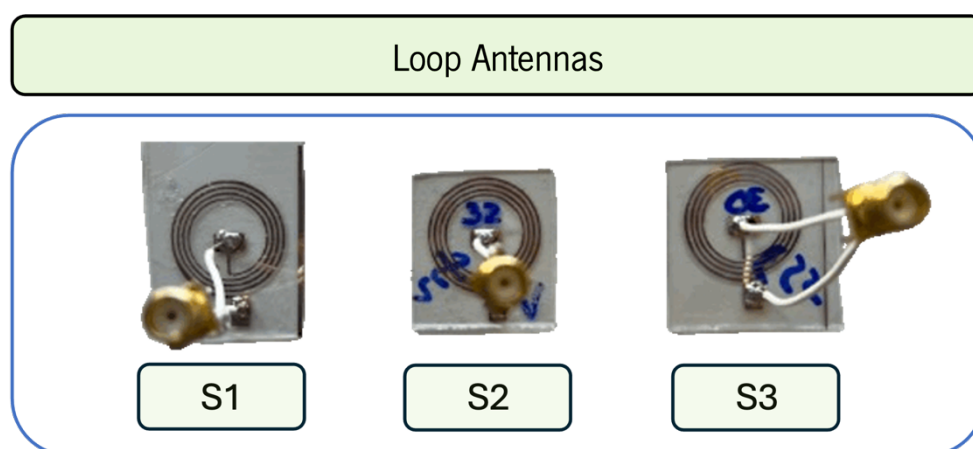


Figure 11. Loop antennas selected for electrical characterisation, identified as S1, S2 and S3.

The electrical parameters of the sensors were analysed using a Lite Vector Network Analyser (LiteVNA) (NanoVNA, Shenzhen, China). Prior to the measurements, the equipment was calibrated, following the sequence recommended by the manufacturer, with the frequency range set to 400 MHz to 3 GHz. Copper (Cu) wires were welded to the sensors and subsequently attached to a straight SMA (SubMiniature version A) female connector, which ensured a stable connection to the LiteVNA throughout the tests. Port 1 of the LiteVNA was connected to the loop antennas to record the S_{11} parameter, which is a reflection coefficient expressed in decibels (dB) that represents the proportion of incident energy that is reflected.¹⁴⁷ The device carries out a frequency sweep and detects resonance when it aligns with the sensor's operating frequency. The resulting output is a plot showing S_{11} as a function of frequency, with peaks that vary in both frequency and amplitude depending on external influences.

The setup for the electrical characterisation is illustrated in Figure 12. Care was taken to maintain consistent conditions across all measurements. The LiteVNA was placed on an isolated surface, as even small movements could cause variations in the signal response. Similarly, the position of the cables and the length of the copper wires were also kept constant to minimise fluctuations in the observed peaks.

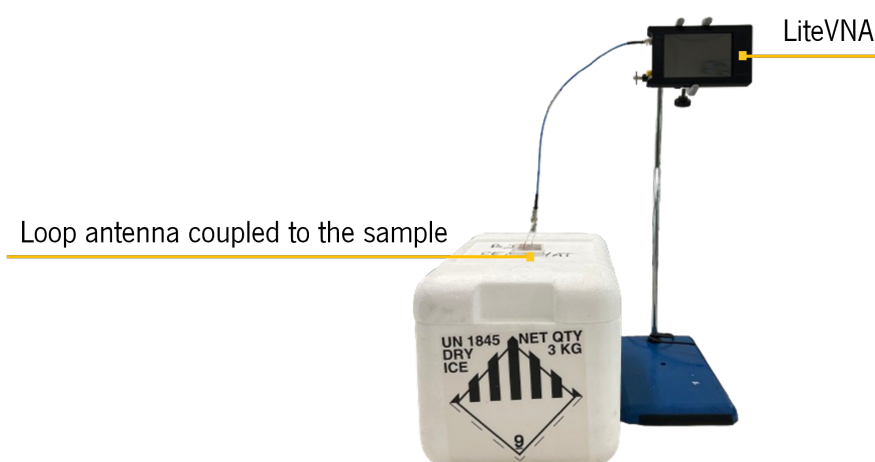


Figure 12. Experimental setup used for electrical characterization with LiteVNA.

The experimental procedure consisted of measuring the sensor response both before and after placing the SPE membranes on the coil area of the loop antennas. The SPE membranes were manually cut with the aim of achieving similar size and shape, and were placed over the coil in a standardised manner for each test, as inconsistencies in membrane dimensions or placement may also contribute to deviations in the sensors' response.

All tests were conducted at room temperature, and each SPE membrane was carefully handled and positioned to avoid any physical damage to the antennas or samples.

3.4. Coin cells

3.4.1. Materials

The materials used for the assembly of the lithium-metal coin-cells included lithium iron phosphate (LFP) single-sided cathode electrodes coated on aluminum (Al) foil featuring a specific capacity of 135 mAh/g and an active material loading of 14 mg/cm² with a mass ratio of 93%. Additional components comprised pre-cut 16 mm diameter lithium (Li) chips anode electrodes with a thickness of 0.45 mm, a porous polypropylene separator (Celgard 2500, 25 µm) and CR2032 stainless steel casings with spacers of 1 mm thickness and cone-shaped springs, all purchased from Cambridge Energy Solutions (Cambridge, United Kingdom). The electrolyte, composed of 1 M LiPF₆ in a 33.33:66.67% (w/w) mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) was obtained from E-Lyte Innovations GmbH (Münster, Germany).

3.4.2. Assembly

Firstly, the purchased materials underwent preliminary preparation. The LFP foil and the separator were cut to precise diameters of 14 mm and 19 mm, respectively, using an MSK-T-06 precision disc cutter (MTI Corporation, Richmond, CA, USA). Afterwards, the casings were cleaned with ethanol and distilled water to remove any residual contaminants. Subsequently, these components were dried in an oven at different temperatures: the separators at 60 °C and the LFP along with the coin cell parts at 80 °C, before being transferred into an argon-filled (Ar) glovebox.

The initial stage of this work involved the assembly of coin cells in lithium metal half-cells configurations. This approach is commonly employed in battery research as a preliminary model to study electrochemical behaviour, since it allows the investigation of a single electrode material against a well-defined lithium reference.^{22,23} At this stage, only commercial materials were used, ensuring the development of stable and reproducible systems, providing a controlled baseline for performance evaluation. These coin cells served

as a benchmark for the subsequent integration of the synthesised SPEs, which were the primary focus of this study.

Approximately 35 coin cells were fabricated during the optimisation stage, aimed at improving performance and reproducibility. Among the tested methods, the assembly process outlined here yielded results that, although not yet comparable to commercial cells, represent the closest approximation achieved so far and indicate promising progress toward that goal.

The assembly of the cells was conducted in the glovebox, where oxygen and moisture levels were carefully controlled to prevent contamination and degradation. The process began by placing the spring inside the housing cover (-), ensuring it was centrally aligned with the larger radius facing upward. A spacer was then positioned on top of the spring, followed by the lithium metal anode.

Approximately half of the required electrolyte, 150 μL , was applied directly onto the anode to ensure complete wetting. The separator was then placed over the anode, and the remaining electrolyte was distributed evenly across its surface to ensure full saturation. The LFP cathode was carefully positioned on top of the separator, with care taken to maintain concentric alignment. The housing (+) was then placed over the assembled components, and the entire assembly was sealed using an MSK-110 hydraulic crimper (MTI Corporation, Richmond, CA, USA) at a pressure of approximately 950 psi. After sealing, the cell was inspected, and any excess electrolyte was wiped clean before storage. The assembled cells were then left to rest for 24 hours at room temperature to ensure stabilisation and proper wetting of the internal components before electrochemical characterisation.

3.4.3. Instrumentation and Analysis Procedure

The performance of the lithium-metal coin cells was assessed using various electrochemical techniques, including CV, EIS, and GCD cycling.

CV measurements were conducted using a VMP-300 potentiostat/galvanostat (Biologic, Seyssinet-Pariset, France). The scans were carried out over a 2.5–3.7 V voltage range, with a rate of 1.0 mV/s, over three cycles at room temperature. Data acquisition was carried out using EC-Lab® software.

EIS was performed using the same potentiostat/galvanostat. An AC voltage amplitude of 10 mV was applied over a frequency range of 100 KHz to 10 mHz at room temperature. The data acquisition was performed using the same software as before, while the analysis was conducted with ZSimpWin software.

GCD cycling was performed using a BTS-4008-5V10mA (Neware Shenzhen, China) battery cycler at room temperature. The tests spanned a voltage range of 2.5–3.7 V, at a C-rate of 0.1C, over 3 to 5 cycles.

CHAPTER 4 – RESULTS AND DISCUSSION

4.1. Overview

This chapter provides a critical analysis of the results, accompanied by relevant discussions to interpret and contextualise the data collected throughout the experimental work. The findings are structured around the same three themes previously outlined.

The opening section focuses on the detailed characterisation of SPEs, covering a broad spectrum of physical, chemical, optical, electrochemical, thermal, mechanical, and surface properties.

The following section examines the electrical interaction between the synthesised membranes and loop antennas, assessing the sensors' capability to detect changes in electrolyte composition. This analysis further explores the relationship between the sensors' electrical response and the properties of the SPEs. Lastly, the final section discusses the electrochemical performance of lithium-metal coin cells.

4.2. Characterisation of Solid Polymer Electrolytes

4.2.1. Macroscopic Analysis

Initially, a general visual analysis of the membranes was conducted, focusing on transparency, uniformity, and surface features. As mentioned in the experimental section, SPEs were synthesised in three batches. This division is essential for the comparative analysis presented here, and therefore, these batches will be identified as Batch 1, 2 and 3. Photographs of the prepared samples are shown in Figure 13.

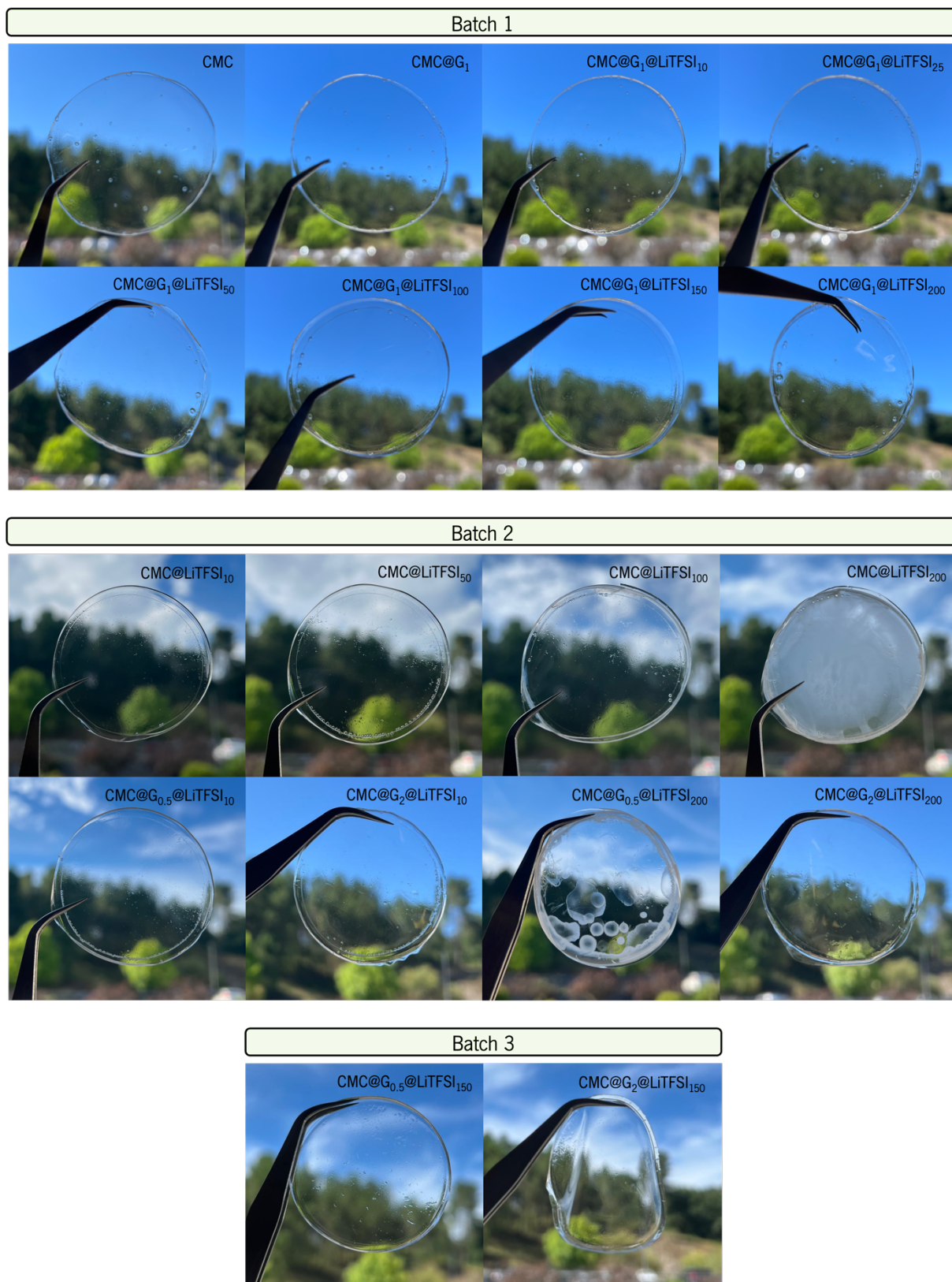


Figure 13. Photographic images of the SPEs under natural light, grouped by synthesis batch.

An important initial observation concerns the small bubbles present on the surface of most membranes. As these are unlikely to be associated with air entrapment during the casting process — since no such formation was evident at that stage — they are probably generated during the drying process, thanks to a high or uneven evaporation rate of the solvent. This hypothesis is corroborated by the results of an initial optimisation conducted for the drying procedure. In the preliminary method, films were dried directly at 60 °C for 24 hours, which resulted in a significantly higher occurrence of bubbles within the films. By implementing the temperature ramp described in the experimental section, the prevalence of bubbles in the samples was notably reduced. It can be inferred that the temperature ramp facilitated a more controlled and balanced solvent evaporation rate. Nevertheless, further optimisation is still required to improve the uniformity and general quality of the samples.

Overall, most membranes appeared transparent, with the exceptions of CMC@LiTFSI₂₀₀ and CMC@G_{0.5}@LiTFSI₂₀₀, which exhibited translucent characteristics. Specifically, CMC@LiTFSI₂₀₀ displayed a uniform white layer across its surface, while CMC@G_{0.5}@LiTFSI₂₀₀ presented irregular white spots of varying sizes and shapes. Transparency was influenced by both glycerol and LiTFSI concentrations. An increase in salt concentration (e.g. 200%) led to white colouration or spots. This result is expected, as an excessively high concentration of the ionic dopant can lead to a non-homogeneous SPE due to the formation of salt clusters or crystals.^{54,85} These limitations are likely attributed to factors such as the proximity of anions and cations, which increases the likelihood of local interactions and promotes the nucleation of clusters, and the insufficient coordination sites by the polymer that may cause lithium cations (Li⁺) to bind predominantly with bis(trifluoromethanesulfonyl)imide anions (TFSI⁻), leading to the eventual formation of salt crystals.^{55,148} However, at this concentration, the incorporation of glycerol, along with an increase in its content, led to more transparent membranes. This outcome suggests that glycerol mitigates the observed phenomenon, as demonstrated in the photographs. According to the literature, its hydroxyl-rich structure enhances the matrix's coordination capacity, providing additional interaction sites for Li⁺ ions.¹⁴⁹ Simultaneously, the high dielectric constant of glycerol facilitates salt dissociation by diminishing the Coulombic forces between the ions.^{55,149,150} Together, these effects likely reduce LiTFSI aggregation and eliminate the visible patches.

Additionally, the flexibility of the SPEs was qualitatively assessed through manual handling of the samples. Given that the tactile perception of flexibility can be influenced by the sequence in which the samples are handled, direct comparisons were conducted predominantly within individual batches to minimise bias. In Batch 1, the CMC membrane was rigid. The addition of glycerol significantly increased flexibility, with further enhancements observed as the salt concentration increased. However, an exception was noted:

the CMC@G₁@LiTFSI₅₀ membrane, which, as seen in Figure 13, exhibits greater flexibility than CMC@G₁@LiTFSI₁₀₀. In Batch 2, the SPEs doped exclusively with LiTFSI demonstrated rigid characteristics, and no clear pattern could be detected with increasing salt concentration. Batch 2 and 3 revealed that SPEs with a 1:2 NaCMC-to-glycerol ratio were consistently more flexible than those with a 1:0.5 ratio, regardless of salt concentration. The dominant effect of glycerol over LiTFSI on flexibility was evident, as membranes with 1:2 ratio exhibited greater flexibility, even compared to membranes with high salt concentrations and a lower amount of glycerol. For instance, the CMC@G₂@LiTFSI₁₀ membrane was more flexible than the membrane CMC@G₁@LiTFSI₂₀₀. The most striking observation of this phenomenon is the transition from near opacity (without plasticiser) to transparency (1:1 and 1:2 NaCMC-to-glycerol ratio) in the membranes containing 200% LiTFSI.

The most flexible sample is the CMC@G₂@LiTFSI₁₅₀. For films with a 1:1 NaCMC-to-glycerol ratio, it was not possible to assess the effect of salt concentration on flexibility. However, this effect could be evaluated in membranes with 1:2 ratio. Among them, an increase in salt concentration enhanced the flexibility of the SPEs by up to 150%. Nevertheless, at a 200% salt concentration, the membrane exhibited reduced flexibility. This behaviour is likely attributed to an increase in the number of charge carriers, such as free ions and ion pairs, which leads to overcrowding of the NaCMC matrix with ions,^{150,151} thereby restricting the motion of the polymer chains.

These findings highlight the predominant role of glycerol in enhancing membrane flexibility by disrupting intermolecular interactions, such as hydrogen bonds, between NaCMC chains, consequently lowering the glass transition temperature (T_g) of the polymer matrix, which facilitates the softening of the backbone, enhancing the segmental motion of the chains. This behaviour reaffirms glycerol's well-established function as a plasticiser.^{74,150} Similarly, the addition of salt contributed to an increase in the flexibility of the SPEs up to a certain concentration, suggesting that the salt also acts as a plasticiser within the studied system. This observation aligns with the findings of Sylla et al.,¹⁵² who demonstrated the plasticising role of LiTFSI in a PEO-based matrix.

4.2.2. Ultraviolet-Visible Spectroscopy

UV-Vis spectroscopy was used to assess the optical transmittance of the polymer films. To ensure reproducibility and statistical reliability, three measurements were taken for each sample at different positions on the membrane surface. The averaged transmittance spectra are shown in Figure 14.

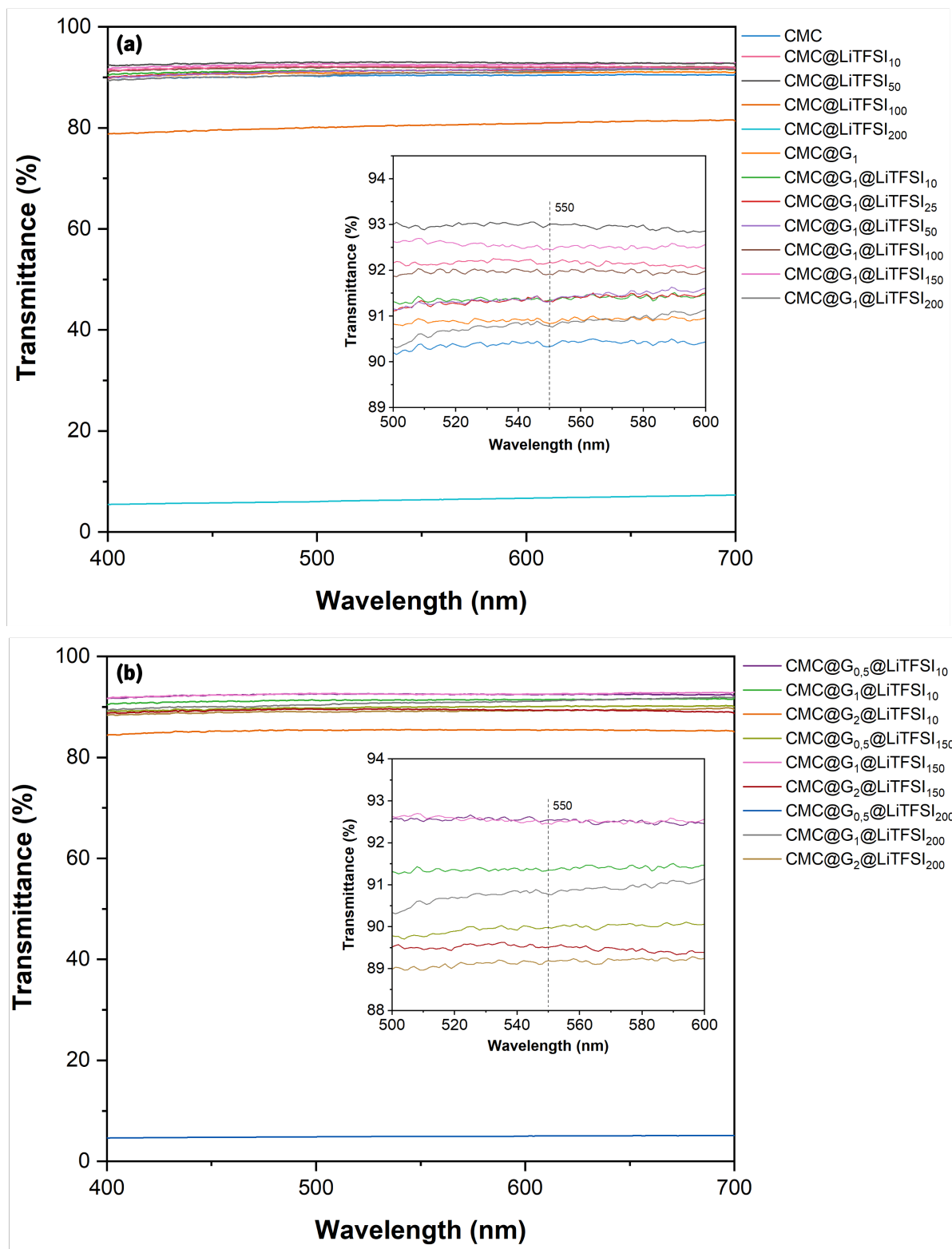


Figure 14. UV-Vis transmittance spectra of the synthesised SPEs: (a) variation in LiTFSI concentration in the absence of glycerol and at fixed 1:1 NaCMC-to-glycerol ratio; (b) variation in glycerol content at fixed salt concentrations of 10, 150 and 200%. Insets display magnified views of the transmittance around 550 nm.

The inset spectra highlight the transmittance at 550 nm, to facilitate differentiation between samples. This specific wavelength was selected due to its central position in the Vis spectrum, where polymeric

materials typically exhibit significant variations in transmittance. Furthermore, it is widely used in the scientific literature as a standard reference.¹⁵³ To further aid in the interpretation of the impact of dopants and their concentration, additional graphs were constructed (Figures 15–17), displaying the average transmittance values at 550 nm along with their corresponding standard deviations, represented as error bars.

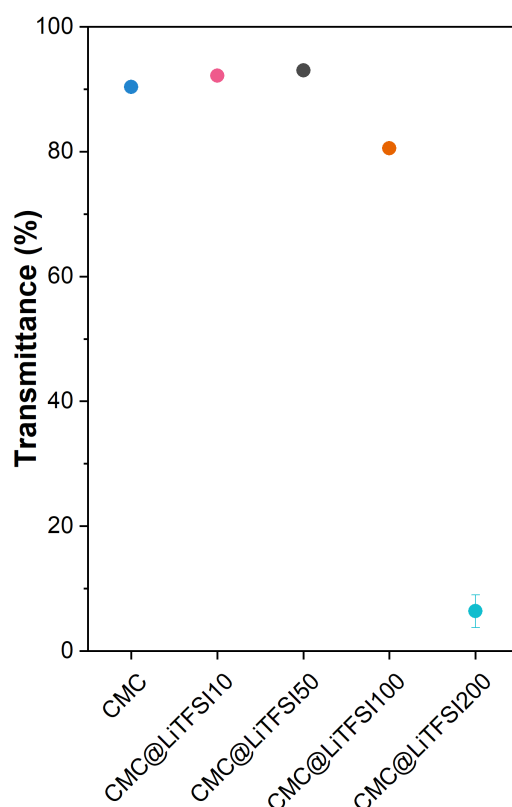


Figure 15. Transmittance at 550 nm for selected SPEs as a function of LiTFSI concentration in the absence of glycerol. Error bars represent standard deviations.

Starting with the polymer matrix, its transmittance at 550 nm is $90.3 \pm 0.1\%$, as shown in Figure 15. When doping it solely with LiTFSI, a general trend is observed. As the salt concentration increases, a slight rise in film transmittance is noted, with an inflection point at 50% LiTFSI ($93.0 \pm 0.2\%$). Beyond this concentration, a pronounced effect of the salt on film transparency becomes evident. A substantial decrease in transmittance is observed, with values dropping to an average of $80.5 \pm 0.5\%$ at 100% salt and $6.4 \pm 2.6\%$ at 200%. This behaviour correlates with the white surface, caused by the formation of salt clusters or crystals, observed in the $\text{CMC@G}_1\text{@LiTFSI}_{200}$ film, confirming that this sample is no longer effectively transparent.

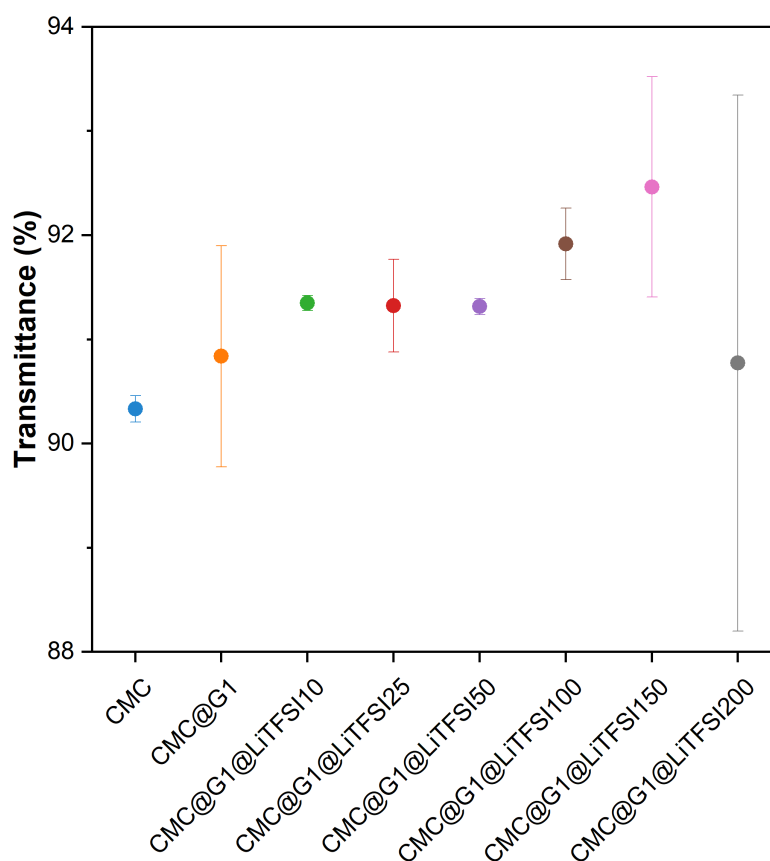


Figure 16. Transmittance at 550 nm for the selected SPEs, as a function of LiTFSI concentration at a fixed 1:1 NaCMC-to-glycerol ratio. Error bars represent standard deviations.

Upon the addition of glycerol, illustrated in Figure 16, the previously discussed effect of LiTFSI appears to be mitigated, as the variations in transmittance values remain within the range of the highest standard deviation. With increasing salt concentration, transmittance exhibits a rising trend, albeit with fluctuations, reaching $92.5 \pm 1.1\%$ at 150% LiTFSI, before decreasing to $90.8 \pm 2.6\%$ at 200%. The difference between this final value and that of CMC@LiTFSI₂₀₀ (6.4%) aligns with expectations, considering that glycerol is known to disrupt LiTFSI aggregates and assist the salt's solubility within the polymer matrix, as stated earlier.^{55,149,150} This observation is further supported by the macroscopic analysis, where the film becomes transparent.

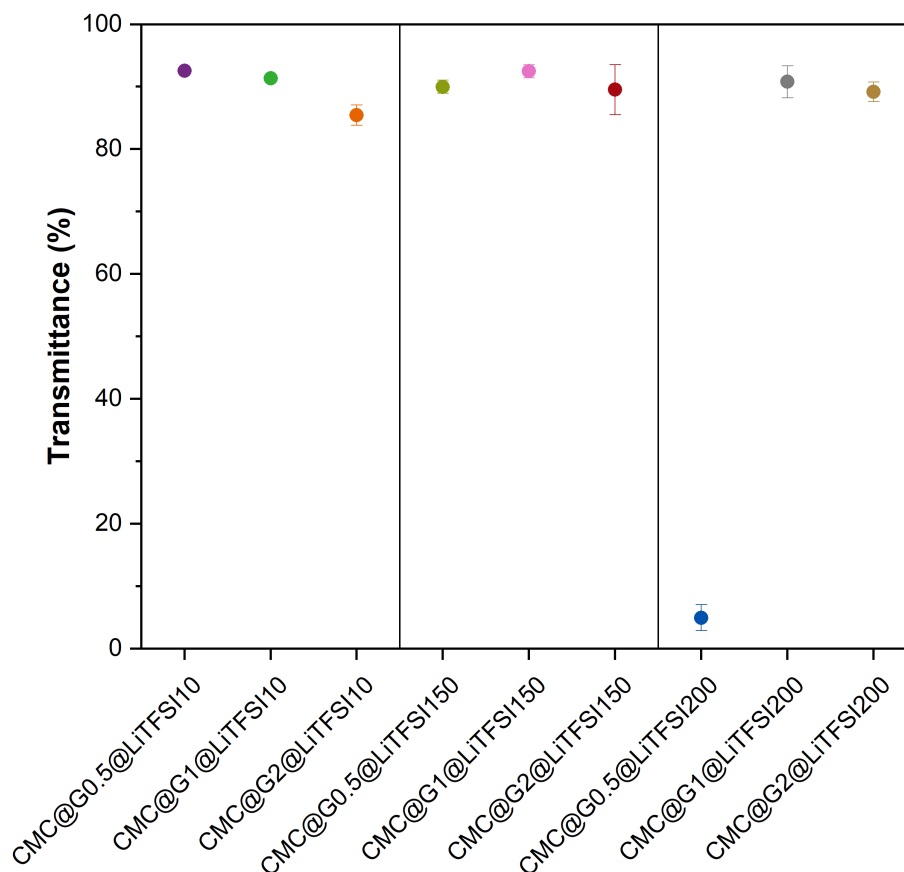


Figure 17. Transmittance at 550 nm for the selected SPEs, as a function of glycerol content at fixed LiTFSI concentrations of 10, 150 and 200%. Error bars represent standard deviations.

Shifting to the effect of glycerol variation on transmittance, represented in Figure 17, a clear synergistic effect of glycerol and LiTFSI doping can be observed. This is evidenced by the fact that the variation in glycerol content at different salt concentrations exhibits distinct trends, making it difficult to isolate the individual impact of glycerol. However, it can be noted that changes in glycerol concentration do not induce significant variations in transmittance values. What is particularly noteworthy is, once again, the effect of glycerol on the transparency of membranes containing 200% LiTFSI. At 1:0.5 NaCMC-to-glycerol ratio, the membrane has visible white patches, whereas at higher glycerol concentrations, it becomes fully transparent, as previously observed. This is supported by the transmittance values, which increase from $4.9 \pm 2.1\%$ at 1:0.5 NaCMC-to-glycerol ratio to $90.8 \pm 2.6\%$ at 1:1 and $89.2 \pm 1.6\%$ at 1:2 ratio. Finally, when analysing the effect of salt concentration at fixed glycerol contents, it becomes clear that at low plasticiser levels (1:0.5 NaCMC-to-glycerol ratio), the salt exhibits the same behaviour as observed in the absence of glycerol. However, at higher glycerol contents (1:1 and 1:2 ratios), the effect of the plasticiser becomes more evident, as membranes with a 1:2 NaCMC-to-glycerol ratio display the same transmittance profile as those with 1:1. This observation suggests that, from a NaCMC-to-glycerol ratio of

at least 1:1, glycerol counteracts the tendency for salt aggregation and thereby attenuates the impact of high salt content on optical clarity.^{55,149,150}

4.2.3. Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy

ATR-FTIR spectroscopy was conducted to investigate the chemical structure, molecular interactions and ionic association within the polymer films. Each SPE was analysed three times at different locations on the membrane surface to ensure result consistency and reproducibility. Since all spectra were identical, a single representative spectrum is displayed for each sample in Figure 18. Additionally, spectra of pure LiTFSI and glycerol, along with the pristine NaCMC membrane, were recorded to identify their characteristic vibrational bands, which are also summarised in the corresponding tables (Table 5–7). These reference spectra serve as a basis for comparison with the doped membranes, enabling the assessment of spectral modifications induced by the incorporation of salt and plasticiser.

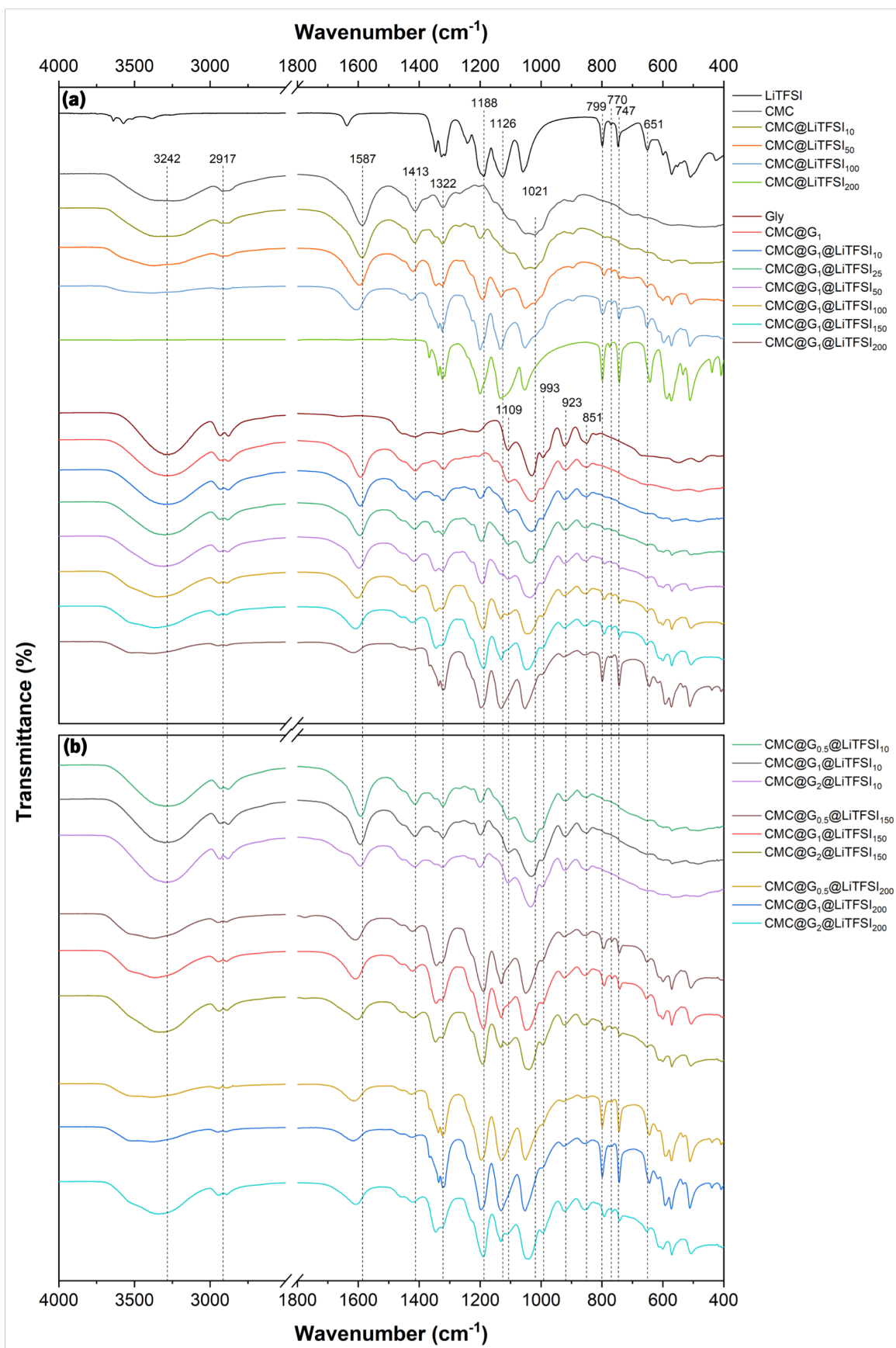


Figure 18. ATR-FTIR spectra of the synthesised SPEs: (a) variation in the LiTFSI concentrations in the absence of glycerol and at fixed 1:1 NaCMC-to-glycerol ratio; (b) variation in glycerol content at fixed salt concentrations of 10, 150 and 200%.

Beginning with the structural characterisation of the NaCMC matrix, whose main vibrational bands are presented in Table 5, the broad band at 3242 cm⁻¹ is assigned to the stretching vibration of hydroxyl (—OH) groups (ν —OH), indicative of extensive hydrogen bonding within the polymer structure.⁷² The absorption at 2917 cm⁻¹ corresponds to the stretching vibrations of C—H bonds (ν C—H).⁷² The carboxylate (—COO) groups present in the polysaccharide chain are identified by two distinct vibration bands: an asymmetric stretching mode (ν_a —COO) at 1587 cm⁻¹ and a symmetric stretching mode (ν_s —COO) at 1413 cm⁻¹.⁷² Additionally, a bending vibration of —OH groups (δ —OH) is observed at 1322 cm⁻¹.⁷² The presence of ether linkages (C—O—C) is confirmed by the vibration band at 1021 cm⁻¹, associated with their stretching modes (ν C—O—C).⁷²

Table 5. Characteristic vibrational modes of the NaCMC membrane (CMC) identified by ATR-FTIR spectroscopy.

Wavenumber (cm ⁻¹)	Vibrational mode	Assignment Description	Reference
3242	ν —OH	Stretching of hydroxyl groups	⁷²
2917	ν C—H	Stretching of C—H bonds	⁷²
1587	ν_a —COO	Asymmetric stretching of carboxylate groups	⁷²
1413	ν_s —COO	Symmetric stretching of carboxylate groups	⁷²
1322	δ —OH	Bending of hydroxyl groups	⁷²
1021	ν C—O—C	Stretching of ether linkages	⁷²

Moving on to the FTIR spectrum of pure LiTFSI, the main vibrational bands identified are listed in Table 6. The asymmetric stretching vibrations of the sulfonyl (—SO₂) group (ν_a —SO₂) appear at 1346 cm⁻¹ and 1327 cm⁻¹,¹⁵⁴ while the C—SO₂—N bending mode (δ C—SO₂—N) is detected at 1188 cm⁻¹.¹⁵⁵ The S=O bending vibration (δ S=O) is present at 1126 cm⁻¹,¹⁵⁵ and the S—N—S asymmetric stretching mode (ν_a S—N—S) is located at 1059 cm⁻¹ and 799 cm⁻¹.^{107,155} Peaks at 770 cm⁻¹ and 747 cm⁻¹ correspond to the trifluoromethyl (—CF₃) group asymmetric bending mode (δ_a —CF₃) and a combination of symmetric CF₃ bending and S—N—S stretching modes (δ_s —CF₃/ ν_s S—N—S), respectively.¹⁰⁷ Finally, the bending vibration of the S—N—S functional group (δ S—N—S) is found at 651 cm⁻¹.¹⁰⁷

Table 6. Characteristic vibrational modes of pure LiTFSI identified by ATR-FTIR spectroscopy.

Wavenumber (cm ⁻¹)	Vibrational mode	Assignment Description	Reference
1346	ν_a -SO ₂	Asymmetric stretching of sulfonyl groups	154
1327			155
1188	δ C-SO ₂ -N	Bending of C-SO ₂ -N linkages	155
1126	δ S=O	Bending of S=O bonds	155
1059	ν_s S-N-S	Asymmetric stretching of S-N-S groups	155
799			107
770	δ_a -CF ₃	Bending of trifluoromethyl groups	107
747	δ_a -CF ₃ / ν_s S-N-S	Bending of trifluoromethyl groups / Symmetric stretching of S-N-S groups	107
651	δ S-N-S	Bending of S-N-S groups	107

Upon the incorporation of LiTFSI into the matrix and with increasing salt concentration, the ν -OH at 3242 cm⁻¹ became broader, less intense, and progressively shifted to higher wavenumbers, reaching 3392 cm⁻¹ at 100% LiTFSI. At the highest salt concentration (200%), the band completely disappeared. The band at 1322 cm⁻¹ (δ -OH) exhibited a slight shift towards higher wavenumbers, attaining 1324 cm⁻¹, along with an increase in intensity. However, this band overlaps with the characteristic ν_a -SO₂ mode of LiTFSI at 1327 cm⁻¹, which may contribute to the observed spectral changes. Despite this, the behaviour observed for the band appears to support the trend observed for the 3242 cm⁻¹ band, indicating disruption of the hydrogen bonding network, potentially due to the coordination of Li⁺ ions with the oxygen atoms of -OH groups, as reported in similar hydroxyl-rich polymer systems.^{156,157} At 200% LiTFSI, the disappearance of the ν -OH band also suggests extensive aggregation or partial crystallisation of the salt, likely due to the saturation of the polymer matrix, confirming previous observations.^{54,55,85,148} The ν_a -COO⁻ and ν_s -COO⁻ bands at 1587 cm⁻¹ and 1413 cm⁻¹, respectively, exhibited a decrease in intensity alongside a progressive shift towards higher wavenumbers, reaching 1607 cm⁻¹ and 1425 cm⁻¹ at 100% LiTFSI. This behaviour suggests increasing coordination of the -COO⁻ groups with Li⁺ ions.^{83,158} At 200% LiTFSI, both bands disappeared, which may indicate complete coordination. This is consistent with the assumption that at this concentration, the polymer matrix reaches its maximum salt solubility, leading to salt crystallization or aggregation.^{54,55,85,148} The ν C-H mode at 2917 cm⁻¹ exhibited a progressive shift towards higher wavenumbers, reaching 2936 cm⁻¹, along with a reduction in intensity. At 200% LiTFSI, the band also

disappeared, further supporting the idea of salt agglomeration at this concentration. The $\nu\text{C—O—C}$ band at 1021 cm^{-1} , remained unchanged, suggesting that the ether functionalities do not partake significantly in coordination with the salt.¹⁵⁹ However, at 200% LiTFSI, once again the band disappeared, likely due to the explanation mentioned before. These observations confirm the biopolymer's ability to dissolve LiTFSI, with increasing coordination primarily through —OH and —COO^- functional groups up to 100% LiTFSI. Nevertheless, at 200%, the solubility limit is reached, leading to salt crystallization or aggregation. As a result, all CMC-related bands disappear, except for the one overlapping with a LiTFSI band.

Moreover, the characteristic peaks of LiTFSI at 1346 cm^{-1} ($\nu_{\text{a}}\text{—SO}_2$), 1327 cm^{-1} ($\nu_{\text{a}}\text{—SO}_2$), 1188 cm^{-1} ($\delta\text{C—SO}_2\text{—N}$), 1126 cm^{-1} ($\delta\text{S=O}$), 1059 cm^{-1} ($\nu_{\text{a}}\text{S—N—S}$), and 651 cm^{-1} ($\delta\text{S—N—S}$) emerged in the doped membranes, progressively increasing in intensity with higher salt concentrations. The $\delta\text{S=O}$ peak at 1126 cm^{-1} exhibited a slight progressive shift towards higher wavenumbers, reaching 1135 cm^{-1} at 100% LiTFSI, followed by a small decrease to 1133 cm^{-1} at 200% LiTFSI. Similarly, the $\delta\text{S—N—S}$ band at 651 cm^{-1} showed a slight shift towards higher wavenumbers, reaching 653 cm^{-1} at 100% LiTFSI. However, at 200%, it shifted back to lower wavenumbers, reaching 643 cm^{-1} . This behaviour suggests that LiTFSI initially interacts strongly with the polymer network at lower doping levels, but as the concentration increases, these interactions weaken due to salt aggregation, with the secondary shift at 200% indicating the formation of salt-rich domains or partial crystallisation within the matrix.^{54,55,85,148} Consistently with this trend, the $\nu_{\text{a}}\text{—SO}_2$ mode at 1346 cm^{-1} exhibited a consecutive shift towards lower wavenumbers, reaching 1337 cm^{-1} at 200% LiTFSI. This shift suggests enhanced TFSI— Li^+ coordination, weakening the S=O bonds and indicating structural reorganization, likely linked to salt-rich domain formation.^{54,160,161} Upon incorporation of 10% LiTFSI, the $\delta\text{C—SO}_2\text{—N}$ peak at 1188 cm^{-1} shifted to 1200 cm^{-1} and remained nearly unchanged with further increases in salt concentration. Additionally, the $\nu_{\text{a}}\text{S—N—S}$ peak at 1059 cm^{-1} experienced a shift towards lower wavenumbers, descending to 1053 cm^{-1} , yet this displacement did not follow a clear pattern with increasing LiTFSI content.

The spectral signature of glycerol, summarised in Table 7, exhibits an $\nu\text{—OH}$ vibration at 3306 cm^{-1} , along with $\nu\text{C—H}$ bands at 2933 cm^{-1} and 2879 cm^{-1} .⁷² The $\nu\text{C—O}$ bands appear at 1109 cm^{-1} and 1031 cm^{-1} .¹⁶² Additional peaks at 993 cm^{-1} , 923 cm^{-1} , and 851 cm^{-1} are associated with skeletal vibrations of the glycerol backbone (C—C).¹⁶²

Table 7. Characteristic vibrational modes of pure glycerol identified by ATR-FTIR spectroscopy.

Wavenumber (cm ⁻¹)	Vibrational mode	Assignment Description	Reference
3306	ν -OH	Stretching of hydroxyl groups	72
2933	ν C-H	Stretching of C-H bonds	72
2879			
1109	ν C-O	Stretching of C-O bonds	162
1031			
993	C-C	Skeletal vibrations of the carbon chain	162
923			
851			

With the addition of glycerol to the membrane, the ν -OH band at 3242 cm⁻¹ became narrower—due to the superposition of the glycerol band at 3306 cm⁻¹—and more intense, shifting to 3272 cm⁻¹. In parallel, the original ν C-H band of CMC at 2917 cm⁻¹ became overlapped by two contributions attributed to glycerol ν C-H vibrations, which appeared slightly shifted at 2931 and 2880 cm⁻¹ (from their typical positions at 2933 and 2879 cm⁻¹). These changes indicate the integration of glycerol within the polymeric matrix and, more specifically, the restructuring of the hydrogen bonding network.¹⁶³ In the wavenumber range of 4000 to 2000 cm⁻¹, the FTIR spectrum of CMC@G₁ closely resembled that of pure glycerol, further reinforcing the strong interaction between the two components.¹⁶⁴ The ν_s -COO⁻ and ν_a -COO⁻ bands at 1587 cm⁻¹ and 1413 cm⁻¹ exhibited a reduction in intensity, with the former shifting to 1592 cm⁻¹, which suggests an interaction with glycerol molecules that alters the hydrogen-bonding network within NaCMC.¹⁶⁵ Similarly, the δ -OH mode at 1322 cm⁻¹ remained at the same position but displayed a noticeable decrease in intensity. These spectral changes suggest the establishment of hydrogen bonding interactions between glycerol and NaCMC, primarily through -OH and -COO⁻ functional groups.¹⁶⁵ Additionally, new bands emerged at 1106, 1031, 997, 921, and 850 cm⁻¹, corresponding to glycerol vibrations, albeit with slightly reduced intensity. The peak at 1031 cm⁻¹ appears broader due to the overlap of two bands—one from NaCMC at 1021 cm⁻¹ and another from glycerol at 1031 cm⁻¹—both associated with the same vibrational mode (ν C-O). The behaviour observed confirms glycerol's role as a plasticising agent, as it disrupts the polymer's intermolecular forces, facilitating chain mobility.^{74,150}

To evaluate the effect of LiTFSI in membranes containing 1:1 NaCMC-to-glycerol ratio, the sample CMC@G₁ was used as the reference. Some spectral modifications observed in these membranes

resemble those previously reported for the salt variation in the pure NaCMC matrix, reinforcing the consistency of the LiTFSI interactions within the system. However, the presence of glycerol introduces specific changes in its coordination dynamics.

The peaks at 3272 (ν -OH), 2931 (ν C-H), 2880 (ν C-H), 1592 (ν_s -COO) and 1413 (ν_s -COO) cm^{-1} exhibit a progressive shift towards higher wavenumbers with increasing salt concentration, reaching 3392, 2950, 2893, 1615, and 1424 cm^{-1} , respectively. This behaviour is consistent with the coordination of Li^+ ions to -OH and -COO $^-$ groups, as previously observed in the glycerol-free system.^{157,160,165} Although these bands show a continuous decrease in intensity with increasing salt content, they remain detectable at 200% LiTFSI—unlike in the absence of glycerol, where they completely disappeared at this concentration. This persistence suggests that the presence of glycerol enhances the coordination capacity of the matrix, thereby delaying or preventing the saturation and subsequent disruption of the polymeric matrix observed in the absence of plasticiser.^{55,149,150} The ν C-O band at 1031 cm^{-1} broadens further due to additional overlap with the 1059 cm^{-1} ν_s S-N-S band. Its intensity increases with higher salt concentrations and a progressive shift towards higher wavenumbers is noted, reaching 1053 cm^{-1} and approaching the original position of the LiTFSI band. Notably, this band remains detectable even at 200% LiTFSI, indicating that the structural integrity of the membrane is maintained. The band at 1321 cm^{-1} , attributed to the overlap between the 1322 cm^{-1} δ -OH band of NaCMC and the 1327 cm^{-1} ν_a -SO $_2$ vibration of LiTFSI, exhibits a continuous increase in intensity with rising salt concentration. It also shows a progressive shift towards higher wavenumbers, reaching 1326 cm^{-1} , followed by a secondary shift back to lower wavenumbers at 200% LiTFSI, settling at 1323 cm^{-1} . Regarding the characteristic peaks of LiTFSI, the bands at 1346, 1188, and 1126 cm^{-1} display a consistent increase in intensity as the salt concentration increases. The ν_a -SO $_2$ band at 1347 cm^{-1} remains stable up to 50% LiTFSI but then undergoes a progressive shift to lower wavenumbers, reaching 1336 cm^{-1} at 200%. The δ C-SO $_2$ -N band at 1199 cm^{-1} shifts slightly to 1189 cm^{-1} and subsequently to 1197 cm^{-1} at 200%, indicating a secondary shift. Meanwhile, the δ S=O band at 1126 cm^{-1} becomes detectable only from 25% LiTFSI onwards and exhibits a progressive shift to lower wavenumbers, reaching 1131 cm^{-1} at the highest salt concentration. The progressive shift of these TFSI related bands towards lower wavenumbers is typically associated with increasing coordination between the anion and Li^+ cations, as such interactions weaken internal TFSI bonds and reduce vibrational frequencies. The occurrence of secondary shifts at 200% LiTFSI further supports this interpretation, suggesting the onset of salt aggregation or early-stage crystallisation phenomena at high salt concentrations.^{160,166} Furthermore, the glycerol-associated peaks generally exhibited a slight shift towards higher wavenumbers and a gradual reduction in intensity with increasing

salt concentration. These spectral changes suggest that the —OH groups of glycerol progressively engage in coordination with Li⁺ ions, which weakens the original hydrogen-bonding network involving glycerol.¹⁶⁷ An exception to this behaviour includes the peak at 997 cm⁻¹ from the skeletal vibrations of the glycerol backbone, which remains unchanged in both position and intensity throughout the entire salt range. Another notable exception is the νC—O band at 1106 cm⁻¹, which also shifts to higher wavenumbers, attaining 1111 cm⁻¹, but progressively decreases in intensity until nearly disappearing at salt concentrations equal to or above 150%, suggesting that LiTFSI not only interacts with the NaCMC matrix but also with specific functional groups within the glycerol structure.¹⁶⁷

The analysis of glycerol variation reveals a slight increase in the intensity of the ν—OH band and the νC—H band at 2917 cm⁻¹ as the plasticiser concentration increases. Similarly, the bands at 993, 923, and 851 cm⁻¹, associated with skeletal vibrations of the glycerol backbone, also intensify, further supporting the progressive incorporation of glycerol within the polymeric network. The νC—O peak at 1109 cm⁻¹, characteristic of glycerol, is present at all concentrations when LiTFSI is at 10%, with its intensity increasing alongside glycerol content. Notably, at this salt concentration, the δS=O peak at 1126 cm⁻¹ is absent, suggesting that the polymer-glycerol interactions predominate at lower salt concentrations, potentially limiting the extent of LiTFSI coordination.¹⁶⁸ However, at higher salt concentrations (150 and 200%), the spectral behaviour shifts: at 1:0.5 and 1:1 NaCMC-to-glycerol ratio, only the δS=O peak at 1126 cm⁻¹ is observed, whereas at 1:2 ratio, both peaks (1109 cm⁻¹ and 1126 cm⁻¹) coexist. This suggests that at lower glycerol content, LiTFSI interacts more strongly with the polymer. As the glycerol concentration increases, competition for coordination sites within the matrix may occur, allowing both glycerol and LiTFSI to be spectrally distinguishable.¹⁶⁸ Furthermore, in the 1:2 ratio and 200% LiTFSI sample, the band incorporating the ν_a—SO₂ (1346 cm⁻¹) and δ—OH (1322 cm⁻¹) modes broadens, and its shape reverts to that observed in samples with lower salt concentrations. This confirms the previously stated assumption that glycerol disrupts salt-rich domains, promoting better salt dispersion within the matrix and mitigating excessive crystallisation.^{55,149,150} Apart from these differences, the spectral changes due to salt variation follow the same trends previously discussed.

In this study, the TFSI⁻ anion was employed as a spectroscopic probe to investigate ionic association within the electrolyte system. The three characteristic vibrational bands of TFSI, previously reported, are clearly identified in Figure 19 at 790 (ν_aS—N—S), 766 (δ_aCF₃), and 741 (δ_sCF₃/ν_sS—N—S) cm⁻¹. Prior studies have shown that the ν_aS—N—S and δ_sCF₃/ν_sS—N—S bands shift depending on the degree of ionic association, with higher wavenumber bands typically associated with contact ion pairs, and lower wavenumber bands corresponding to free TFSI⁻ anions.^{107,169}

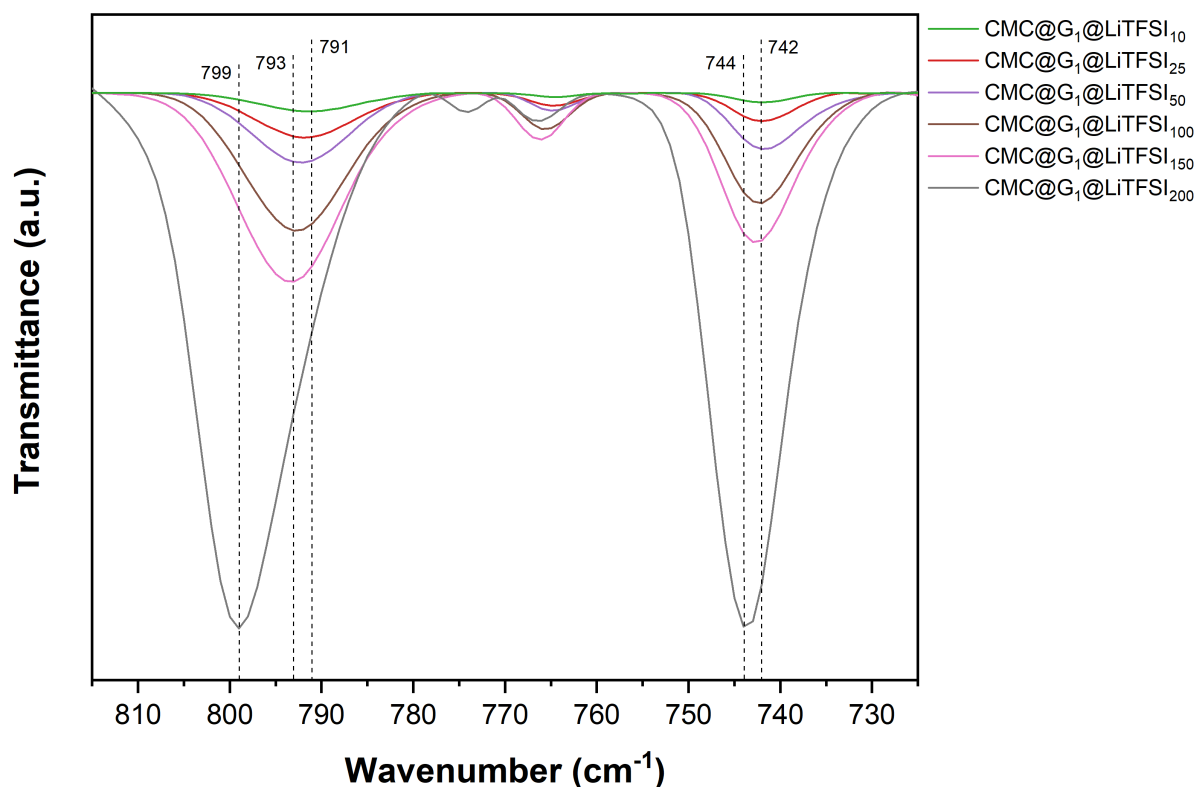


Figure 19. Overlaid ATR-FTIR spectra of selected SPEs (730-810 cm^{-1}) as a function of LiTFSI concentration at fixed 1:1 NaCMC-to-glycerol ratio.

To evaluate the effect of salt concentration on ionic association, the IR spectra reveal a systematic shift of these bands towards higher wavenumbers with rising LiTFSI content. Specifically, the left-side band shifts from 791 cm^{-1} at 10% salt to 793 cm^{-1} at 150% and further to 799 cm^{-1} at 200%, while the right-side band shows a smaller shift, moving from 742 cm^{-1} at 10% to 744 cm^{-1} at 200% LiTFSI. This trend strongly indicates a gradual enhancement of ionic association, as the relative abundance of free TFSI⁻ anions decreases in favour of contact ion pairs and possibly higher-order aggregates.^{107,169} In parallel, the gradual increase in band intensity also supports the formation of more structured ionic domains within the matrix. This behaviour is expected at higher salt concentrations, where the density of both cations and anions rises, enhancing the probability of ion-ion interactions. The resulting overcrowded environment promotes the formation of contact ion pairs and, ultimately, the emergence of larger ionic clusters. These observations are consistent with findings from FTIR and complementary analytical techniques, reinforcing the hypothesis that, at 200% LiTFSI, salt aggregation or clustering phenomena are taking place.

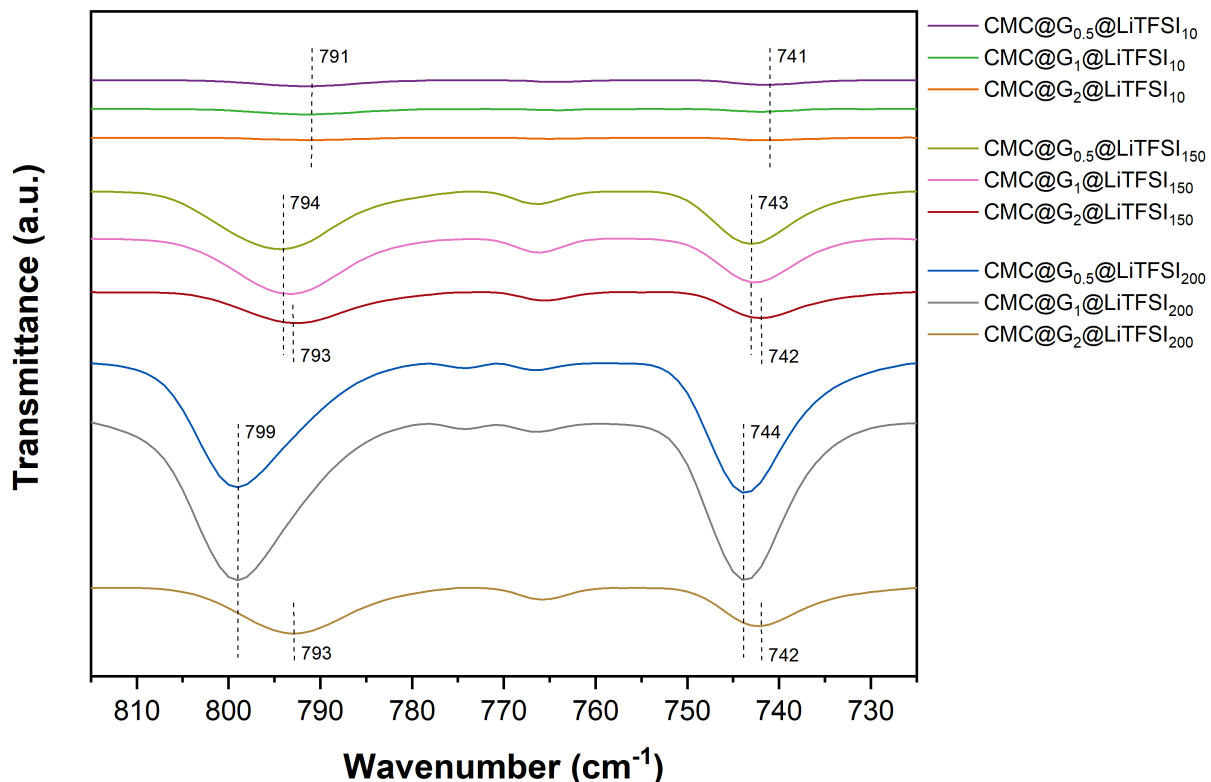


Figure 20. Overlaid ATR-FTIR spectra of selected SPEs (730-810 cm^{-1}) as a function of glycerol content at fixed LiTFSI concentrations of 10, 150 and 200%.

The influence of plasticiser content was examined across different salt concentrations in the Figure 20 spectra. At 10% LiTFSI, the characteristic $\nu_s\text{S}-\text{N}-\text{S}$ and $\delta_s\text{CF}_3/\nu_s\text{S}-\text{N}-\text{S}$ vibrational bands of TFSI remain centred at 791 and 744 cm^{-1} , respectively, regardless of glycerol content. However, at 150% LiTFSI, a slight and progressive shift towards lower wavenumbers is observed as the plasticiser concentration increases, with the bands shifting from 794 and 743 cm^{-1} , at 1:0.5 NaCMC-to-glycerol ratio, to 793 and 742 cm^{-1} at 1:2 ratio. At 200% LiTFSI, the band positions remain stable at 799 and 744 cm^{-1} for 1:0.5 and 1:1 NaCMC-to-glycerol ratio, but a marked shift occurs at a 1:2 ratio, where the bands shift down to 793 and 742 cm^{-1} . These shifts to lower wavenumbers are typically associated with an increased population of free TFSI anions and, consequently, a reduction in ionic association.^{107,169} The pronounced change observed under these conditions suggests that higher glycerol content may disrupt salt aggregation by favouring ion pair dissociation and enhancing the presence of uncoordinated anions within the matrix. Across all salt concentrations—and particularly at 200%—band intensities remained relatively stable between 1:0.5 and 1:1 ratios but decreased markedly at 1:2. This intensity drop further supports the hypothesis that excess glycerol interferes with ionic interactions, reducing the extent of ion pairing.

4.2.4. Electrochemical Impedance Spectroscopy

EIS was employed to evaluate the ionic conductivities of the synthesised SPEs. This analysis was conducted in two stages. Initially, EIS measurements were performed at room temperature shortly after the drying process of the samples was completed. Subsequently, new measurements were conducted to include temperature variations. This approach was adopted because it enabled the selection of a moderately sized batch of samples for further advanced characterisation outside the University of Minho, as such techniques were not conducted in-house. The selection process was based on the ionic conductivity values of the membranes at room temperature, as this property is critical for electrolytes — particularly in view of the intended application. Without sufficient ionic conductivity, the SPEs cannot fulfil their fundamental role of transporting ions between electrodes.

The ionic conductivity values for the eighteen synthesised samples at room temperature are presented in Figure 21.

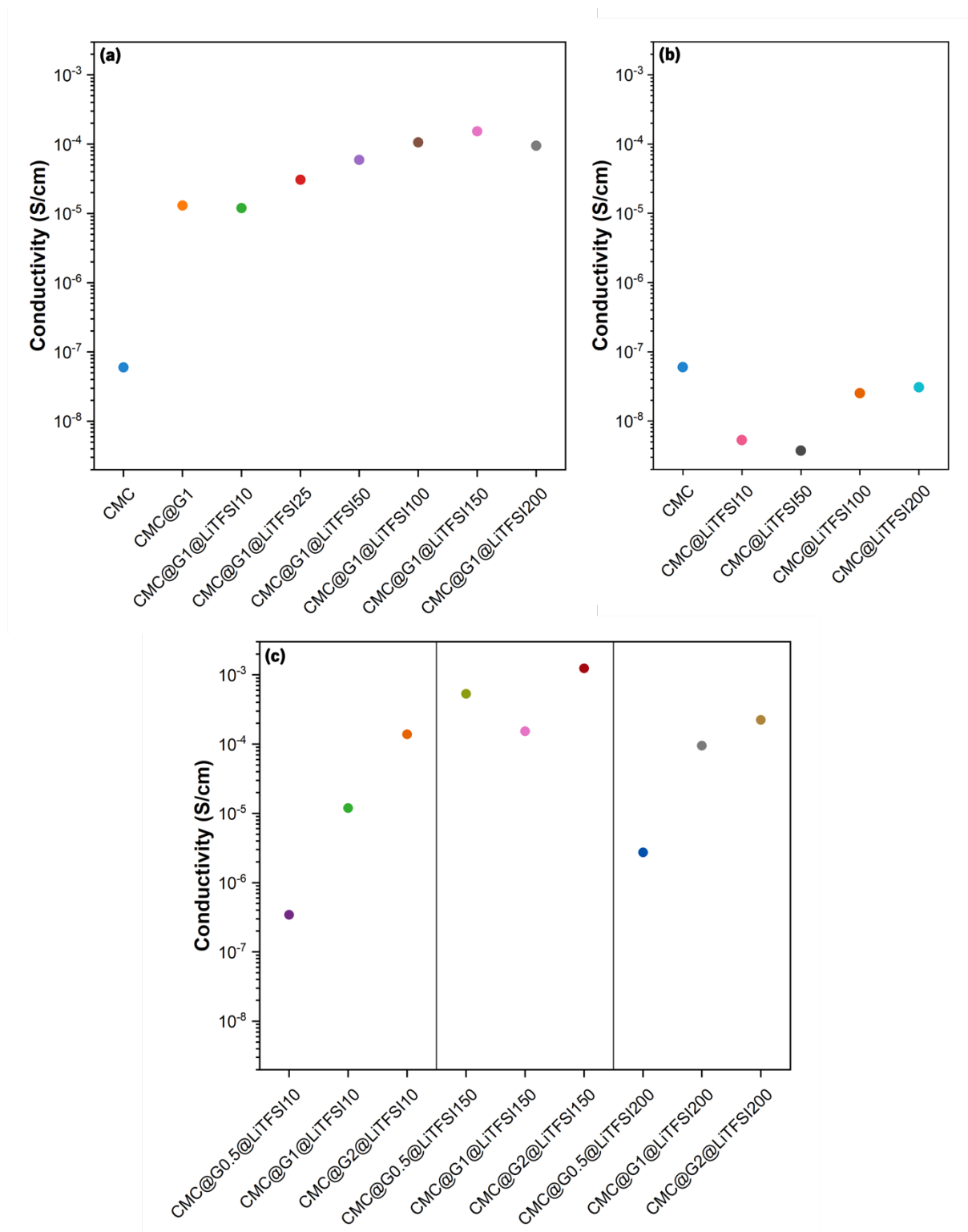


Figure 21. Ionic conductivity of the synthesised SPEs at room temperature, measured by EIS: (a) variation in LiTFSI concentration at fixed 1:1 NaCMC-to-glycerol ratio; (b) variation in LiTFSI concentration in the absence of glycerol; (c) variation in glycerol content at fixed salt concentrations of 10, 150 and 200%.

Based on these results, it was therefore possible to proceed with the selection of the samples. The membranes doped solely with LiTFSI were excluded from the group of handpicked samples since none

of them reached the minimum conductivity threshold value of 10^{-5} S/cm, required for practical use in electrochemical devices, such as LIBs.¹⁰⁷ Additionally, the CMC@G_{0.5}@LiTFSI₂₀₀ and CMC@G₂@LiTFSI₂₀₀ membranes were also excluded due to a consistent decline in conductivity values compared to their analogues of 150% concentration, indicating that the salt incorporation limit had been exceeded, supporting what can be seen in Figure 21(a). Thus, the twelve samples selected for further in-depth characterisation were: CMC; CMC@G₁; CMC@G₁@LiTFSI₁₀; CMC@G₁@LiTFSI₂₅; CMC@G₁@LiTFSI₅₀; CMC@G₁@LiTFSI₁₀₀; CMC@G₁@LiTFSI₁₅₀; CMC@G₁@LiTFSI₂₀₀; CMC@G_{0.5}@LiTFSI₁₀; CMC@G₂@LiTFSI₁₀; CMC@G_{0.5}@LiTFSI₁₅₀ and CMC@G₂@LiTFSI₁₅₀.

Although the subsequent analyses will focus exclusively on the twelve selected SPEs, the discussion presented here will continue to include data from all eighteen samples to provide a complete and unbiased overview of the initial findings. Additionally, from this point onwards, it will focus on the data obtained from the second set of measurements under varying temperature conditions.

The Nyquist plots resulting from these EIS measurements at room temperature were used to determine the bulk resistance (R_b) of the membranes, a crucial parameter for calculating ionic conductivity. Each Nyquist plot was analysed by identifying the intersection of the semicircle (or the high-frequency region) with the real axis (Z'), corresponding to the R_b value. The ionic conductivity (σ , S/cm) was then calculated using Equation 9.¹⁵⁰

$$\sigma = \frac{d}{R_b A} \quad \text{Equation 9}$$

where d is the thickness of the membranes (cm), R_b is the bulk resistance obtained from the Nyquist plot (Ω), and A is the electrode-electrolyte contact area (cm²).

Typically, the Nyquist plots of SPEs exhibit two distinct regions: an incomplete semicircle at high frequencies corresponding to charge transfer resistance, and a straight line (spur) at low frequencies associated with ionic diffusion. However, the majority of the plots, especially the ones referring to the most conductive samples, only reveal a straight line, indicating that the conductivity is predominantly governed by ionic transport.¹⁵¹

Moreover, the Nyquist plots for the pure NaCMC membrane and those doped exclusively with LiTFSI exhibited highly scattered and non-converging data at numerous temperatures, making it impossible to accurately determine the bulk resistance (R_b) and preventing their study under different temperature conditions. In the control sample (CMC) case, this outcome is anticipated, as the material is inherently non-conductive owing to the absence of sufficient free charge carriers within the matrix and the restricted

movement of its chains. For the SPEs composed solely of NaCMC and LiTFSI, this behaviour can be explained by the rigid nature of the host matrix that results in constrained mobility of the polymer chains, which is a fundamental part of the ion-hopping mechanism responsible for ionic transport in such systems, rendering the conductivity negligible. In this mechanism, Li^+ ions, released by the dissociation of LiTFSI as it dissolves into the matrix, jump to neighbouring coordination sites within the polymer structure.^{54,55} Due to these limitations, it was only possible to calculate the ionic conductivities of thirteen out of the eighteen synthesised samples. These values were subsequently plotted against temperature in Arrhenius plots, which are presented in Figure 22.

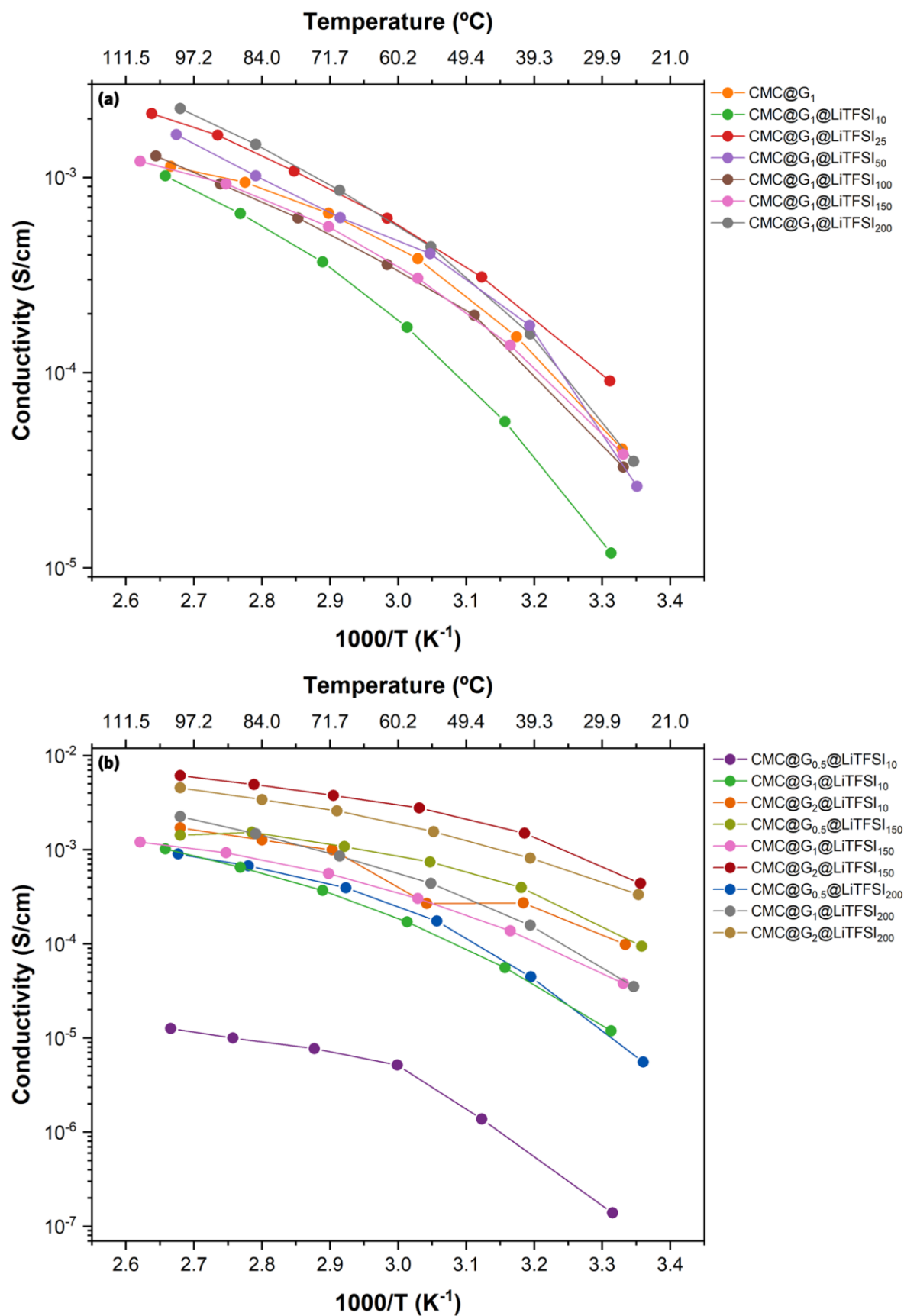


Figure 22. Arrhenius plots of ionic conductivity for the synthesised SPEs: (a) variation in LiTFSI concentration at fixed 1:1 NaCMC-to-glycerol ratio; (b) variation in glycerol content at fixed salt concentrations of 10, 150 and 200%.

The data presented indicate that the conductivity of the membranes follows a VTF-like behaviour, rather than a typical Arrhenius trend. This is evidenced by the non-linear dependence of conductivity on the reciprocal of temperature, confirming that ion transport in these membranes is governed by an ion-hopping mechanism coupled to the segmental dynamics of the polymer chains. An exception to this general trend is observed for the sample CMC@G₂@LiTFSI₁₀, which shows a drop at approximately 55.6 °C before resuming the expected VTF-like behaviour at higher temperatures. According to the literature, an increase in temperature enhances segmental motion and correspondingly increases the fraction of free volume within biopolymer electrolyte systems. This combined effect facilitates faster ionic movement and creates pathways for ion transport, thereby significantly improving conductivity.⁵⁵

Figure 22(a) shows that increasing the salt concentration does not lead to significant variations in ionic conductivity among the samples at room temperature, as most values remain within the same order of magnitude (10^{-5} S/cm). However, when examining Figure 23, which depicts a closer look at these ionic conductivities, a general trend can be identified.

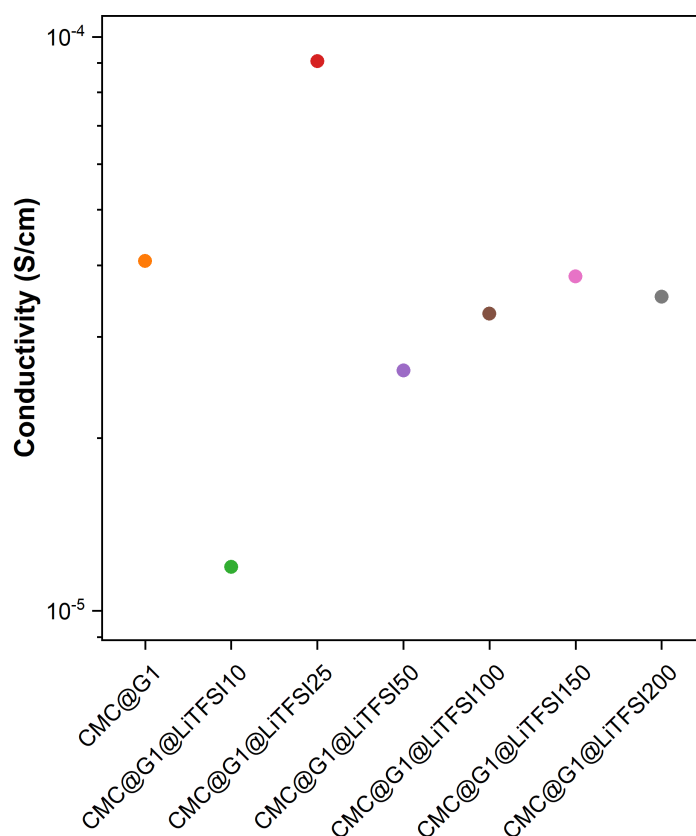


Figure 23. Ionic conductivity of selected SPEs at room temperature, measured by EIS, as a function of LiTFSI concentration at fixed 1:1 NaCMC-to-glycerol ratio.

It is worth noting that slight fluctuations can be detected by comparing these results with the ones presented before (Figure 21(a)). Although the differences between the two obtained ionic conductivity for each sample are not substantial, two specific values, corresponding to CMC@G₁ and CMC@G₁@LiTFSI₂₅, stand out in the later plot for having higher conductivities than expected. In the earlier analysis, their values aligned closely with the expected effect of LiTFSI on ionic transport within SPEs. This suggests that they may be anomalous and should be disregarded. Despite efforts to control humidity, such as storing samples in a desiccator, discrepancies in the obtained values, particularly for these samples, are likely due to residual moisture, which may have affected ion mobility.

As the salt concentration increases, ionic conductivity also slightly increases, with the exception discussed earlier, before reaching a maximum of 3.82×10^{-5} S/cm at 150%. Beyond this point, conductivity decreases. This behaviour aligns with the typical trend of polymer-salt complexes, where an increase in the number of charge carriers enhances the SPE's conductivity. On the other hand, beyond an optimal concentration, this increase leads to an overload of ions, obstructing ionic pathways. As charge carriers become too closely packed, recombination is facilitated, thereby reducing the density of free ions available for transport.^{85,150,151,170} In addition, some authors,^{171,172} have attributed the improvement of the conductivity to a reduction in the crystallinity of the NaCMC structure, which can be explained by the physical interaction occurring between the polymer and the ions.⁸⁵ However, at 200% salt concentration, the critical limit has been surpassed and it may instead promote localised crystallinity due to the surplus of ions, further hindering ionic transport,⁸⁵ as it is traditionally established that effective conductivity primarily occurs within the amorphous regions of the polymeric matrix as a result of lower energy barriers.¹⁷³ To further improve the ionic conductivity of SPEs, the enhancement of the amorphous content is pursued through dopants;⁸² in this case, glycerol was used.

Returning to Figure 22(a) and evaluating now the conductivity values across the entire temperature range, the CMC@G₁@LiTFSI₁₀ sample consistently shows low ionic conductivity, with values extending from 1.19×10^{-5} S/cm at 27.3 °C to 1.14×10^{-3} S/cm at 102.0 °C. This result is anticipated because a low salt concentration is insufficient to produce adequate ionic density, resulting in a limited number of free ions.^{150,151} In addition, at 200% salt concentration (CMC@G₁@LiTFSI₂₀₀), the ionic conductivity is notably reduced at lower temperatures, 3.52×10^{-5} S/cm, as previously explained. With increasing temperature, this sample exhibits a significant rise in conductivity, achieving the highest observed value of 2.26×10^{-3} S/cm.

Turning now to Figure 22(b) and starting by analysing the ionic conductivities of the SPEs at room temperature, illustrated in Figure 24, an increase in the amount of glycerol consistently leads to an

enhancement in ionic conductivity, irrespective of the salt concentration. A significant effect is observed, considering that, with the lowest LiTFSI concentration of 10%, the conductivity can increase from 1.39×10^{-7} S/cm (CMC@G_{0.5}@LiTFSI₁₀) to 9.87×10^{-5} S/cm (CMC@G₂@LiTFSI₁₀). This observation reinforces the critical role of glycerol in enhancing the system's conductivity. As a plasticiser, glycerol increases the flexibility of the polymer matrix and promotes the dissociation of LiTFSI.^{55,150} This, in turn, facilitates the ion-hopping mechanism, thereby improving ionic mobility within the material.⁵⁴ These findings further support the VTF-type conduction behaviour observed in the membranes. Furthermore, the inclusion of glycerol establishes alternative ionic pathways for the migration of free ions in the plasticizer-rich phase and boosts the amorphous nature of the samples, which also plays a significant role in contributing to conductivity enhancement.^{55,150,170}

The effect of LiTFSI concentration in the SPEs with 1:0.5 and 1:2 NaCMC-to-glycerol ratio mirrors the behaviour observed in the 1:1 (Figure 23), where a conductivity threshold is reached at 150% salt concentration.

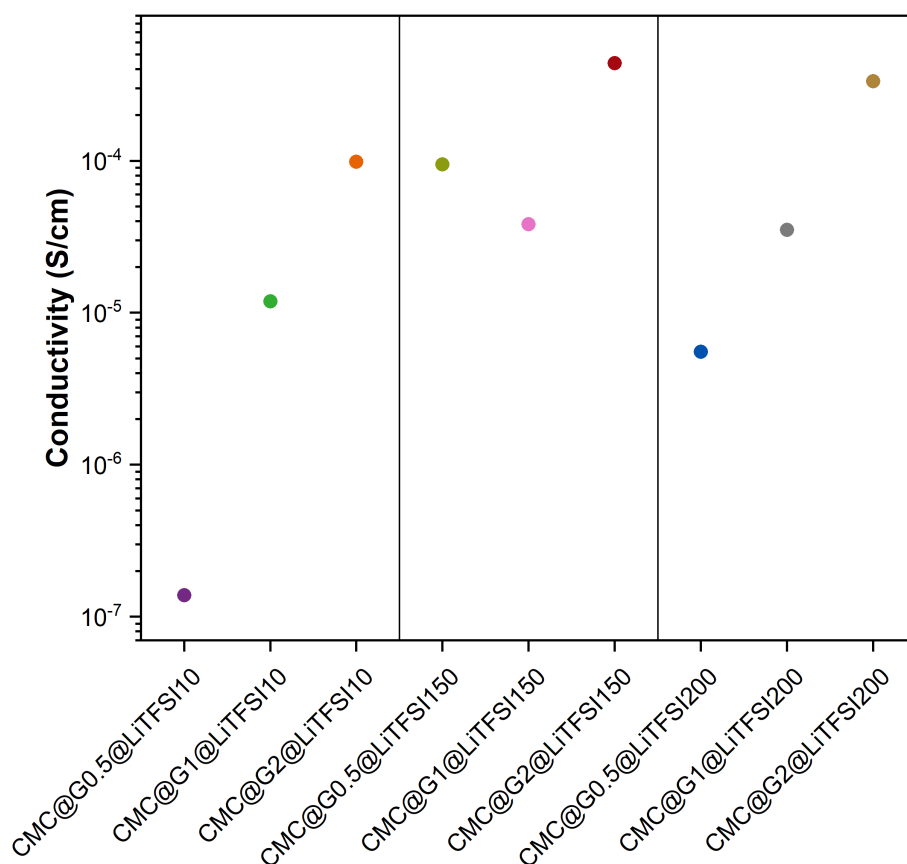


Figure 24. Ionic conductivity of selected SPEs at room temperature, measured by EIS, as a function of glycerol content at fixed LiTFSI concentrations of 10, 150 and 200%

The sample exhibiting the highest ionic conductivity values across all temperatures is CMC@G₂@LiTFSI₁₅₀, ranging from 4.40×10^{-4} to 6.14×10^{-3} S/cm at 24.9 and 100.1 °C, respectively. This highlights the synergistic effect of glycerol and LiTFSI in enhancing the system's overall ionic transport.

The sample with the second-highest ionic conductivities is CMC@G₂@LiTFSI₂₀₀, spanning from 3.35×10^{-4} S/cm at 25.1 °C to 4.56×10^{-3} S/cm at 100.0 °C. The observed increase in conductivity at 200% salt concentration with the addition of glycerol, further validates the earlier discussions on the macroscopic analysis of the SPEs. Glycerol promotes the dissociation of LiTFSI crystals or agglomerations within the NaCMC matrix, thereby improving ionic mobility.^{55,150} However, despite this improvement, the conductivity remains slightly lower than that of the 150% salt concentration sample.^{85,150,151}

The CMC@G_{0.5}@LiTFSI₁₀ SPE stands out by displaying significantly lower ionic conductivity across all measured temperatures. This outcome is anticipated, as the reduced ionic mobility results from the limited motion of the polymer chains and the insufficient availability of charge carriers.^{55,150}

In summary, the findings discussed above highlight that considering only ionic conductivity, the most promising SPE for the intended application appears to be CMC@G₂@LiTFSI₁₅₀, exhibiting a conductivity of 4.40×10^{-4} S/cm at room temperature. However, while ionic conductivity is indeed the critical property for this purpose, it is not the sole factor that must be considered. Another essential parameter for SPEs is their mechanical robustness. From the initial analysis, this film was observed to be extremely flexible and challenging to handle, which raises concerns regarding its suitability for battery integration. Further insights into this issue will be explored in the tensile test section. Thus, if a sample from films with 1:1 NaCMC-to-glycerol ratio were to be chosen, where the glycerol content appears more balanced—since it increases the system's conductivity compared to 1:0.5 membranes without compromising its ease of handling and potentially its mechanical strength—then CMC@G₁@LiTFSI₅₀ could be the most appropriate election. Neglecting the deviant values, this SPE presents the overall highest ionic conductivities (2.62×10^{-5} S/cm). At this level, the ionic density is sufficient, and no significant ion aggregation effects are detected, achieving an optimal equilibrium between performance and material consumption where minimising resource use is preferable.

4.2.5. X-Ray Diffraction

XRD was conducted to assess the crystalline structure and phase composition of the samples. Due to time constraints, only ten out of the twelve samples analysed in the other characterisation techniques were successfully measured. Despite this limitation, the selected SPEs provide a representative overview

of the structural characteristics of the studied films. Figure 25 and Figure 26 present the diffraction patterns obtained during the analysis. Since it was not possible to perform an XRD analysis of the LiTFSI salt used in this study, reference data from the literature was consulted.

In general, both diffractograms indicate that the synthesised SPEs are mainly amorphous. This finding is consistent with previous studies on CMC films.^{174,175}

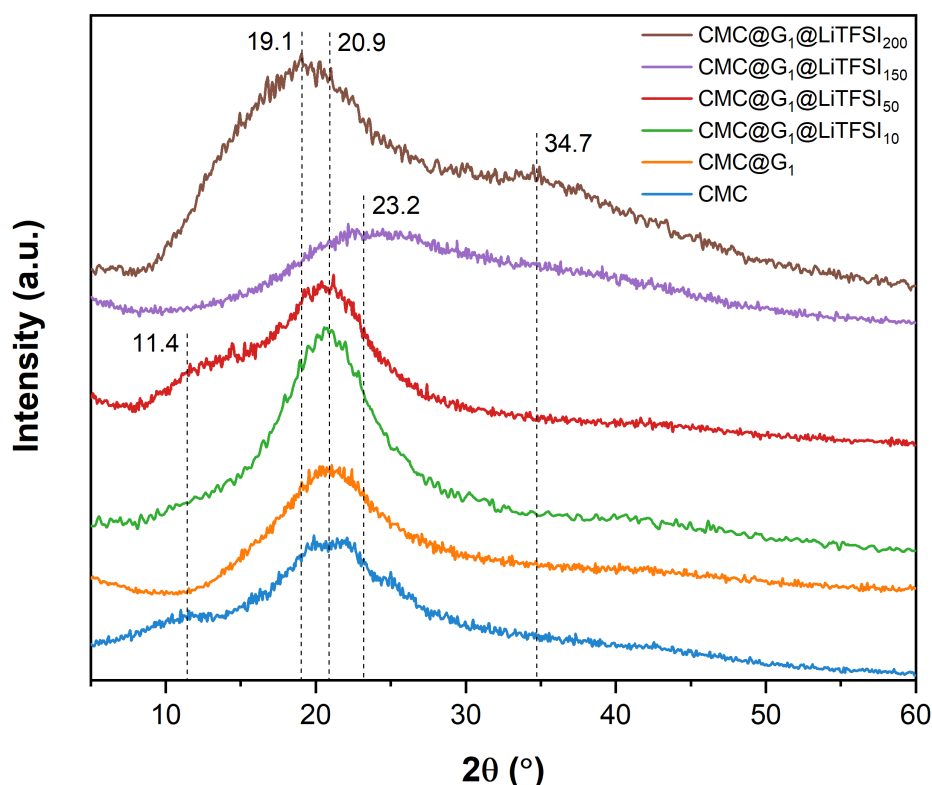


Figure 25. XRD patterns of selected SPEs, as a function of LiTFSI concentration at fixed 1:1 NaCMC-to-glycerol ratio.

A detailed inspection of Figure 25 shows the crystalline pattern of the pristine matrix with two broad peaks centred at Bragg angles of $2\theta = 11.4^\circ$ and 20.9° , corresponding to (110) and (200) lattice plane of reflection.¹⁷⁶⁻¹⁷⁹ (177–180) These are characteristic of the NaCMC structure, and arise from intramolecular and intermolecular hydrogen bonding, which contributes to its semi-ordered arrangement.^{83,85,180} The lower-angle peak (11.4°), upon doping the matrix with glycerol, disappears, suggesting a partial desintegration of the polymer's crystalline structure. This effect is observed in most samples and can be attributed to the electrostatic interactions between the dopants and NaCMC, leading to disruption of the hydrogen bonding network within the polymer chains, thereby hindering the arrangement of ordered phases and therefore reducing the crystallinity,^{83,157,160,163,165} however, the peak reappears in the CMC@G₁@LiTFSI₅₀ and

CMC@G_{0.5}@LiTFSI₁₀ samples. In the former, no significant shift is detected, while in the latter, the peak is displaced to a higher 2θ value of 14.0° , suggesting a structural compression effect, possibly due to reduced plasticisation and the strengthening of electrostatic interactions between LiTFSI and the matrix.⁸² The second peak (20.9°), which represents the biopolymer backbone, remains present in all samples, as expected. Moreover, its Bragg angle, intensity, and width are unchanged upon glycerol incorporation. With the addition of LiTFSI, although variations in intensity and peak width are observed across the samples, no clear trend is established with increasing salt concentration. However, the peak exhibits the highest intensity at 200%, which is anticipated, as the crystallisation and/or agglomeration of LiTFSI at this concentration caused a reduction in ion conductivity. This interpretation is further supported by FTIR analysis, which confirmed structural changes compatible with salt aggregation, in agreement with the trends suggested by the previous characterisation techniques. This structural rearrangement is further evidenced by the emergence of a new peak at a Bragg 2θ value of 34.7° , which corresponds to a reference peak of the crystalline LiTFSI, as identified in a published XRD pattern of the salt.¹⁸¹ Notably, no other characteristic peaks of crystalline LiTFSI are observed in the remaining SPEs, confirming the complete dissolution of the salt within the polymer matrix and thus the formation of ion-dipole complexes.¹⁸² Furthermore, up to 50%, the Bragg angle associated with the polymer remains unchanged. Beyond this concentration, a shift occurs towards higher diffraction angles (23.2°) at 150% LiTFSI, suggesting a contraction of the polymeric structure due to strong electrostatic interactions between Li⁺ ions and the functional groups of the matrix.^{83,157,160,163,165} However, at 200% LiTFSI, a shift towards lower angles (19.1°) is observed, which may indicate an expansion of the polymer network due to excessive salt incorporation, leading to partial crystallisation or agglomeration, thereby increasing the intermolecular spacing.^{54,82}

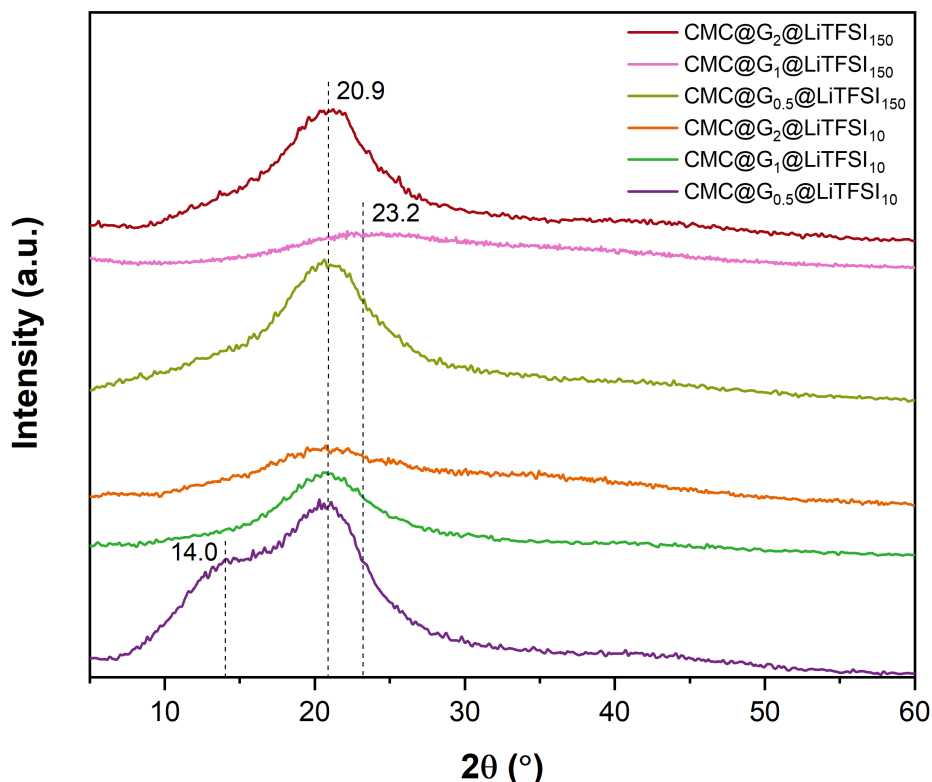


Figure 26. XRD patterns of selected SPEs, as a function of glycerol content at fixed LiTFSI concentrations of 10, 150 and 200%.

Moving on to the analysis of Figure 26, and first considering the peaks associated with the NaCMC backbone, it is evident that both remain present in the CMC@G_{0.5}@LiTFSI₁₀ sample, as discussed earlier. In the remaining membranes within this diffractogram, the same behaviour observed previously occurs—the leftmost peak disappears, likely due to the same structural modifications. Examining the peak at $2\theta = 20.9^\circ$, variations in glycerol concentration influence the crystalline structure of the sample, as evidenced by changes in relative intensity and peak broadening/narrowing. At a 10% LiTFSI concentration, the expected effect of glycerol, as indicated by our results and previously reported in the literature, is clearly observable. As its concentration increases, a progressive weakening of the peak intensity occurs, indicating a rise in amorphicity.¹⁵⁰ This increase is associated with the disruption of the network of hydrogen bonds in the polymer backbone, as previously discussed.^{83,85} However, this trend is no longer evident at 150% LiTFSI, suggesting that the effect of the salt surpasses that of the glycerol, likely dominating the structural modifications within the system. Additionally, The Bragg angle remains unchanged, except in the case of CMC@G₁@LiTFSI₁₅₀, which was also discussed in the previous paragraph.

4.2.6. Polarised Optical Microscopy

POM was utilized to investigate the morphological characteristics of the films. The obtained micrographs, illustrated in Figure 27 and Figure 28, confirm the predominantly amorphous nature of the samples, referred to in the previous section.



Figure 27. POM micrographs of selected SPEs, as a function of LiTFSI concentration at fixed 1:1 NaCMC-to-glycerol ratio, acquired at 4× and 10× magnifications.



Figure 28. POM micrographs of selected SPEs, as a function of glycerol content at fixed LiTFSI concentrations of 10 and 150%, acquired at 4× and 10× magnifications.

Moreover, upon doping the matrix with LiTFSI and glycerol, birefringent domains emerge, suggesting the presence of submicrometric anisotropy. These entities are attributed to the formation of crystalline phases induced by ionic interactions between the dopants and the polymeric matrix, as typically observed in SPEs.^{183,184} Such findings are consistent with the overall structural behaviour identified throughout this study.

4.2.7. Scanning Electron Microscopy

SEM was employed to investigate the samples' surface morphology and structural features. Figure 29 and Figure 30 present the micrographs captured during the analysis.

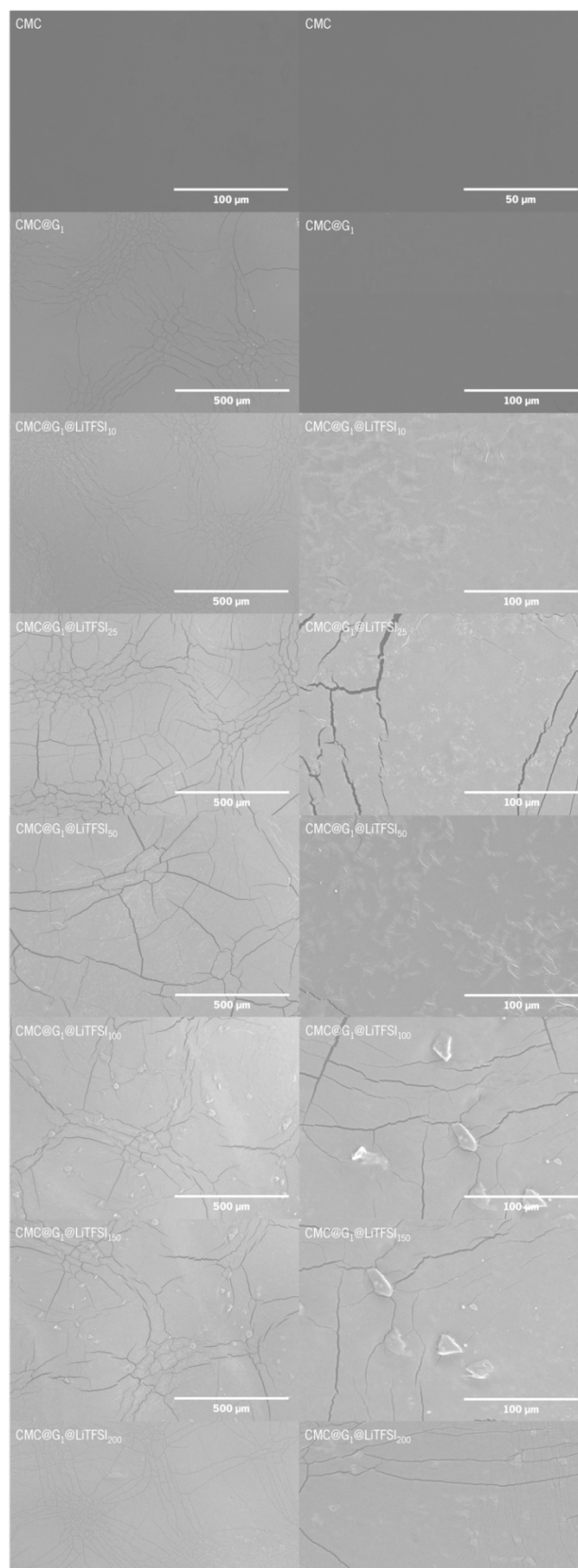


Figure 29. SEM micrographs of selected SPEs, as a function of LiTFSI concentrations at fixed 1:1 NaCMC-to-glycerol ratio, acquired at 100× and 500× magnifications.

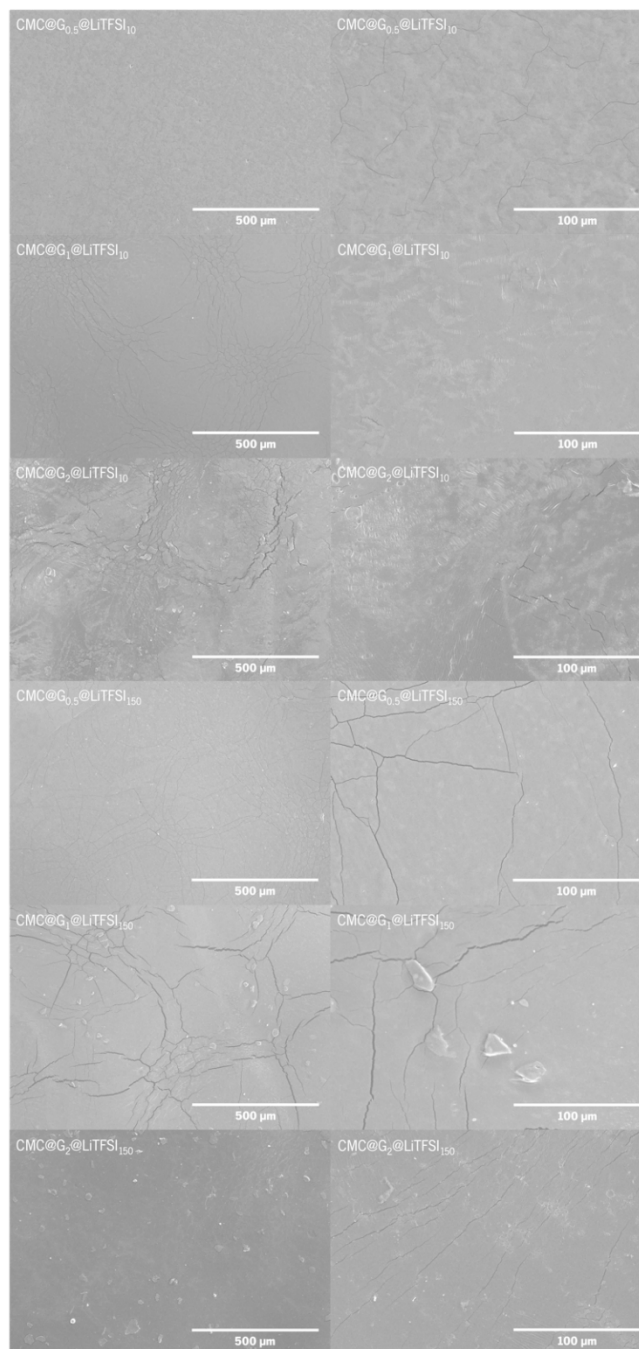


Figure 30. SEM micrographs of selected SPEs, as a function of glycerol content at fixed LiTFSI concentrations of 10, 150 and 200%, acquired at 100× and 500× magnifications.

In Figure 29, it can be observed that the surface of the CMC sample is homogeneous and presents a nonporous and smooth texture, free from significant imperfections. However, upon doping the matrix with glycerol (CMC@G_i), cracks are evident across the surface of the sample. At higher magnification, it becomes clear that the regions without cracks still retain a uniform morphology, indicating that the glycerol content is well dispersed on the surface. The cracks appear to be a direct result of the properties imparted to the films by the addition of glycerol, regardless of its concentration, as they are present in all

samples containing this component in their structure. It can be inferred that these cracks may result from one of two mechanisms: (1) the potentially high and uneven solvent evaporation rate, or (2) the irreversible stretching of the membranes during their removal from the Petri dishes. The latter was unavoidable due to the strong adhesion of the membranes to the dishes. Although efforts were made to control the solvent evaporation rate, as described earlier, these measures may have been insufficient. To conclusively determine the cause of the observed phenomenon, additional analyses would be required. It is worth noting that the adhesion of the membranes to the Petri dishes is desirable for the intended application. In electrochemical devices, full adhesion of the electrolyte to the electrodes is crucial. From an industrial perspective, if the cracks are indeed caused by irreversible stretching during removal, this would not pose a significant issue, as the polymeric solutions are intended to be directly deposited onto the electrodes in battery applications.

When incorporating different amounts of LiTFSI, as shown in Figure 29, the surface of the samples appears to develop some roughness. Higher salt concentrations are generally expected to favour the formation of visible agglomerates, particularly beyond the threshold at which the polymer matrix can no longer effectively accommodate or dissociate the added salt (e.g. 200%).^{54,55,85,148} This expectation is partially supported by the present data, as crystalline domains—possibly corresponding to salt aggregates—were only observed from 100% LiTFSI loading onwards. However, the absence of detectable aggregates at 200% may reflect a higher degree of salt dispersion in this particular sample—potentially resulting from localised microstructural variations or artefacts in sample preparation.

In general, it is not possible to draw definitive conclusions regarding the influence of increasing glycerol concentrations, illustrated in Figure 30, on the features assessed by this technique, as the variations observed do not exhibit a clear trend. Nonetheless, based on literature reports and consistent with other findings in this thesis, glycerol is known to promote salt dissociation, which would be expected to reduce the presence of salt aggregates as its concentration increases.^{55,149,150}

4.2.8. Thermogravimetric Analysis

TGA was conducted to assess the thermal stability and decomposition profile of the synthesized SPEs, with the resulting thermograms presented in Figure 31 and Figure 32.

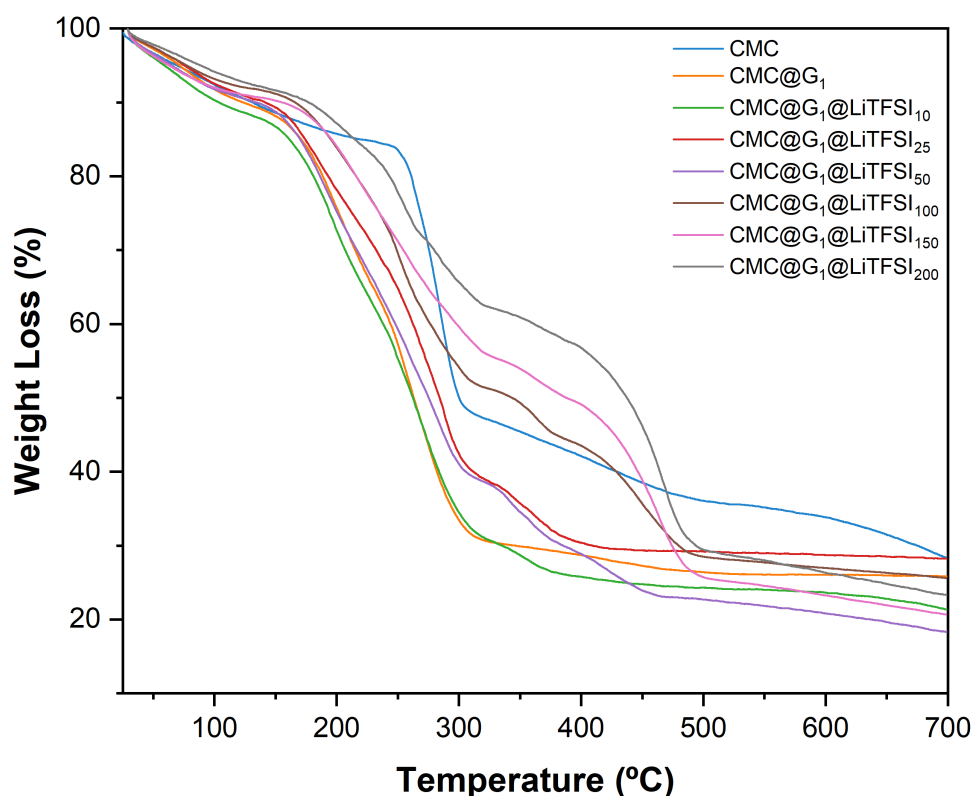


Figure 31. TGA thermograms of selected SPEs as a function of LiTFSI concentration at fixed 1:1 NaCMC-to-glycerol ratio.

The analysis of the NaCMC film, shown in Figure 31, reveals three distinct thermal stages. The first one, with an onset temperature of 28.5 °C is associated with the release of absorbed moisture and residual water,¹⁸⁰ with the maximum evaporation rate occurring at 134.0 °C, accounting for 15.67% weight loss. The second stage, where the thermal decomposition begins, starting at 261.2 °C and reaching the highest degradation rate at 283.0 °C, is attributed to the breakdown of the polysaccharide backbone, leading to depolymerisation and the most significant mass loss (37.22%).⁸³ Finally, the third stage, initiated at 360.2 °C corresponds to the decarboxylation of the COO⁻ groups within the polymeric structure,⁸³ and reached the maximum degradation rate at 426.0 °C, resulting in an additional 11.26% weight loss. At 700.0 °C, approximately 28.34% of the initial mass remains.

The incorporation of glycerol into the NaCMC matrix resulted in a reduction of its thermal stability, as indicated by a shift towards lower decomposition temperatures (173.1 °C). Moreover, the thermogram reveals the presence of two partially overlapping decomposition stages. The first stage is associated with the degradation of glycerol,¹⁸⁵ exhibiting a maximum rate of mass loss at 191.0 °C and accounting for 25.75% of the total weight loss. The second stage is attributed to the depolymerisation of the NaCMC backbone, occurring at 246.7 °C — a lower temperature compared to the pristine polymer — with a mass

loss of 32.79% and a peak decomposition rate at 270.0 °C. This earlier decomposition can be attributed to two main factors: Firstly, glycerol interacts with NaCMC through hydrogen bonding, disrupting the polymer's inter and intramolecular network. This structural alteration weakens the cohesive forces within the matrix, thereby lowering the energy required for thermal degradation. Secondly, during the glycerol decomposition process, volatile by-products and reactive species, such as free radicals, may be generated, which can further catalyse the breakdown of the biopolymer.¹⁶³ The absence of a distinct decomposition peak up to 500 °C suggests that no major phase in the composite exhibits a specific thermal behaviour. The gradual weight loss between 320 °C and 500 °C is likely due to residual volatiles and partially stable CMC side chains.¹⁸⁵ The stabilisation of the residual mass at high temperatures suggests that inorganic components persist beyond 500 °C.¹⁸⁶

The study of the effect of increasing LiTFSI concentration in the membranes reveals a complex behaviour, with no straightforward trend in thermal stability. The overall degradation profile remains similar to that of the glycerol-doped matrix, indicating that glycerol exerts a more pronounced influence on the thermal behaviour than the salt. However, a key distinction emerges with increasing LiTFSI concentration: the appearance of a new thermal event at 25% LiTFSI, with a maximum degradation rate of 340 °C. The peak, which becomes more pronounced in samples with higher salt content, is likely associated with the decomposition of LiTFSI crystallites embedded within the polymer matrix, as reported in the literature.⁵⁴ This interpretation is supported by the progressive increase in weight loss observed during this decomposition stage, from 8.33% in CMC@G₁@LiTFSI₂₅ to 28.47% in the formulation containing 200% salt. The growing intensity of this thermal event suggests an increasing presence of crystalline salt domains, confirming that above a certain doping threshold, LiTFSI tends to crystallise instead of remaining fully solvated within the polymeric network.^{54,55,85,148} Such behaviour is consistent with previous characterisation techniques, which show that the phenomenon is particularly evident in the membrane doped with 200% salt (CMC@G₁@LiTFSI₂₀₀). Furthermore, these results indicate that the system's thermal response is influenced not only by the salt content but also by the degree of salt dispersion and interaction within the matrix, albeit to a lesser extent.

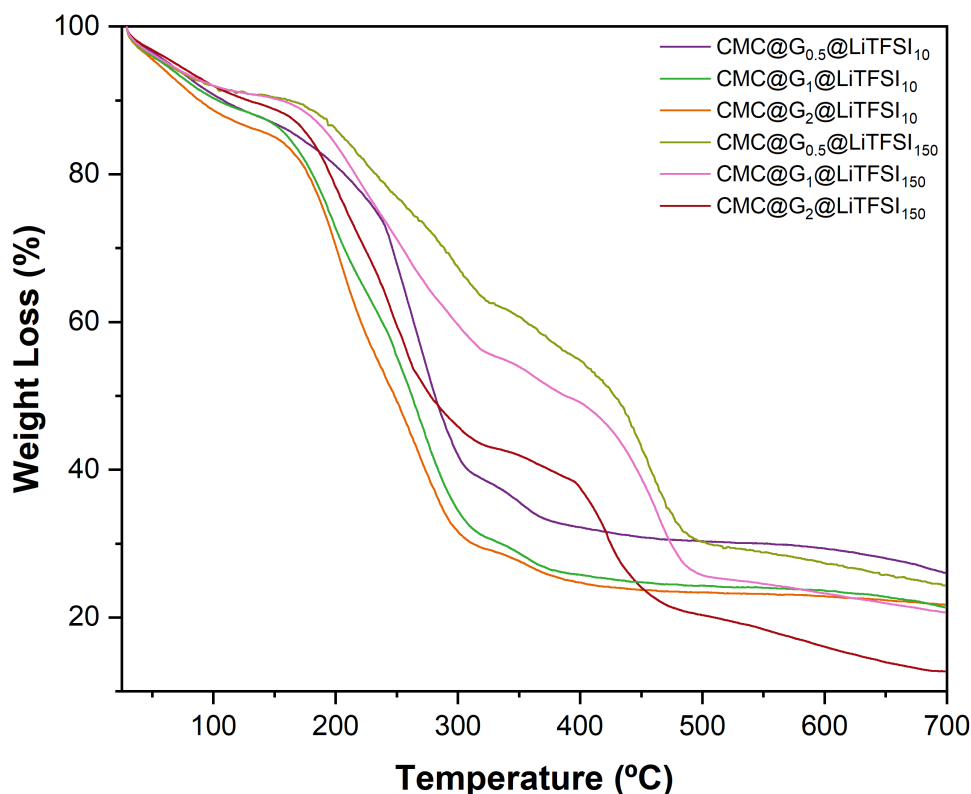


Figure 32. TGA thermograms of selected SPEs as a function of glycerol content at fixed LiTFSI concentrations of 10 and 150%.

Transitioning to the study of glycerol's effect, illustrated in Figure 32, the results partially corroborate previous assumptions regarding its influence on thermal stability. For both 10% and 150% LiTFSI, increasing the glycerol content from a 1:0.5 to a 1:1 NaCMC-to-glycerol ratio leads to a marked decrease in the initial decomposition temperature — from 233.6 °C to 173.9 °C for 10% LiTFSI, and from 191.4 °C to 181.6 °C for 150% LiTFSI. However, a further increase to a 1:2 ratio results in a slight rise in this parameter (174.6 °C and 188.1 °C, respectively), deviating from the expected trend of continuous thermal destabilisation. A comparable behaviour is observed in the residual mass profile at 10% LiTFSI, where a significant reduction is noted from 26.01% (1:0.5) to 21.35% (1:1), followed by a slight increase to 21.74% at 1:2. In contrast, at 150% LiTFSI, the anticipated trend is confirmed, with the residual mass decreasing from 24.36% at 1:0.5 to 12.72% at 1:2. These findings indicate that although glycerol typically promotes early volatilisation due to its high vapour pressure,¹⁶² its influence on the thermal behaviour of the membranes is not strictly linear. Regarding the variation in salt concentration, the trends observed earlier are reinforced, with the thermal events corresponding to LiTFSI agglomeration being significantly more pronounced at 150% compared to 10%.

To conclude, the thermal stability of the synthesised SPEs must be evaluated in the context of their intended application in batteries. In such systems, materials are often subjected to elevated temperatures, making thermal resistance a critical parameter for ensuring structural integrity and operational reliability.¹⁸⁷ Thermal stability is also a key factor in improving the safety of solid-state lithium batteries, as it helps ensure the structural and electrochemical integrity of SPEs under elevated temperatures, thereby reducing the risk of degradation and thermal failure under abuse conditions.^{187,188} The films selected for implementation in solid-state lithium battery systems exhibit thermal stability up to approximately 160–230 °C. Although a slight reduction in thermal stability is observed with the incorporation of dopants, the materials retain sufficient resistance to thermal degradation for their intended use. Additionally, the presence of salt and plasticiser contributes positively to other essential parameters, including ionic conductivity and mechanical flexibility, as evidenced by the results obtained in this work, thereby reinforcing the overall suitability of these formulations for integration in electrochemical devices.

4.2.9. Tensile Testing

Tensile testing was performed to characterise the mechanical behaviour of the different SPEs. Each sample was cut into three strips, and tests were conducted on all three to ensure reliable results. Figure 33 shows a representative stress–strain curve selected from the measurements carried out for each film, serving as an example of their observed mechanical response.

deviations, providing a clearer visualisation of the variations and trends observed across the different membranes.

Table 8. Mechanical properties of the SPEs, including maximum force, elongation at break, and Young's Modulus, presented as mean values accompanied by their respective standard deviations.

Sample ID	Maximum Force (N)	Elongation at Break (%)	Young's Modulus (MPa)
CMC	51 ± 16	1.48 ± 0.43	2440 ± 330
CMC@G ₁	2.59 ± 0.34	126.0 ± 5.6	4.30 ± 0.38
CMC@G ₁ @LiTFSI ₁₀	4.0 ± 3.5	131.7 ± 5.2	5.2 ± 3.6
CMC@G ₁ @LiTFSI ₂₅	0.93 ± 0.33	87 ± 21	0.418 ± 0.012
CMC@G ₁ @LiTFSI ₅₀	1.50 ± 0.14	126.0 ± 5.3	1.12 ± 0.13
CMC@G ₁ @LiTFSI ₁₀₀	2.65 ± 0.25	134.2 ± 8.9	0.947 ± 0.024
CMC@G ₁ @LiTFSI ₁₅₀	5.7 ± 4.3	137 ± 23	0.77 ± 0.38
CMC@G ₁ @LiTFSI ₂₀₀	2.15 ± 0.34	100.8 ± 9.8	0.60 ± 0.21
CMC@G _{0.5} @LiTFSI ₁₀	30.7 ± 5.7	4.9 ± 1.5	508 ± 93
CMC@G ₂ @LiTFSI ₁₀	0.65 ± 0.13	93 ± 14	0.225 ± 0.066
CMC@G _{0.5} @LiTFSI ₁₅₀	12.04 ± 0.99	45.9 ± 8.5	42.2 ± 16.2
CMC@G ₂ @LiTFSI ₁₅₀	0.82 ± 0.25	93 ± 20	0.133 ± 0.021

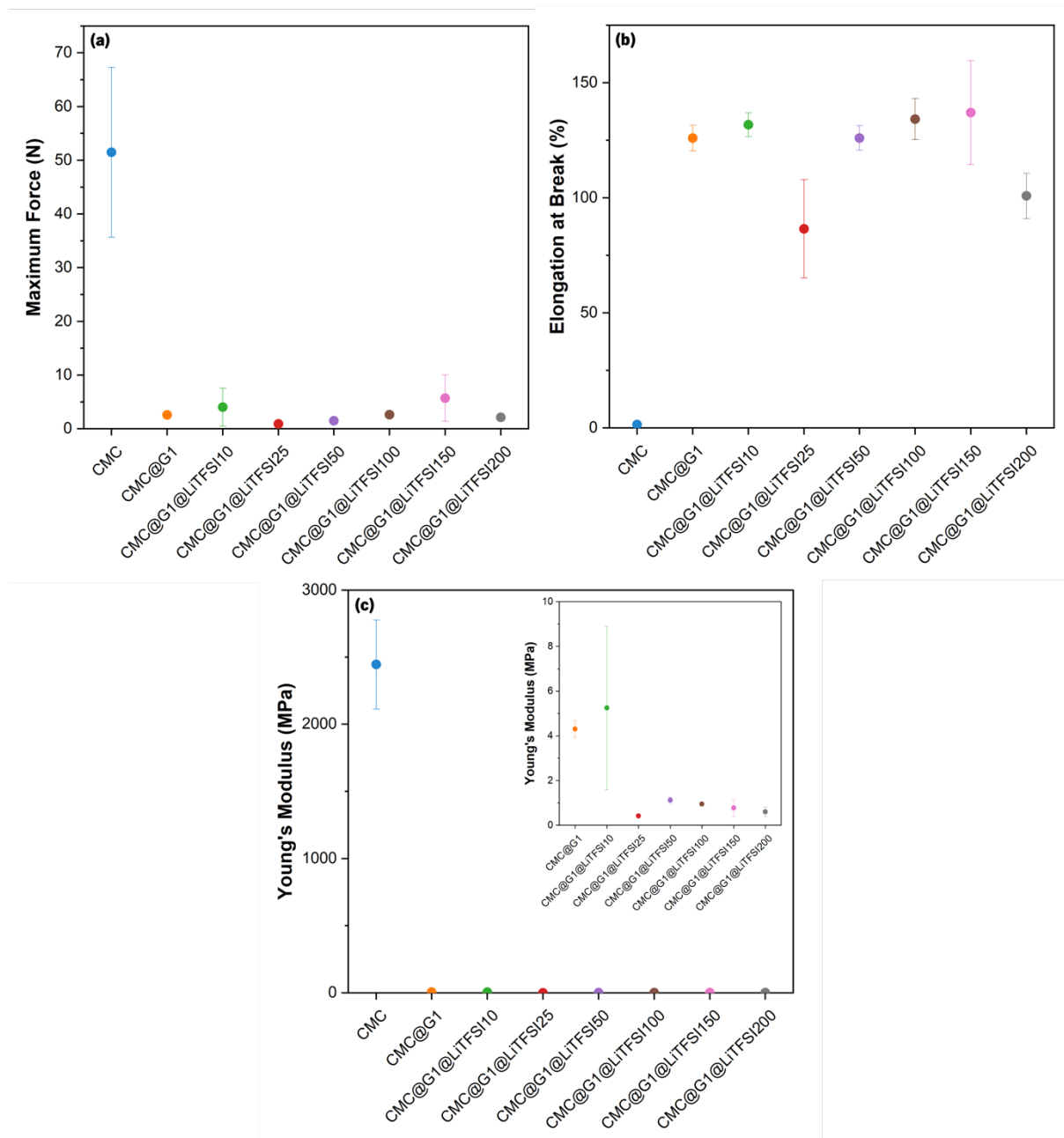


Figure 34. Mechanical properties of selected SPEs as a function of LiTFSI concentration at fixed 1:1 NaCMC-to-glycerol ratio. (a) Maximum force; (b) Elongation at break; (c) Young's Modulus (main plot and magnified inset). Error bars represent standard deviations.

Examining Figure 34, it is possible to infer the impact of LiTFSI doping on the system. Starting with Figure 34(a), the highest $F_{\max}$ value is observed for the CMC sample, with 51 ± 16 N, indicating it possesses the greatest tensile strength. Upon doping with glycerol, this value drops significantly to 2.59 ± 0.34 N. With the incorporation of 10% LiTFSI, it reaches 4.0 ± 3.5 N and this difference is no longer statistically significant. As the salt concentration increases, a decrease is observed in the CMC@G₁@LiTFSI₂₅ sample

(0.93 ± 0.33 N), and from that point, the $F_{\max}$ slightly rises, peaking at 150% LiTFSI concentration with a value of 5.7 ± 4.3 N, followed by a decline to 2.15 ± 0.34 N for CMC@G₁@LiTFSI₂₀₀.

Focusing on the ϵ_b parameter, as showcased in Figure 34(b), the lowest value, as expected, is observed for the pristine CMC SPE ($1.48 \pm 0.43\%$), which highlights its brittle nature. The addition of glycerol renders the film significantly more ductile, increasing ϵ_b to $126 \pm 5.6\%$. Incorporating 10% LiTFSI leads to a further increase, reaching $131.7 \pm 5.2\%$. At 25% salt, however, a reduction is noted ($87 \pm 21\%$) followed by a general trend of increasing ϵ_b with higher LiTFSI concentrations. The parameter peaks at $137 \pm 23\%$ for the CMC@G₁@LiTFSI₁₅₀ sample, before decreasing to $100.8 \pm 9.8\%$ for CMC@G₁@LiTFSI₂₀₀. As for the Young's modulus in Figure 34(c), the highest value is observed for the host matrix, at 2440 ± 330 MPa, reflecting its rigid nature. The incorporation of glycerol induces a significant reduction, with E decreasing to 4.30 ± 0.38 MPa. Further doping with 10% salt results in a slight increase to 5.2 ± 3.6 MPa, although this change is not statistically significant. No clear pattern emerges with increasing LiTFSI concentration; however, a gradual reduction of the E values is noticeable from CMC@G₁@LiTFSI₅₀ onwards reaching 0.60 ± 0.21 MPa for the CMC@G₁@LiTFSI₂₀₀ sample, indicating that the films become more flexible.

Overall, the predominant effect of glycerol is evident. The variations induced by its incorporation are significantly greater than those observed with salt doping in all three parameters. While variations are observed with increasing LiTFSI concentration, an analysis of the associated standard deviations reveals that most of these differences are not statistically significant.

It is also important to highlight a distinctive trend observed in the data, where the values for 10% and 25% salt concentrations seem to consistently deviate from the overall expected pattern. As previously discussed in relation to humidity, despite efforts to control as many variables as possible, certain factors proved difficult to manage, potentially introducing variability into the results. In this case, the anomalous behaviour could be linked to the presence of cracks in the samples, as identified in SEM micrographs. These structural imperfections are known to likely affect mechanical properties, though their influence is not always consistent or predictable.

The progressive increase in $F_{\max}$ and ϵ_b , up to a certain point, by LiTFSI doping can be explained by what has been described in previous studies. The effect on tensile strength can be attributed to the reinforcement of intermolecular forces within the SPEs. This arises from the establishment of ion–dipole interactions between Li⁺ and TFSI⁻ ions and the NaCMC chains, which significantly enhance the structural stability of the material.⁵⁴ When examining the elastic behaviour of the membranes, the hypothesis proposed by Ndruru et al.¹⁸⁹ is supported, suggesting that lithium salts can improve this property by

disrupting their crystalline phase, which leads to greater amorphicity.⁸³ However, as the LiTFSI content exceeded the critical threshold of 150%, the formation of salt clusters led to an uneven distribution of LiTFSI within the polymeric matrix. This inhomogeneity in the interactions reversed the previously reported beneficial effects.⁵⁴

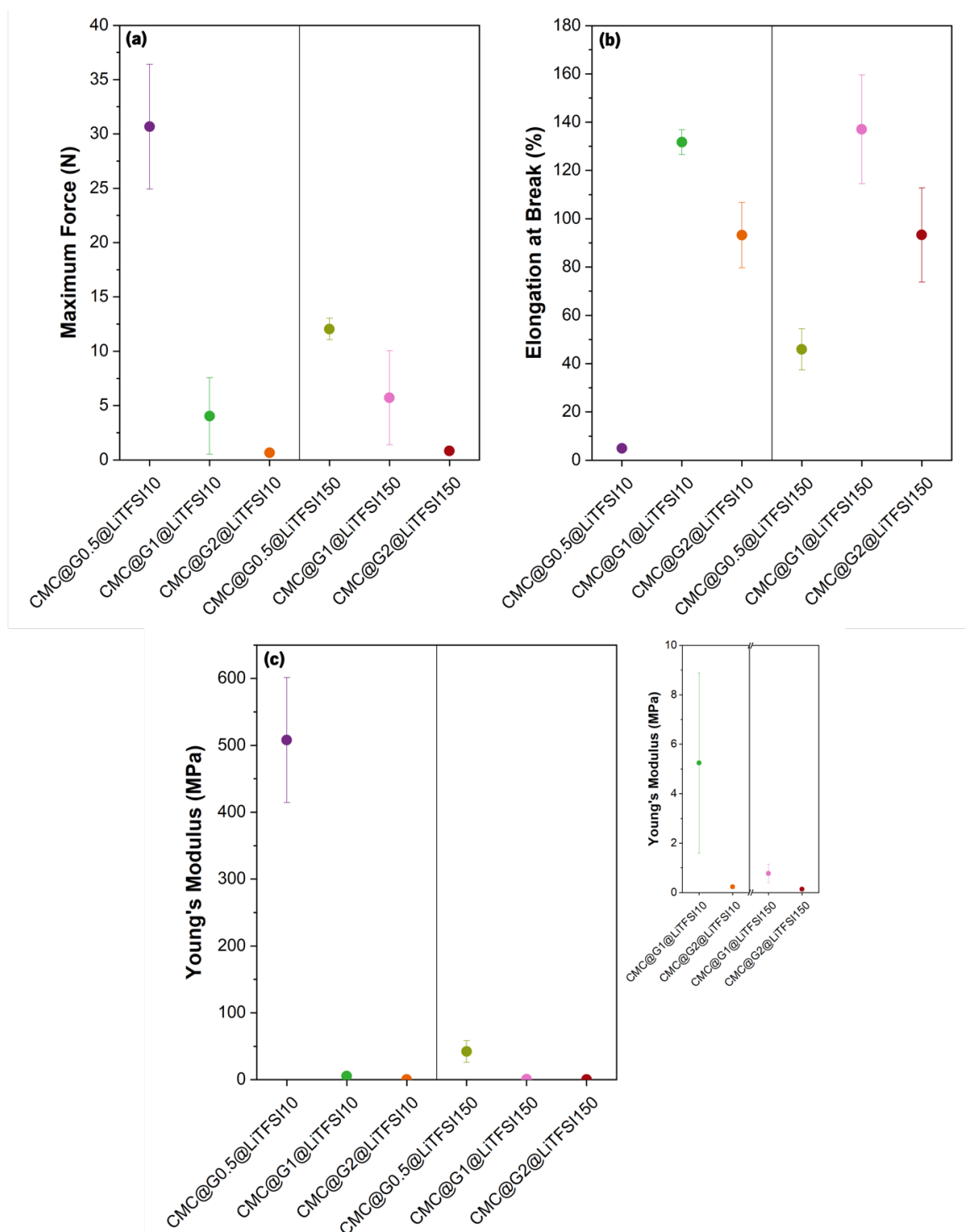


Figure 35. Mechanical properties of selected SPEs as a function of glycerol content at fixed LiTFSI concentrations of 10 and 150%. (a) Maximum force; (b) Elongation at break; (c) Young's Modulus (main plot and magnified inset). Error bars represent standard deviations.

Moving on to the analysis of glycerol's effect, illustrated in Figure 35, and examining Figure 35(a), it can be observed that as glycerol concentration increases, a reduction in $F_{\max}$ is observed at both 10% and 150% salt concentrations. This can be attributed to the plasticising effect of glycerol, which reduces the tensile strength of the materials.

Regarding Figure 35(b), an increase in glycerol concentration correlates with higher ϵ_b values, reaching an inflection point at a 1:1 NaCMC-to-glycerol ratio. Beyond this, a decrease is noted. This trend is consistent across both LiTFSI concentrations. The observed behaviour arises from the increased ductility imparted by glycerol. However, when the concentration exceeds the critical threshold, the membranes become excessively flexible, compromising their structural integrity.

The E parameter, depicted in Figure 35(c), decreases with increasing glycerol concentration, irrespective of the salt concentration, providing enhanced flexibility to the SPEs.

For all these parameters, the transition from 1:0.5 NaCMC-to-glycerol ratio to 1:1 results in the most significant changes, with the impact being particularly pronounced at 10% salt concentration. Conversely, the transition from 1:1 to 1:2 ratio shows a continuation of the plasticising effect, though the differences are not always statistically significant.

Moreover, glycerol doping resulted in a general decrease in $F_{\max}$ and E, alongside an improvement in ϵ_b , dose-dependently, evidence that aligns with those reported in the literature. This can be attributed to the ability of glycerol's hydroxyl groups to form hydrogen bonds with both the carboxyl and hydroxyl groups within the NaCMC matrix, thereby increasing the free volume of the system. Additionally, this interaction reduces both inter- and intramolecular interactions among the biopolymer chains, consequently enhancing the mobility within the host matrix.^{162,163} As a result, the behaviour of NaCMC-based films transitions from brittle to flexible, with higher glycerol content further promoting their ability to deform and enhancing their ductility.

In general, glycerol acts as a plasticiser, enhancing both flexibility and plasticity while reducing tensile strength. LiTFSI counterbalances this loss by reinforcing the matrix. On top of that, the overall results are consistent with the findings and observations presented in the previous analyses. As anticipated, membranes with higher glycerol content (1:2 NaCMC-to-glycerol ratio) demonstrated superior flexibility and ductility, corroborating the conclusions drawn from the macroscopic evaluation, where the dominant effect of glycerol on deformability was evident. Furthermore, the suspicion raised in the EIS section—that 1:2 ratio membranes may have compromised mechanical properties due to their extreme flexibility—has been confirmed. The tensile testing outcomes revealed a significant decrease in the ϵ_b values for these films, indicating a limit in mechanical performance at glycerol concentrations beyond this ratio.

For the intended application, SPEs must possess robust mechanical properties to ensure both the performance and safety of batteries. These, combined with elevated ionic conductivity, play a crucial role in suppressing the formation of lithium dendrites by promoting homogeneous lithium metal deposition.⁵⁴ Moreover, mechanical strength enhances the durability of SPEs by preventing structural failures, such as cracks or deformations, which may arise from the stress and pressure associated with battery operation or assembly, as well as from dendrite-induced damage. Such failures increase the risk of electrode particle intrusion into the polymeric membrane, potentially causing electrical short circuits.^{54,83} In addition, SPEs need to exhibit sufficient flexibility to relax elastically during the repeated charging and discharging cycles, thereby maintaining the functional reliability of the battery, even under demanding operating conditions. In the context of large-scale production, it is equally important for SPEs to exhibit sufficient elasticity to accommodate the stresses generated during assembly, storage, and consumption.⁸²

To summarise, good mechanical properties can be achieved by balancing these three parameters, ensuring durability and adaptability under all kinds of stresses. The mechanical robustness observed in the CMC@G_i@LiTFS₁₅₀ film makes it a strong candidate, as it demonstrates a higher E , without significantly compromising $F_{\max}$ and ϵ_b . This sample effectively combines sufficient mechanical strength with enhanced conductivity, as previously highlighted, further supporting its potential for practical battery integration.

4.2.10. Contact Angle Measurements

Contact angle (θ_c) measurements were conducted to assess the surface hydrophilicity of the various films. To ensure reproducibility and statistical reliability, three CAMs were performed for each sample at distinct points on the film surfaces. The mean values of the obtained results and their respective standard deviations are first summarised in Table 9 and subsequently plotted in Figure 36 and Figure 37.

Table 9. Contact angle values of the SPEs, presented as mean values accompanied by their respective standard deviations.

Sample ID	Contact Angle (°)
CMC	69.6 ± 4.9
CMC@G ₁	65.3 ± 3.3
CMC@G ₁ @LiTFSI ₁₀	55.0 ± 2.9
CMC@G ₁ @LiTFSI ₂₅	54.6 ± 5.4
CMC@G ₁ @LiTFSI ₅₀	59.2 ± 4.0
CMC@G ₁ @LiTFSI ₁₀₀	53.6 ± 5.0
CMC@G ₁ @LiTFSI ₁₅₀	58.8 ± 2.5
CMC@G ₁ @LiTFSI ₂₀₀	61.5 ± 2.0
CMC@G _{0.5} @LiTFSI ₁₀	66.5 ± 3.5
CMC@G ₂ @LiTFSI ₁₀	61.6 ± 3.5
CMC@G _{0.5} @LiTFSI ₁₅₀	62.7 ± 3.9
CMC@G ₂ @LiTFSI ₁₅₀	59.6 ± 2.1

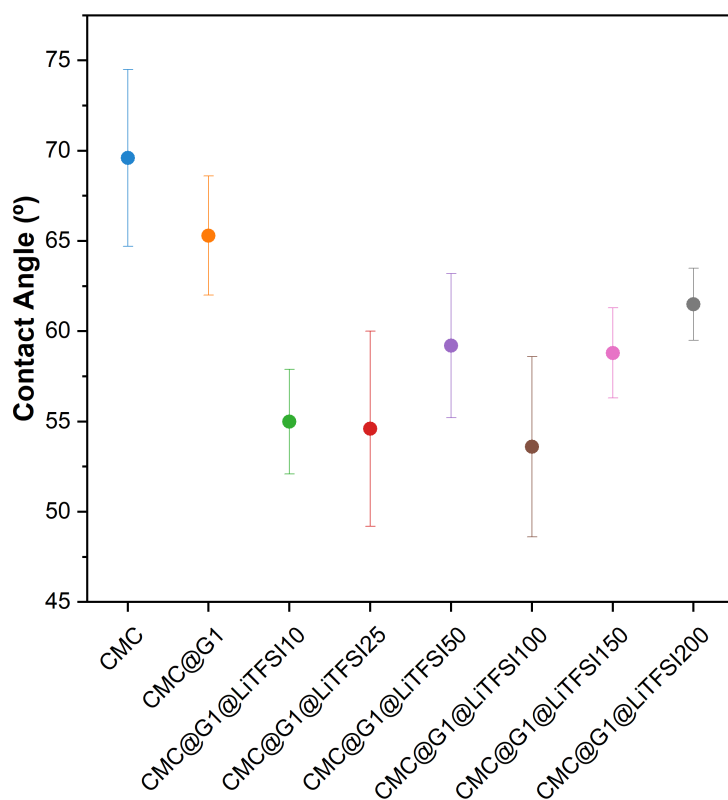


Figure 36. Contact angle values of selected SPEs as a function of LiTFSI concentration at fixed 1:1 NaCMC-to-glycerol ratio. Error bars represent standard deviations.

The highest contact angle value, $69.6 \pm 4.9^\circ$, was observed for the pristine NaCMC matrix, which is inherently hydrophilic and water-soluble.¹⁹⁰ Upon doping, first with LiTFSI and then with glycerol, the matrix became more hydrophilic, as evidenced by a decrease in contact angle values, to $65.3 \pm 3.3^\circ$ and further to $55.0 \pm 2.9^\circ$. Yet, the only statistically significant difference is observed with the addition of LiTFSI.

However, as the salt concentration increased, Figure 36, a general trend of rising contact angle values was noted (e.g., the 200% concentration exhibited a higher contact angle than the 10% concentration), indicating an increase in hydrophobicity. This behaviour could be attributed to the competition between water molecules and Li^+ ions in binding with the host matrix carboxylate groups. It is worth noting that the $\text{CMC@G}_1\text{@LiTFSI}_{50}$ contact angle appears to deviate from the pattern. Finally, although variations are observed with augmenting salt concentration, they are not particularly significant, since most values fell within the range defined by the largest standard deviation of the $\text{CMC@G}_1\text{@LiTFSI}_{25}$ sample, $54.6 \pm 5.4^\circ$, except for the $\text{CMC@G}_1\text{@LiTFSI}_{200}$ value of $61.5 \pm 2.0^\circ$.

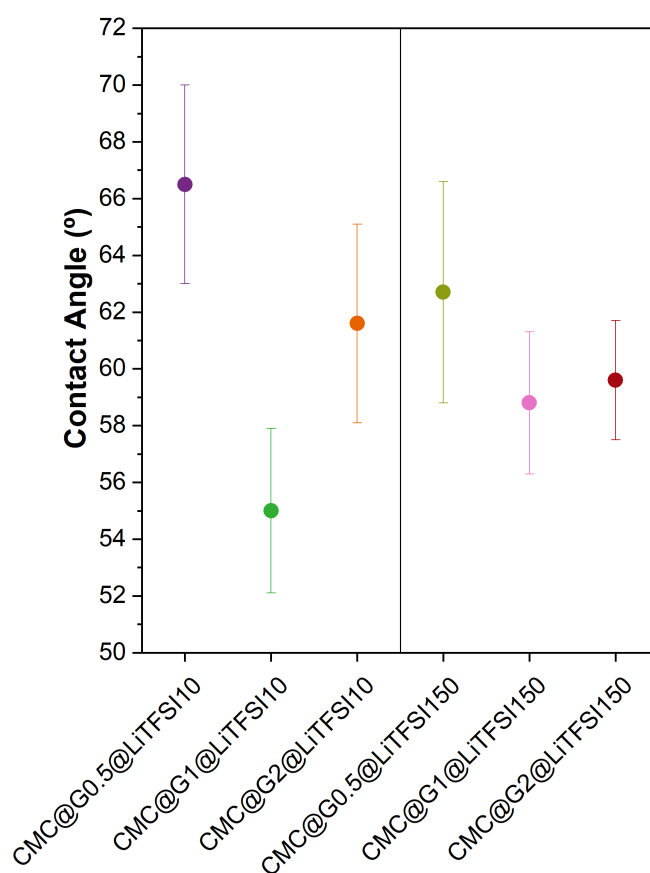


Figure 37. Contact angle values of selected SPEs as a function of glycerol content at fixed LiTFSI concentrations of 10 and 150%. Error bars represent standard deviations.

When examining Figure 37, the overall trend suggests that glycerol reduces the contact angle (e.g., the 1:0.5 NaCMC-to-glycerol ratio membranes exhibited a higher contact angle than the 1:2), thereby enhancing the hydrophilicity of the SPEs by providing additional interaction sites for water molecules through its hydroxyl groups. However, a limit to this effect seems to be reached at a 1:1 glycerol-to-NaCMC ratio. This conclusion aligns with the profile observed at both 10% and 150% salt concentrations, although the limited dataset does not allow for definitive assertions. Similarly, in this case, the differences are not statistically significant, as most values lie within the range defined by the CMC@G₁@LiTFSI₂₅ sample, $54.6 \pm 5.4^\circ$, except for the value of $66.5 \pm 3.5^\circ$ (CMC@G_{0.5}@LiTFSI₁₅₀), which stands out. Collectively, these results indicate that the SPEs exhibit a moderate degree of hydrophilicity, which appears advantageous for enhancing ionic conductivity.¹⁹¹ At the same time, such wettability may help ensure adequate interfacial contact with electrode materials.¹⁹² However, highly hydrophilic systems risk retaining trace amounts of moisture or carbon dioxide (CO₂) prior to cell fabrication, which, upon contact with lithium metal, can trigger spontaneous interfacial degradation reactions, including the formation of lithium hydroxide (LiOH) and, eventually, lithium carbonate (Li₂CO₃). These by-products form passivation layers that significantly increase interfacial resistance and impair ion transport, as demonstrated in studies incorporating both garnet-type and PEO-based solid electrolytes.^{193,194} Striking an appropriate balance is therefore critical. The ability to modulate surface wettability through variations in salt and plasticiser content suggests that the materials developed in this work exhibit a promising compromise between electrochemical performance and interfacial compatibility, supporting their potential suitability for integration into SSB architectures incorporating embedded sensors.

4.3. Electrical Characterisation of Sensor-SPE Interaction

The electrical characterisation of the interaction between the SPEs and the loop antennas was conducted through *S11* parameter analysis using a LiteVNA. As mentioned before, to guarantee consistency and minimise variability, the measurements were conducted under controlled conditions, and the procedure was replicated for three sensors with comparable resistance values. Since two of the three sensors displayed identical trends and the third deviated only slightly for one sample, sensor S3 — representative of the majority behaviour — was selected for illustration. The curves obtained are plotted in Figure 38(a) and Figure 39(a).

Initially, the *S11* data were normalised to the maximum peak intensity within each dataset, allowing for direct comparison of the resonance behaviour across samples regardless of absolute signal strength. The reproducibility of the baseline signal, i.e., the sensor response prior to membrane application, was then assessed. For each of the three sensors, the baseline curves showed minimal variation across repeated measurements, with the traces displaying significant overlap throughout the scanned frequency range. Given this high consistency, an average curve was calculated for each sensor by determining the mean *S11* value at each frequency point. This averaged baseline was then used as the reference against which the response of the SPEs was evaluated. For clarity, two distinct frequency regions were selected for further analysis. Region 1 spans approximately 0.50–0.78 GHz, while Region 2 covers the range between 2.45 and 3.00 GHz. These were chosen based on the presence of well-defined peaks that allowed the assessment of systematic shifts in the resonance behaviour. The evolution of resonance frequencies in both regions, as a function of LiTFSI and glycerol content, is presented in Figure 39 and Figure 41.

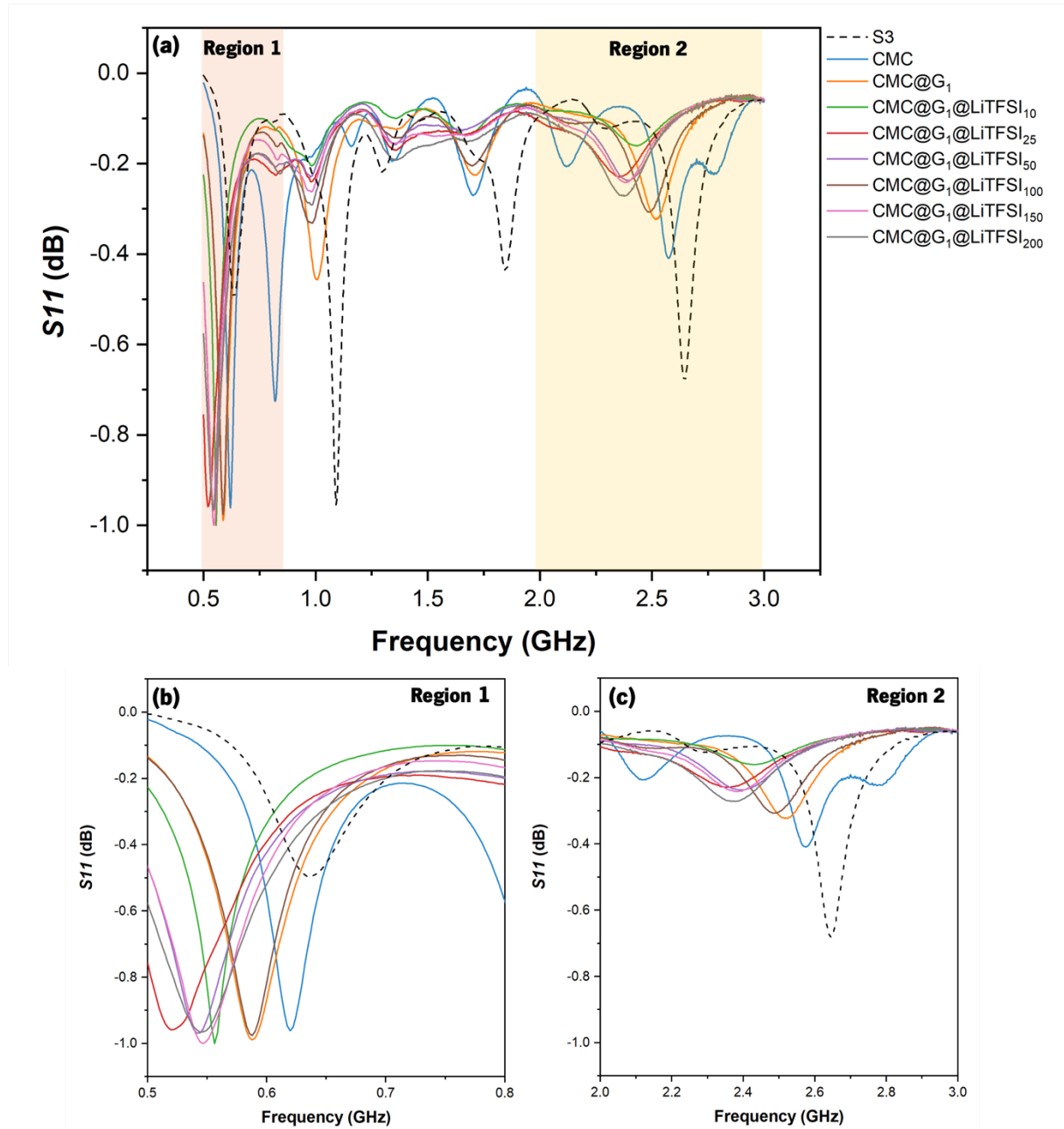


Figure 38. Resonance peaks obtained with the loop antenna (S3) after deposition of selected SPEs, as a function of LiTFSI concentration at fixed 1:1 NaCMC-to-glycerol ratio. (a) Full S_{11} response in the 0.5-3.0 GHz range; (b) and (c) show insets with magnified views of region 1 and 2, respectively. The dashed line (S3) corresponds to the bar antenna without any SPE deposited.

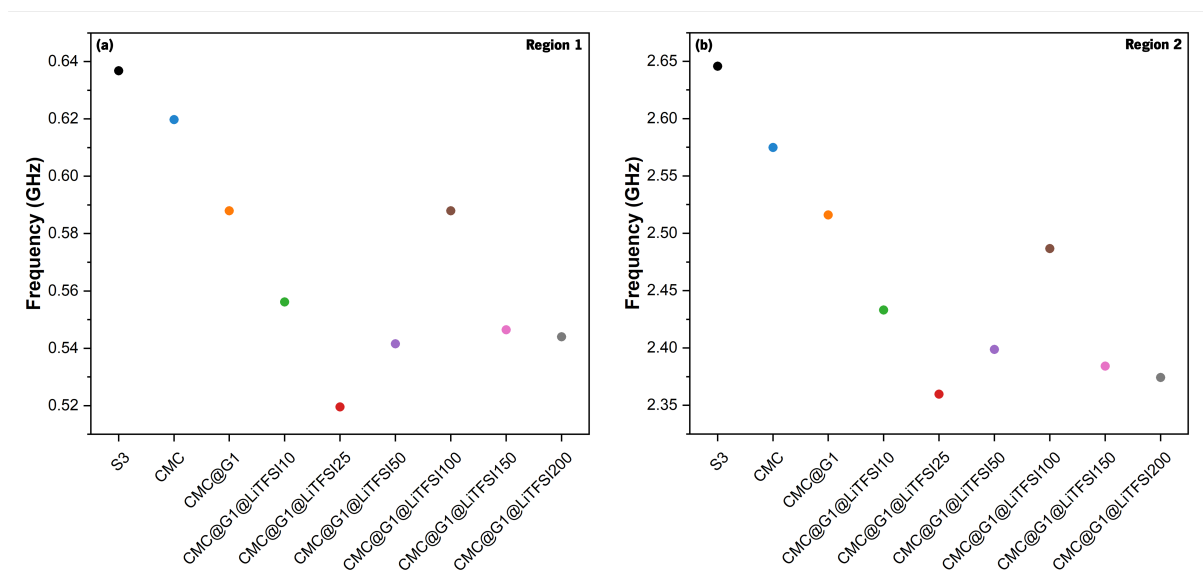


Figure 39. Resonance peak frequencies of selected SPEs as a function of LiTFSI concentration at a fixed 1:1 NaCMC-to-glycerol ratio for Regions 1 (a) and 2 (b).

Comparing the resonance behaviour between the reference sensor and the CMC and CMC@G₁ membranes, prior to any LiTFSI addition, a progressive shift of the peak in Region 1 (Figure 38(b) and Figure 39(a)) was observed—from 0.637 GHz for the bare sensor, to 0.620 GHz with the pure matrix, and further to 0.588 GHz with glycerol doping. A similar trend was observed in Region 2 (Figure 38(c) and Figure 39(b)). These progressive shifts towards lower frequencies indicate an increase in dielectric loading. This effect reflects the introduction of increasingly polarisable media over the sensor, due to the presence of polar functional groups in NaCMC and the enhanced molecular mobility induced by glycerol. The influence of salt concentration was then assessed. The selected regions exhibited identical non-linear trends in response to increasing salt concentration. In Region 1, the peak initially shifted progressively towards lower frequencies, reaching a minimum of approximately 0.520 GHz for the CMC@G₁@LiTFSI₂₅ sample. From this point, the frequency increased again up to 0.589 GHz at 100% LiTFSI, before decreasing once more to 0.544 GHz for the 200% sample. Region 2 displayed the same sequence of shifts, indicating a consistent response pattern across both bands.

Although the SPEs were stored under dry and sealed conditions and characterised within a week of synthesis, the transport period between research facilities — during which the samples were vacuum-packed with silica desiccant but not kept in a desiccator — may have allowed for minor physicochemical changes. These could include solvent absorption or internal reorganisation,^{195,196} potentially contributing to the observed response. Despite the non-uniform nature of the variation, all salt-containing samples exhibited frequencies lower than that of the reference (CMC@G₁), suggesting an overall increase in the

dielectric loading of the system. This effect has been previously reported for conjugated polymers, where the incorporation of LiTFSI significantly enhanced the static dielectric permittivity of the blend.¹⁹⁷ Furthermore, the shifts observed in Region 2 were generally more pronounced than those in Region 1, indicating higher sensitivity at these frequencies.

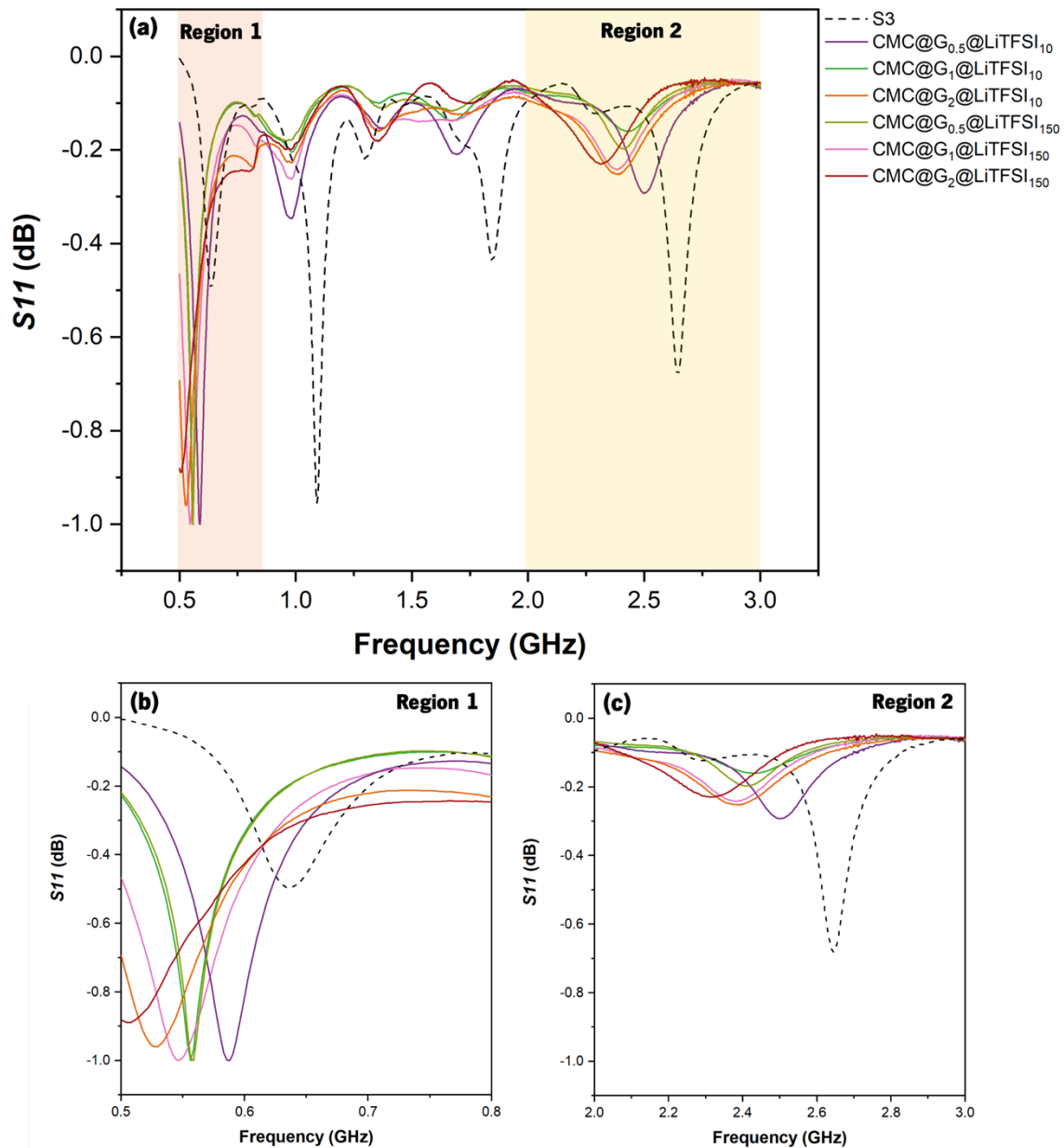


Figure 40. Resonance peaks obtained with the loop antenna (S3) after deposition of selected SPEs, as a function of glycerol content at fixed LiTFSI concentrations of 10 and 150%. (a) Full S_{11} response in the 0.5-3.0 GHz range; (b) and (c) show insets with magnified views of region 1 and 2, respectively. The dashed line (S3) corresponds to the bar antenna without any SPE deposited.

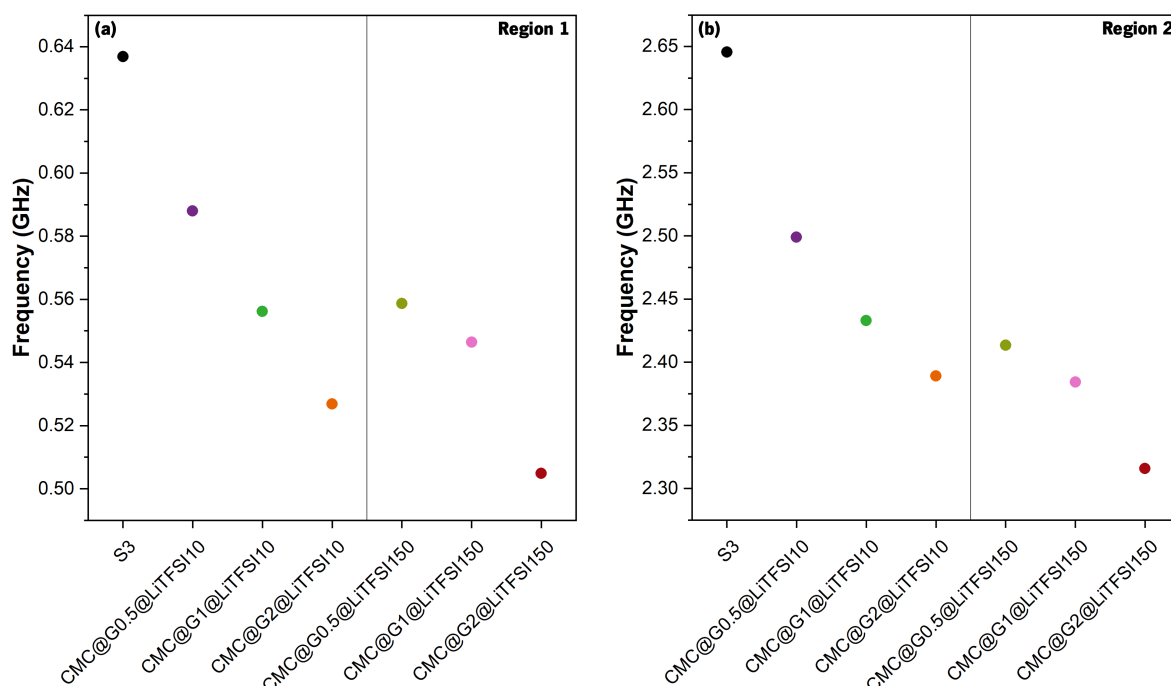


Figure 41. Resonance peak frequencies of selected SPEs as a function of glycerol content at fixed LiTFSI concentrations of 10 and 150% for Regions 1 (a) and 2 (b).

Similarly, the effect of glycerol content was investigated and in both cases, the resonance peaks in Regions 1 (Figure 40(b) and Figure 41(a)) and 2 (Figure 40(c) and Figure 41(b)) followed a clear linear trend, shifting progressively towards lower frequencies with increasing glycerol concentration. This behaviour is consistent with the known effect of glycerol in enhancing segmental mobility, thereby increasing the material's polarisability. As a result, the effective dielectric constant increases and the resonance frequency decreases.^{79,198} The identical trends observed across both resonance regions reinforce the reliability of the sensor response and indicate that the effect of plasticiser on the membrane's dielectric behaviour is systematic and concentration-dependent. As previously noted, the shifts were more pronounced in Region 2, suggesting once again a higher sensitivity at higher frequencies.

Overall, the ability of the loop antennas to interact with the SPEs and produce measurable shifts in resonance signals – independently of specific compositional variations – confirms their potential for embedded applications, namely real-time monitoring in SSB environments. Furthermore, their clear sensitivity to changes in membrane composition further reinforces their suitability for the intended sensing approach.

4.4. Electrochemical Characterisation of Coin Cells

The electrochemical characterisation of the lithium metal coin cells followed an iterative process, during which different techniques and experimental parameters were tested to establish an appropriate analysis protocol. Initially, it was necessary to determine the most efficient sequence of measurements, ensuring that each stage provided complementary information without compromising the integrity of the cell. Multiple approaches were evaluated until a reproducible method was established, allowing for the monitoring of internal resistance evolution, electrochemical activity, and system stability throughout the initial cycling process.

Among the techniques tested, CV was selected as the first electrochemical test, performed at a relatively fast scan rate to minimise excessive lithium consumption and potential side reactions, while verifying the presence of electrochemical activity. This step was essential to assess whether the assembled coin cells exhibited reversible redox behaviour before proceeding to further characterisation.

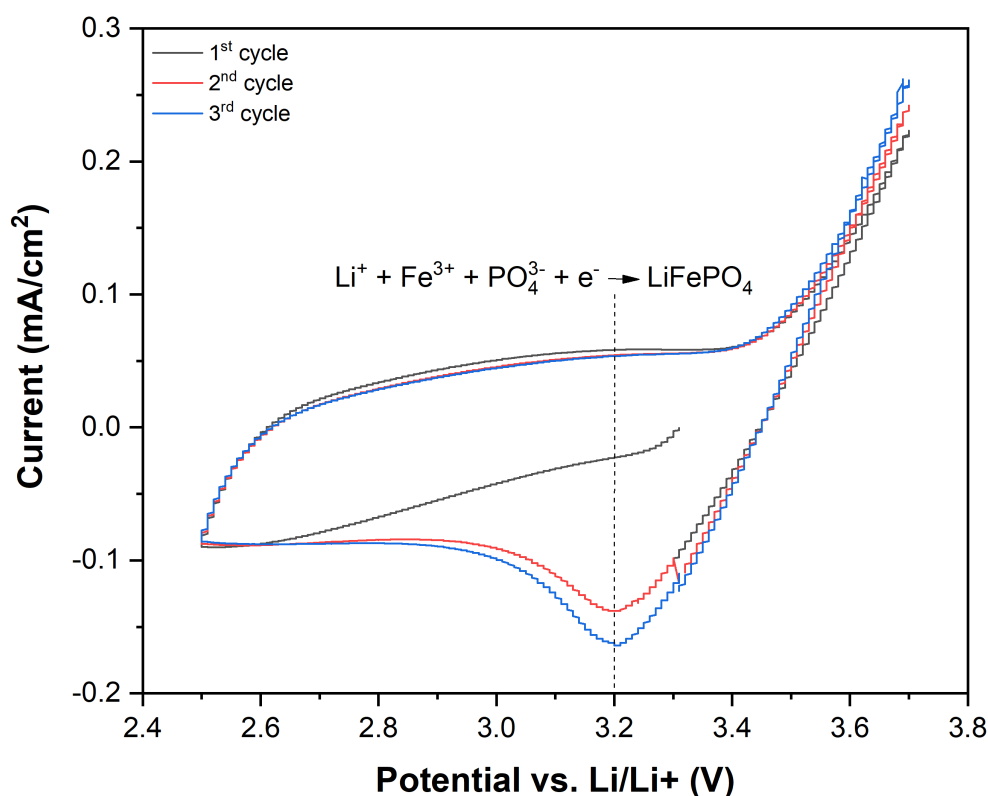


Figure 42. Cyclic voltammograms of a representative LFP | Li half-cell recorded at a scan rate of 1 mV/s over three consecutive cycles.

Figure 42 presents the voltammogram of one of the tested LFP || Li half-cells, recorded at 1 mV/s over three consecutive cycles. In the first cycle, a diffuse response is observed, which may be attributed to an initial stabilisation of the system. In the subsequent cycles, a certain degree of reversibility in the redox process can be observed. The data reveal a well-defined cathodic peak (3.2 V vs. Li⁺/Li), associated with the reduction reaction of the active material, confirming the presence of electrochemical activity in the cell.¹⁹⁹ However, the corresponding anodic peak is less pronounced.

Afterwards, EIS is typically performed. This measurement provides insight into the internal resistance of the cell and helps assess the interfacial properties before any significant electrochemical changes occur. However, for the specific coin cell previously discussed, no EIS analysis was carried out at this stage. To illustrate the expected behaviour, a Nyquist plot from a similar coin cell is presented, in Figure 43, as a reference. The equivalent electrical circuit (EEC) used to model the electrical response of the LFP || Li half-cell configuration is also illustrated in the corresponding diagram. While this does not allow for a direct correlation with the CV results, it provides a qualitative example of the impedance response observed in comparable conditions. The data were fitted using an EEC composed of two RQ elements in series, followed by a standalone constant phase element (Q). This configuration is often used in lithium battery studies to model the electrolyte and charge transfer resistances, while the final Q element is associated with an incomplete Warburg-type diffusion process, typically observed at low frequencies in systems where ion transport within the electrode becomes rate-limiting.

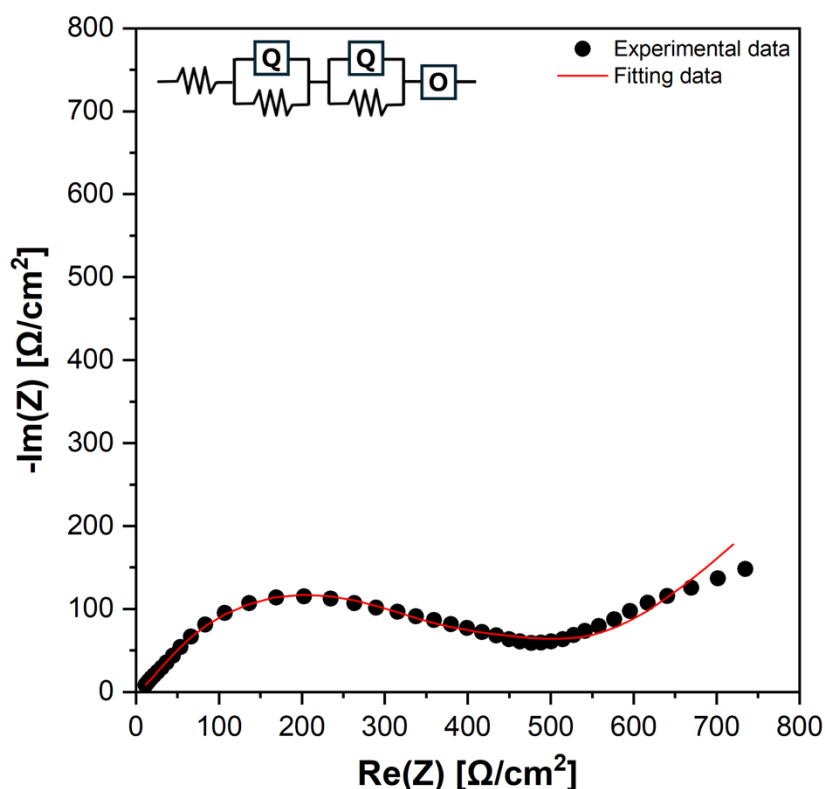


Figure 43. Nyquist plot of a representative LFP || Li half-cell, showing experimental impedance data and corresponding fitting curve. The graph includes the equivalent circuit model used for fitting.

This is a typical Nyquist plot of a LFP || Li half-cell before the formation of the SEI, which is a confirmation of what is expected. It exhibits a well-defined semicircle in the mid frequency range, corresponding to the charge transfer resistance (R_{ct}) at the electrode/electrolyte interface.²⁰⁰ At lower frequencies, the curve transitions into an inclined line, characteristic of the Warburg impedance (Z_w), which represents the diffusion-controlled transport of Li^+ ions within the cathode material.²⁰⁰ The internal resistance of the coin cell is approximately $500 \text{ } \Omega/\text{cm}^2$, determined by summing the ohmic resistance (R_s)—obtained from the intercept of the Nyquist plot with the real axis at high frequencies, which accounts for contributions from the electrolyte, current collectors, and electrical contacts—and the R_{ct} , represented by the diameter of the semicircle. This relatively high internal resistance may be influenced by the fact that the SEI layer has not yet fully developed, meaning that the interfacial resistance has not stabilised. Nevertheless, this measurement is important to establish a baseline for comparison with the post-cycling impedance analysis.

The next step consists of performing three GCD cycles at a C-rate of 0.1C, to promote the formation of the SEI. This process is crucial for enhancing the long-term performance of the coin cell and ensuring a

stable electrode/electrolyte interface. Throughout this stage, the electrochemical behaviour is monitored to evaluate the activation of the cell prior to conducting additional analysis.

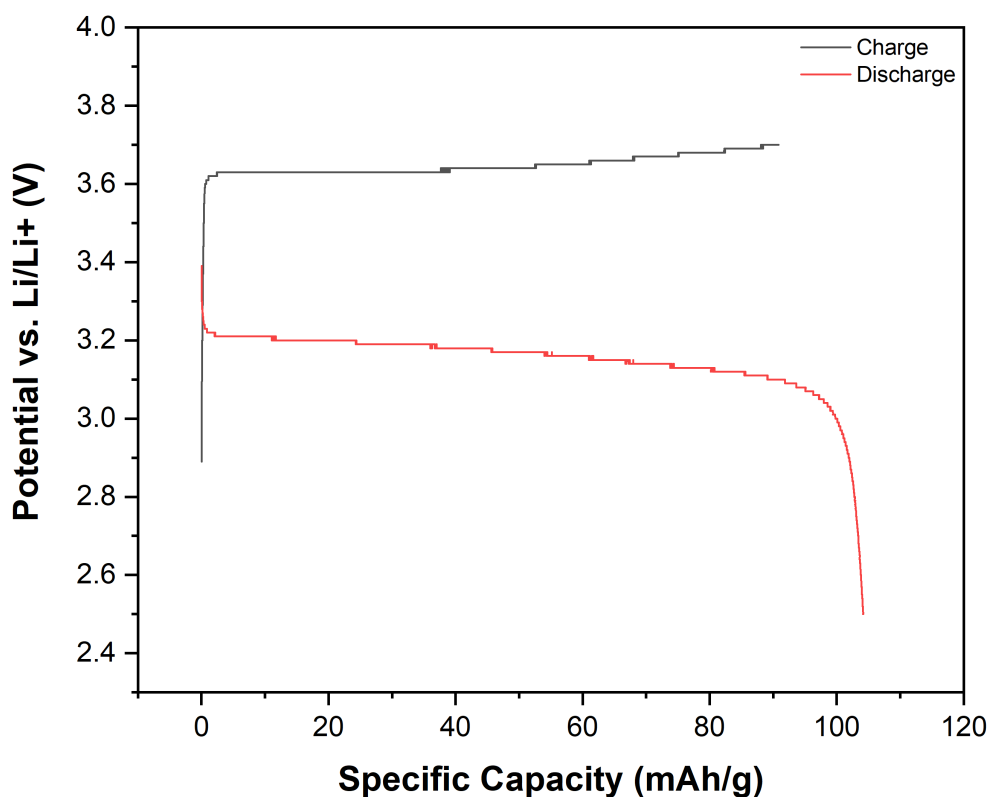


Figure 44. Galvanostatic charge-discharge profiles of a representative LFP | Li half-cell from the third cycle.

In Figure 44, The charge-discharge curves from the third cycle of the same LFP | Li half-cell of the CV analysis are displayed, as this stage provides a more representative assessment of the cell's performance. To begin with, it is worth noting that the charge-discharge profiles exhibit discrete steps instead of a smooth profile, which can be attributed to the data acquisition settings. The measurement was performed with an insufficient resolution to capture the continuous voltage variation during rapid cycling. The voltage plateau observed in both charge and discharge reflects the two-phase coexistence region between LiFePO_4 and FePO_4 during lithium intercalation/deintercalation.²⁰¹ The plateau in charge has a slightly higher potential than in discharge, a behaviour consistent with the intrinsic electrochemical hysteresis of LiFePO_4 .²⁰² The curves demonstrate the characteristic voltage plateau of the LiFePO_4 system at approximately 3.2 V vs. Li^+/Li . The specific capacity reaches a maximum of 120 mAh/g, which is slightly lower than the nominal value (135 mAh/g) provided by the manufacturer. Such deviations are commonly reported and may be attributed to the formation of lithium dendrites and excessive growth of the SEI, both of which can lead to partial loss of active material during cycling.^{203,204}

EIS was intended to be performed after cycling to compare the Nyquist plot with the one obtained before, enabling the assessment of changes in internal resistance. This analysis would provide insight into the formation of the SEI layer, which is expected to modify the impedance response due to the stabilisation of interfacial processes. However, it was not possible to obtain this measurement within the required timeframe. The appearance of a second semicircle at high frequencies would have been expected, corresponding to the resistance of the SEI layer (R_i), along with a decrease in internal resistance.²⁰⁰

The rationale behind this preliminary characterisation was to establish a robust screening process before proceeding to long-term performance evaluations. Only after a set of half-cells (usually three to five) containing the same materials successfully passed the initial electrochemical tests would it be considered worthwhile to advance that setup to extended cycling experiments. This stepwise approach ensures that only the most promising configurations undergo thorough evaluation, optimising experimental resources and enhancing the reliability of subsequent findings. Long-term performance analysis typically includes galvanostatic cycling over hundreds of cycles to assess capacity retention, coulombic efficiency, and potential degradation mechanisms. Moreover, aging tests, such as prolonged open-circuit storage and rate capability studies, would provide further insights into the stability of the electrolyte and electrode materials under real operating conditions.

CHAPTER 5 – CONCLUSION AND FUTURE PERSPECTIVES

This dissertation explored the synthesis and characterisation of a NaCMC-based SPE, aiming to contribute to the advancement of safer and more sustainable materials for SSBs. A systematic approach was adopted to investigate the influence of varying concentrations of LiTFSI and glycerol on the physical, chemical, mechanical, optical, and electrochemical properties of the membranes.

Through comprehensive characterisation, a consistent behavioural pattern was identified: the dissociation capacity of the polymer matrix towards the salt was confirmed to reach its limit at approximately 150% LiTFSI loading, with crystallisation observed at 200% in the absence or at low levels of plasticiser. This crystallisation was progressively mitigated with increasing glycerol concentrations, highlighting its critical role in promoting salt dispersion. Furthermore, the experimental results aligned with previous literature reports, confirming that LiTFSI enhanced the number of charge carriers and, consequently, the ionic conductivity, up to an optimal concentration (in this case, 150% salt) beyond which a reverse effect was observed. In parallel, glycerol incorporation not only improved the mechanical flexibility of the membranes but also facilitated polymer chain mobility, thereby further promoting ionic transport.

Key electrochemical and physicochemical results further validate the system's potential. Although the 1:2 NaCMC-to-glycerol ratio and 150% LiTFSI loading (CMC@G₂@LiTFSI₁₅₀) film exhibited the highest ionic conductivity (4.40×10^{-4} S/cm), its mechanical fragility and limited handling stability rendered it less practical for further application. Therefore, the 1:1 NaCMC-to-glycerol ratio and 50% LiTFSI loading (CMC@G₁@LiTFSI₅₀), presenting a conductivity of 2.62×10^{-5} S/cm with more consistent ionic behaviour over a temperature range and reduced material consumption, was identified as the most promising formulation. This selection reflects an optimal compromise between electrochemical performance, mechanical integrity, and sustainability considerations.

In terms of mechanical performance, glycerol incorporation enhanced membrane flexibility, but excessive plasticiser content was observed to compromise tensile strength. A comparison between formulations highlights this trade-off: CMC@G₂@LiTFSI₁₅₀ presented a $F_{\max}$ of 0.82 ± 0.25 N, an ϵ_b of $93 \pm 20\%$, and a E of 0.133 ± 0.021 MPa, whereas CMC@G₁@LiTFSI₅₀ exhibited superior mechanical robustness, with $F_{\max} = 3.0 \pm 1.4$ N, $\epsilon_b = 58 \pm 15\%$, and $E = 0.51 \pm 0.10$ MPa.

Additionally, the membranes exhibited thermal stability up to approximately 160–230 °C, ensuring their suitability for battery integration.

Morphological features and surface wettability of the SPEs were also studied, confirming the predominantly amorphous character of the membranes and their moderate hydrophilicity, which is advantageous for promoting ionic conductivity and ensuring good interfacial contact with the electrodes. Overall, the developed SPEs exhibited promising properties for battery integration, including flexible mechanical behaviour, satisfactory thermal stability and moderate hydrophilicity. Nonetheless, their ionic conductivity remained below the ideal threshold of 10^{-3} S/cm, highlighting a common limitation observed in SPEs. Achieving a balanced trade-off between conductivity, mechanical robustness, and interfacial compatibility will be critical for future optimisation efforts.

The interaction between the SPEs and loop antenna sensors confirmed that the membranes influenced the dielectric environment of the sensors, leading to measurable shifts in resonance peaks. These preliminary findings suggest the feasibility of integrating such flexible electrolytes into passive wireless sensing platforms for *in situ* and *in operando* monitoring of SSBs.

In parallel, the assembly and initial testing of lithium half-cells provided valuable groundwork for subsequent investigations. Although the direct integration of the synthesised SPEs into coin cells was not achieved, the protocols established during this phase—despite requiring further optimisation—provided valuable insights into the challenges of achieving reproducibility and may serve as a solid foundation for future electrolyte evaluation.

While this research advances the understanding of NaCMC-based SPEs, certain limitations were identified. The drying process, although improved by the implementation of a temperature ramp, could benefit from further optimisation to enhance membrane uniformity and minimise surface defects. Additionally, the potential sensitivity of the membranes to ambient humidity warrants further investigation, particularly in the context of long-term battery operation. From a compositional standpoint, exploring intermediate salt concentrations around the 150% threshold, together with a more detailed assessment of the optimal plasticiser content, could enable the identification of formulations offering the best compromise between critical properties for battery integration, while potentially enhancing material sustainability.

Building upon the foundations established in this work, future research should aim on testing the most promising SPE formulations in lithium-metal half-cell configurations, in order to systematically evaluate their practical electrochemical performance. It is essential to recognise that the formulation exhibiting the highest ionic conductivity may not necessarily deliver the best overall performance, given the critical need to preserve mechanical and thermal properties. Therefore, several formulations demonstrating a balanced combination of these attributes should be shortlisted for further development.

Subsequently, efforts should focus on continuing the experimental work required to integrate the sensors into the membranes, as an initial step before advancing to battery testing and progressing towards the development of multifunctional SSBs.

Ultimately, the insights generated by this research pave the way for a holistic approach to battery development, where electrolyte engineering and smart sensing technologies converge to address the challenges of next-generation ESSs.

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