

**STUDY OF POLYMER ELECTROLYTE
FOR ENERGY STORAGE DEVICE**

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**A project report submitted in partial fulfilment of the
requirements for the award of Bachelor of Materials
Engineering with Honours**

**Lee Kong Chian Faculty of Engineering and Science
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ABSTRACT

The development of high-performance solid polymer electrolytes (SPEs) is critical for the advancement of safe and efficient solid-state energy storage devices, such as Electric Double-Layer Capacitors (EDLCs). This study investigates the enhancement of a poly(ethyl methacrylate) (PEMA) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) host matrix through the incorporation of various ceramic fillers, specifically Barium Titanate (BaTiO_3), Lithium lanthanum zirconium tantalum oxide (LLZTO), Titanium Dioxide (TiO_2), and Zinc Oxide (ZnO). Using the solution casting method, composite membranes were fabricated and characterized to evaluate their structural and electrochemical properties. Material characterization via XRD and SEM revealed that while the electrolytes remained predominantly amorphous, the micro-sized ($\sim 20\text{ }\mu\text{m}$) filler particles led to localized dispersion challenges and interfacial wetting issues. Electrochemical analysis identified the 2 wt% BaTiO_3 formulation (BSPE-2) as the optimal composition, achieving a superior ionic conductivity of $5.28 \times 10^{-5}\text{ S/cm}$ and an exceptionally wide stability window of 6.2 V. When integrated into an EDLC, the system demonstrated a specific capacitance of 11.02 F/g, an energy density of 0.462 Wh/kg, and a power density of 83.14 W/kg. However, cyclic stability testing showed a significant 55.5% energy density drop over 500 cycles, indicating poor long-term durability. It is concluded that while BaTiO_3 significantly boosts short-term performance and voltage stability, the large particle size contributes to mechanical degradation. Future recommendations include transitioning to nano-sized fillers and refining fabrication techniques, such as doctor blade coating and the addition of solid plasticizers, to ensure interfacial integrity and commercial viability.

Keywords: Solid polymer electrolyte; PEMA; BaTiO_3 ; EDLC; Ionic conductivity; Ceramic fillers

Subject Area: Materials Science / Energy Storage

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CHAPTER 1 INTRODUCTION

1.1 General introduction

Electricity is a foundational invention that brings convenience to our lives. It not only frees our hands, saves our time, and even brings entertainment to us, letting us have more opportunities to develop this world. According to technological development, the demand for electricity is increasing. This shows that technology is becoming more critical in managing electricity to use energy more efficiently and reduce waste. In an electrical cycle, there is the source (production), intermediate (power transmission, storage), and terminal (usage). The total electrical efficiency is directly affected by each part of them; all phases in the cycle are critical for continuous research and development. For example, the source is the power plant; to increase its efficiency through increasing the conversion ratio, for power transmission it can be through reducing the electrical resistance and increasing the transmission voltage, and for the terminal phase through reasonable allocation of energy usage with the software system and so on.

In these related important techniques, energy storage is one of the parts which is a process of storing energy produced continuously for future use; it helps to balance the mismatching between relatively continuous and stable energy production with chaotic and disordered energy demand. For a simple example, coal fuel power plants have stable production while urban electricity usage is usually high demand at night, low demand at noon. A good energy storage system absolutely has high strategic significance in balancing energy supply and demand because it is essential for grid stability and efficient energy use, especially with intermittent renewable energy. Besides, the portable energy storage components are important in mobile devices, such as smartphones, automobiles, and so on. The characteristics of this kind of energy storage are being relatively lightweight, suitable for easy loading and unloading, and usually designed to have high energy density and power density for better and more efficient performance to increase product competitiveness. Typical energy storage types include batteries and supercapacitors, of which supercapacitors have several branches such as electric double-layer capacitors (EDLCs), pseudo capacitors, and hybrid supercapacitors (Chen & Holze, 2024). Although these energy storage components have been separated into several different categories, their basic mechanisms are the same: storing the electrical energy in a different energy form

during charging and converting the corresponding energy to electrical energy to be powered into the connected circuit during discharging. At the same time, energy storage does not have any internal power generation characteristic, meaning that they are energy limited, and recharging is required. Based on the different energy storing mechanisms, batteries have higher energy density but lower power density than supercapacitors. These properties show that batteries have deeper and larger capacity that can store more energy at one time while supercapacitors have higher power rates that can rapidly produce a large amount of energy in a while and store energy faster during charging. Since the power density of supercapacitors is extremely higher than batteries, it has huge potential in the energy storage field if its energy density property can have a breakthrough.

Among three categories of supercapacitors, EDLCs have the highest power density, so this project will mainly focus on them. As a capacitor, the EDLCs' basic components are electrodes, electrolyte, conductive ions, and so on. Here, the development of EDLCs is focused on the electrolyte, specifically the polymer electrolyte. Different from liquid electrolyte, polymer electrolyte offers a potential solution for safety, smaller density, and flexible energy storage devices. Polymer electrolytes present in gel, solid, or composite form physical properties which reduce the risk of leakage and thermal evaporation, impart better mechanical flexibility and processability, lightweight properties for convenient portability, and so on (Chen & Holze, 2024). Significant work since the 1970s (starting with PEO: Li systems) has focused on improving conductivity and mechanical stability to make them viable for energy storage applications. This has been followed by a lot of related research to expand and develop the technology level in the polymer electrolyte field, increasing the safety, energy storing capacity, and mechanical properties without compromising the power density.

1.2 Important of Study

Energy storage plays an important role in the modern sustainable energy intermediate transition. While lithium-ion batteries occupy the mainstream in this field due to their excellent energy density and relatively high voltage provided, they have drawbacks regarding safety concerns (flammability, thermal runaway, and potential leakage problems) and limited lifetime durability due to uncontrollable charging deposition positions.

EDLCs matched with polymer electrolytes are highly capable of solving these issues regarding both safety and lifetime. So, the development of polymer electrolytes for EDLCs offers a feasible solution to these challenges, making this study important for several reasons:

- Safety and Stability Enhancement

Traditional liquid electrolytes have strong fluidity properties, which easily lead to leakage problems during use. At the same time, the solutes of the electrolyte usually have highly active properties for better storing performance; their risk factors are increased also. Once the electrolyte leaks and the active elements directly contact the oxygen atmosphere, spontaneous combustion is unavoidable, which brings flammability issues (Chattopadhyay et al., 2023). In contrast, polymer electrolytes are almost always tailored and designed in gel or solid form, eliminating these potential hazards by providing a non-leaking and relatively thermally stable medium for ion transport (Chen & Holze, 2024).

- Longer Lifespan and Durability

One of the critical advantages of polymer electrolytes is their ability to significantly extend the lifespan of EDLCs. Traditional liquid electrolytes degrade over time due to solvent decomposition, electrode corrosion, and side reactions, leading to capacity fading and requiring maintenance. In contrast, polymer electrolytes impart superior cycling stability. This extended lifespan reduces maintenance costs and enhances the economic viability of EDLCs for long-term applications such as renewable energy storage and industrial power backup systems (Chen & Holze, 2024).

- Flexibility and Device Integration

Due to the two main physical forms of polymer electrolytes, it is possible to tailor the suitable form for specific energy storage devices depending on their requirements. Solid form polymer electrolytes provide extra support to the EDLCs, which are suitable for devices that usually experience shocks or semi-permanent devices (which last a longer time and reduce maintenance fees). Gel form and solid thin-film polymer electrolytes impart flexibility, making them suitable for wearable electronics and flexible displays. Unlike the limitations of rigid liquid-based systems, polymer electrolytes also can be tailored into various geometries, improving electrode-electrolyte contact and device durability (Chattopadhyay et al., 2023).

- Improved Energy and Power Density

As energy storage devices, EDLCs have a serious drawback: extremely low energy density properties compared to batteries. This is like a bank, but the savings limit is only 1000. In contrast, they have high power density, which means a faster charging and discharging rate. So, scientists and engineers try to develop EDLCs for larger energy storage capacity without compromising their power density simultaneously. Power density is decided by the ionic conductivity in the electrolyte medium; while liquid-based electrolytes usually have higher ionic conductivity than polymer electrolytes, solid forms especially have the poorest conductivity (Muñoz et al., 2024).

- Advancing Next-Generation Energy Storage

The integration of polymer electrolytes into EDLCs supports the transition toward clean energy systems. Renewable energy sources like solar and wind require efficient storage solutions to mitigate intermittency. EDLCs with high-performance polymer electrolytes can provide rapid and wide energy buffering, grid stabilization, and regenerative braking in electric vehicles. What is certain is that no matter how fast the technological progress and iteration are in the future, EDLCs will still be a major trend in the future energy storage direction (Chen & Holze, 2024).

1.3 Problem Statement

Although polymer electrolytes impart many advantages in EDLCs, there are still some critical challenges that remain without a solution, limiting the overall performance and obstructing their widespread application. Their limitations mainly come from fundamental inherent material properties and engineering obstacles which lower their competitiveness with traditional liquid electrolytes. The key problems are:

- Low Ionic Conductivity at Room Temperature

Most polymer electrolytes have significantly lower ionic conductivity (10^{-5} – 10^{-3} S/cm) compared to liquid electrolytes (above 10^{-2} S/cm) at room temperature. This problem, particularly in pure solid polymer electrolytes such as PEO, is more severe, slowing down the charging and discharging times. This results in higher internal resistance and reduced power delivery (lower power density), especially in high-current applications (Chen & Holze, 2024).

- Trade-Off between Mechanical Properties and Ionic Conductivity

While increasing polymer flexibility enhances ionic conductivity through the addition of plasticizers, it compromises the electrolytes' mechanical strength. Suitably optimizing the mechanical strength and ion conductivity of polymer electrolytes requires engineering tailored with balance; it is quite a challenge to maintain the overall performance (Chen & Holze, 2024).

- Interfacial Resistance at Electrode-Electrolyte Boundary

Poor adhesion between rigid polymer electrolytes and porous carbon electrodes creates high charge-transfer resistance, reducing effective capacitance and energy efficiency. Besides, polymer electrolytes have poor fluidity and high viscosity compared to liquid-based electrolytes; it is difficult for them to immerse themselves completely into the porosity of electrodes, which also causes the negative impacts above because these electrode-electrolyte boundaries are critical in EDLC energy storage (Zhao et al., 2025).

- Environmental Sensitivity

Polymer electrolytes may degrade with cycling or environmental exposure, affecting capacitance, leakage resistance, and performance. Hydrogel-based polymer electrolytes often suffer from water evaporation in dry conditions or swelling in humid environments, causing performance degradation. Since polymer materials are inherently heat sensitive, and the application scenarios of energy storage usually are accompanied by high temperatures, degradation is almost unavoidable (Foran et al., 2020).

1.4 Aim and Objective

1.4.1 – Aim

To develop and optimize a solid polymer electrolyte (SPE) membrane based on poly(ethyl methacrylate), PEMA incorporated with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and ceramic additives (BaTiO₃, TiO₂, LLZTO, ZnO) for application in EDLCs, focusing on enhancing ionic conductivity, mechanical stability, and electrochemical performance.

1.4.2 - Objective

1. To formulate and fabricate solid polymer membrane electrolytes composed of PEMA + LiTFSI with varying concentrations of additives via appropriate solution casting or melt mixing techniques.
2. To characterize the structural and morphological properties of the developed electrolytes using techniques such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) to determine crystallinity, functional group interactions, and the dispersion of additives.
3. To measure ionic conductivity using electrochemical impedance spectroscopy (EIS).
4. To compare the effects of different ceramic additives on overall performance to identify the most promising formulation for high-performance EDLC applications.
5. To assess the electrochemical stability window and capacitance performance of the optimized electrolyte through cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), and linear sweep voltammetry (LSV) using electrochemical stability tests in EDLC configurations.

1.5 Scope and Limitation

1.5.1 - Scope

This study focuses on the performance of EDLCs, with the main emphasis on polymer electrolytes. The key scope points are:

- The study focuses on the performance of EDLCs, with the electrolyte as the main research target.
- A PEMA-based solid polymer electrolyte membrane is investigated due to its safety and potential lifespan advantages.
- LiTFSI is used as the ionic salt at a fixed concentration, providing mobile ions for conductivity.

- The main variable studied is the addition of ceramic additives to improve ionic conductivity.
- Carbon-based electrodes are kept constant to minimize experimental variability.
- As the electrolyte is in solid membrane form, no separator is required.
- Lab-scale EDLCs are fabricated and tested under identical conditions for reliable comparison.
- Electrochemical and structural performance is evaluated using advanced characterization methods.

1.5.2 - Limitation

This study is limited in several aspects. The study focuses only on certain materials and is conducted under laboratory conditions. The key limitations include:

- The study is limited to PEMA-based solid polymer electrolytes with selected ceramic additives.
- LiTFSI concentration is fixed and not optimized.
- Electrode properties are not modified or optimized.
- The work is restricted to lab-scale fabrication and testing under controlled conditions.
- Long-term stability, scalability, cost, and environmental impact are not assessed.

1.5 Contribution of Study

This research contributes significantly to the study of PEMA-based electrolytes for EDLCs by identifying the optimal weight percentage of additives to achieve good performance. A major contribution is the identification of BaTiO₃ as a highly effective filler, expanding the electrochemical window to 6.2 V and increasing conductivity to the 10⁻⁵ S/cm range. By transitioning to this solid-state system, the study promotes safer energy storage that eliminating risks like electrolyte leakage, internal shorting, and the production of harmful gases. Finally, the discovery of a 55.5% energy density reduction after 500 cycles provides a critical baseline for long-term reliability, proving that high conductivity must be balanced with operational durability.

1.6 Outline of Report

This section discusses five sequential chapter content:

- i) **Chapter 1 Introduction** – Introduces the research background, problem statement, objectives, and the significance of the study.
- ii) **Chapter 2 Literature Review** – Establishes a theoretical framework for the study through academic studies and research.
- iii) **Chapter 3 Methodology and Workplan** – Describes the materials, fabrication techniques for the samples, the analytical equipment used, and the research plan.
- iv) **Chapter 4 Results and Discussion** – Presents the experimental results and provides a critical analysis and comparison of the findings against established studies.
- v) **Chapter 5 Conclusions and Recommendations** – Summarizes the key findings in relation to the research objectives and proposes directions for future work.

CHAPTER 2 LITERATURE REVIEW

2.1 Introduction

The fabrication of electric double-layer capacitors with solid polymer electrolytes typically begins with electrode preparation, gel formation, cell assembly, and thermal treatment. Activated carbon is commonly used as the electrode material because of its high surface area, which is essential for forming an effective double-layer charge storage interface. The activated carbon is mixed with a conductive additive, such as carbon black, and a binder to form a slurry. This slurry is then uniformly coated onto aluminium foil, which serves as the current collector, and dried to form a stable electrode layer (Arora et al., 2024).

For the electrolyte, the polymer, lithium salt, and other components such as plasticizers or fillers are dissolved in a suitable solvent to form a homogeneous gel precursor. Instead of forming a separate SPE film, the gel is directly introduced during assembly. In the assembly stage, the gel is evenly applied between the two prepared electrodes, ensuring intimate contact with both the electrode layers and the aluminium collectors. This configuration forms a compact sandwich structure where the gel completely infiltrates the porous structure of the electrodes, which enhances ionic transport and interfacial adhesion.

Once the assembly is complete, the entire structure is subjected to oven baking or thermal treatment under controlled conditions. This process evaporates the residual solvent and solidifies the gel into a uniform solid polymer electrolyte layer, effectively converting the gel form into a stable SPE while maintaining strong adhesion between the electrolyte and the electrodes. The result is a robust, integrated EDLC cell with minimized interfacial resistance and improved mechanical stability (Arora et al., 2024).

After fabrication, the EDLC undergoes comprehensive electrochemical characterization. Tests such as cyclic voltammetry, galvanostatic charge-discharge, and electrochemical impedance spectroscopy are performed to evaluate capacitance, ionic conductivity, internal resistance, and cycling performance. This fabrication method, combining direct gel infiltration within situ SPE formation, provides excellent electrode-electrolyte contact, leading to improved performance and scalability for both laboratory studies and industrial production (Arora et al., 2024).

2.1.1 - Energy Storage

Energy storage devices are systems that store energy for later use, helping to balance supply and demand, improve efficiency, and make renewable energy more practical. They can be classified in different ways, but in electrochemical applications, the main types are batteries, supercapacitors, and hybrid devices. Each has its own energy storage mechanism, performance characteristics, and application range.

Batteries store energy through chemical reactions inside the electrodes and electrolyte. When charging, electrical energy is converted into chemical energy by moving ions from one electrode to another, and during discharge, the chemical energy is converted back into electrical energy. The reaction is reversible so the battery can be reused, but over time the electrode materials degrade and capacity drops. Common battery types include lithium-ion, lead-acid, nickel-metal hydride, and sodium-ion. Lithium-ion batteries are widely used because they have high energy density and good efficiency; they typically have a gravimetric energy density (energy per unit weight) in the range of 150–250 Wh/kg. However, they have moderate power density and a limited lifetime compared to supercapacitors (Official, 2025).

Supercapacitors store energy without chemical reactions, using electrostatic charge separation or fast surface redox reactions, so they can charge and discharge very quickly and last for hundreds of thousands of cycles. There are three main types which are shown in Fig 2.1. Electric Double Layer Capacitors (EDLC) store charge through the formation of electric double layers at the electrode–electrolyte interface. Typical EDLC devices have energy densities in the range of 5–6 Wh/kg (Burke & Zhao, 2022).

Pseudocapacitors store energy through fast, reversible faradaic reactions at or near the electrode surface, giving higher capacitance but slightly lower cycle life than EDLCs. Hybrid capacitors combine features of both EDLCs and pseudocapacitors, with one electrode storing charge electrostatically and the other through faradaic reactions, resulting in higher energy density than EDLCs but still being faster than batteries (Chen & Holze, 2024) (Elalfy et al., 2024).

Hybrid energy storage devices combine battery-type electrodes with capacitor-type electrodes in the same system to balance energy density and power density. In a typical hybrid mode, one electrode works like a battery (faradaic reaction) and the other like a capacitor (electrostatic storage) (Elalfy et al., 2024). Lithium-ion capacitors (LICs) are an

example where the negative electrode is usually pre-lithiated carbon (battery-like) and the positive electrode is activated carbon (capacitor-like). This design allows for higher energy density than supercapacitors and higher power density than batteries, making hybrids suitable for applications where both quick bursts of power and decent storage capacity are required.

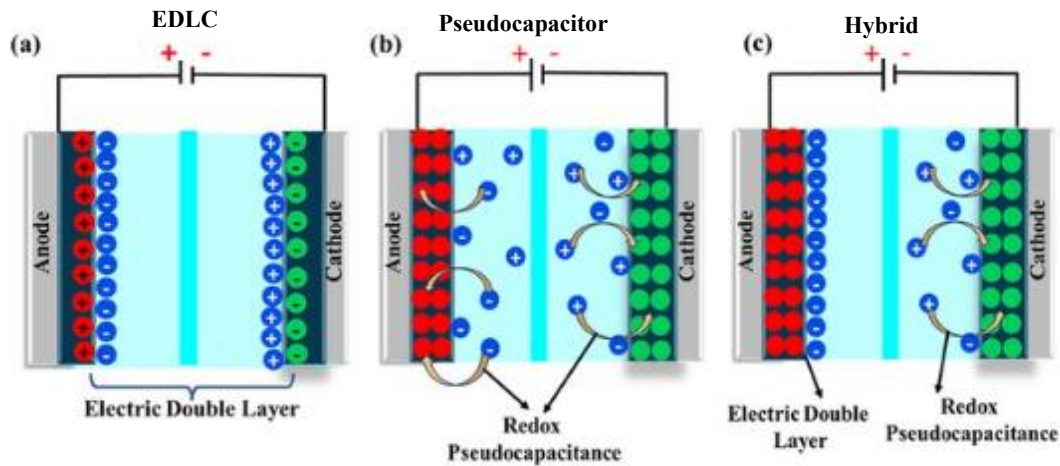


Fig 2.1 Schematic illustration and charge storage mechanism of a) EDLC, b) Pseudocapacitor, and c) Hybrid supercapacitor (Iqbal et al., 2025).

In summary, batteries are best for high energy density but have slower charge/discharge and shorter cycle life. Supercapacitors, especially EDLCs, are best for high power and long life but have lower energy density. Hybrid devices aim to bridge this gap by combining the advantages of both systems. The choice between these devices depends on the application's needs for power, energy, cycle life, cost, and safety; ongoing research focuses on improving materials and designs to make them more efficient and versatile.

2.1.2 - EDLC Working Principle

An Electric Double Layer Capacitor is a type of energy storage device that stores electrical energy by the electrostatic separation of charges at the interface between the electrode and the electrolyte. It does not use a dielectric layer like a normal capacitor but stores energy through the formation of an electric double layer on the electrode surface. When voltage is applied, ions from the electrolyte move and arrange themselves at the surface of the porous

electrode with opposite charges, forming two layers separated by a very small distance (nanometer scale). Because of this very small separation and the large surface area of the electrode, EDLCs can achieve much higher capacitance than normal capacitors. The charge storage process in an EDLC is non-faradaic, meaning no chemical reaction happens, so the device can have a very long cycle life, fast charging and discharging, and high-power density (Elalfy et al., 2024).

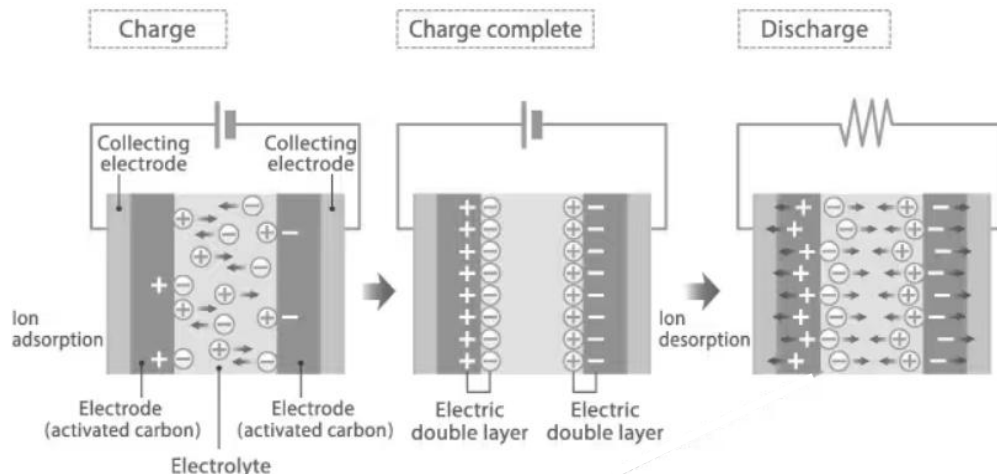


Fig 2.2 EDLC Charge/Discharge (EDLC: High-Power Energy Storage, 2026)

An EDLC is usually made from two high surface area carbon-based electrodes (such as activated carbon, carbon nanotubes, or graphene), a conductive current collector, and an electrolyte, which is shown in Fig 2.2. The current collector allows electrons to be collected from the electrodes into the connected circuit. The electrolyte can be aqueous, organic, or an ionic liquid, and the choice will affect the device performance. During charging, cations move toward the negative electrode and anions move toward the positive electrode, creating the electric double layer at both sides. Because no chemical change occurs, EDLCs can be charged and discharged for hundreds of thousands of cycles with very little performance loss (Aziz et al., 2019).

EDLCs can be divided into different types based on the electrolyte or the electrode design. Based on the electrolyte, the aqueous type (such as KOH or Na₂SO₄ solution) has high ionic conductivity and low resistance, but the working voltage is limited to around 1 V because of water decomposition. The organic type (such as TEABF₄ in acetonitrile or propylene carbonate) allows a higher voltage of around 2.5–3 V, giving higher energy density, but the conductivity is lower and the solvents can be flammable. The ionic liquid

type can work up to around 4 V and has high thermal stability, but the viscosity is high and the cost is higher. Based on electrode design, EDLCs can be symmetric, where both electrodes are made of the same material, or asymmetric/hybrid, where the electrodes have different surface properties to improve ion storage (Balducci, 2016; Mendhe & Panda, 2023).

The performance of an EDLC mainly depends on the surface area and pore structure of the electrode, the conductivity and stability of the electrolyte, and the compatibility between the electrode and electrolyte. To get high performance, the electrolyte should have high ionic conductivity, a wide voltage window, good thermal stability, and be stable with the electrode material. Because of this, many studies are now focusing on polymer electrolytes—such as solid polymer, gel polymer, or composite polymer electrolytes—as an alternative to liquid systems. By improving both the electrode and electrolyte, EDLCs can offer a balance between high power density, fast charge/discharge, and a long lifetime, making them suitable for applications ranging from portable devices to large energy storage systems.

2.1.3 – Ion Transport Mechanism in Polymer Electrolytes

The first step for ion transport in polymer electrolytes is the dissociation of the lithium salt inside the polymer host. When the salt dissolves, it separates into mobile cations and bulky anions. The anions are usually less mobile, while the cations interact with polar functional groups in the polymer, such as ether oxygen or carbonyl oxygen atoms. After dissociation, the cations can migrate through several different transport mechanisms.

One of the main mechanisms is polymer segmental migration (continuous motion), where the mobility of the polymer backbone segments helps to carry the ions along with the chain movement. The dynamic motion of the polymer opens and closes free volume in the matrix, creating a continuous pathway for cation migration, which is shown in Fig 2.3.

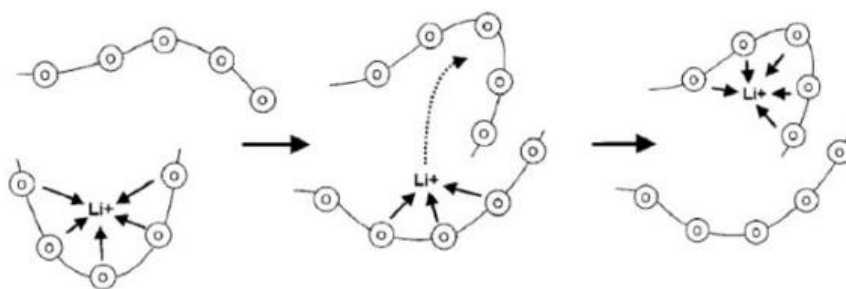


Fig 2.3 Polymer Segmental Migration (Yang & Hou, 2012)

Another mechanism is called vehicular transport, which occurs when ions move together with a coordinating group or solvent molecule that acts as a “vehicle.” In this case, the ion is not moving independently but is transported as part of a larger complex through the polymer matrix.

The third mechanism is ion hopping, where the ions jump from one coordinating site to another within the polymer host. These coordination sites are usually provided by polar atoms like oxygen, and the hopping process occurs when an ion breaks the temporary bond at one site and re-associates at the next site.

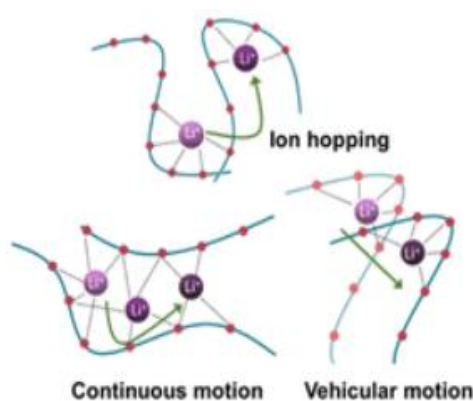


Fig 2.4 Ions Transport Mechanism (Gudla et al., 2025)

In practice, the overall ion transport in solid polymer electrolytes is the result of a combination of these processes. Salt dissociation provides the mobile charge carriers, while polymer segmental motion, vehicular transport, and ion hopping together enable the continuous movement of ions through the electrolyte matrix.

2.1.4 - Polymer Electrolyte

Polymer electrolytes are a type of electrolyte where a polymer-based matrix is used to hold and transport ions. They are usually in solid or gel form, and the ion transport happens through the movement of ions in the polymer chain. Compared to liquid electrolytes, polymer electrolytes can offer better safety because they have less leakage and are generally more stable to use. They also have advantages such as being flexible, lightweight, and easy

to shape into thin films, which makes them suitable for compact or flexible energy storage devices.

The ion conductivity of polymer electrolytes depends on several factors, such as the mobility of the polymer chains, the number of available ion carriers, and the interaction between the ions and the polymer. Lowering the crystallization level and increasing the amorphous phase in the polymer can improve ion mobility, because the polymer chains have more flexibility and it is easier for ion movement. However, polymer electrolytes usually have lower ionic conductivity compared to liquid systems, especially at room temperature. To overcome this problem, different modification methods can be applied, such as adding plasticizers to increase chain mobility or adding fillers to improve ion conductivity and mechanical properties (Mendhe & Panda, 2023).

Another important feature of polymer electrolytes is their ability to provide a wider electrochemical stability window. This allows them to be used in devices that operate at higher voltages without decomposing. They can also act as both the electrolyte and separator, simplifying the design of the device. Due to these benefits, polymer electrolytes are widely developed for applications in various electrochemical systems, including EDLCs where a well-balanced ion conduction and good mechanical integrity are needed for long-term cycling and high performance.

2.1.5 – Comparison between Gel and Solid PE

Gel polymer electrolytes (GPEs) and solid polymer electrolytes (SPEs) are both polymer-based systems for ion conduction, but they have different structures and performance characteristics. A GPE contains a liquid electrolyte trapped inside a polymer matrix, giving it high ionic conductivity close to that of liquid systems, because the liquid phase provides continuous ion transport pathways. The gel form also maintains flexibility and good contact with the electrode surface, which helps to reduce interfacial resistance. However, the presence of liquid components can affect long-term stability and safety, especially at high temperatures or over long cycling periods, as there is still a risk of solvent evaporation or leakage (Pour et al., 2024).

An SPE, on the other hand, is a completely solid system where ion transport happens through the polymer chains without any liquid phase. This gives higher safety, better mechanical strength, and better thermal stability compared to GPEs. An SPE can also act as both electrolyte and separator, which can simplify the device design. The main drawback is that SPEs usually have lower ionic conductivity at room temperature, because ion movement is limited by the segmental motion of the polymer chains. To improve this, methods like blending, adding fillers, or using plasticizers are often applied (Latif et al., 2021). Overall, GPEs offer higher conductivity and better interfacial contact, while SPEs provide better safety, mechanical stability, and structural integrity. The choice depends on the application needs and operating conditions.

2.2 Polymer Electrolyte Host Material

A polymer electrolyte host material is the main polymer matrix that holds the salt and provides the ion transport medium. The host material must have the ability to dissolve the salt and interact with the ions so that the ions can move through the polymer electrolyte structure. Generally, ion transportation in a polymer electrolyte happens through the movement of the polymer chain segments in the amorphous phase, so the material should have enough flexibility and a low glass transition temperature to allow chain movement (Mendhe & Panda, 2023).

At the same time, it needs to have good mechanical strength to form a stable membrane and maintain contact with the electrodes during device operation. Other important properties include a high decomposition voltage so the electrolyte can operate in a wide voltage window without decomposing, good thermal stability so it can work safely at elevated temperatures, and high wettability to impart good adhesion and low interfacial resistance. Polymers that have polar functional groups, such as ether, carbonyl, or nitrile, are generally more suitable because these groups can coordinate with the salt cations and help dissociate the salt into free ions. The choice of host material will strongly affect the ionic conductivity, mechanical stability, and electrochemical performance of the polymer electrolyte, so it is important to select or design a polymer that can balance these properties for the intended application.

2.2.1 - Polyethylene Oxide, PEO

Polyethylene oxide is a polymer with a linear chain structure that has ether oxygen atoms along the backbone. These oxygen atoms can coordinate strongly with lithium cations, which makes PEO good at dissolving lithium salts. PEO has both crystalline and amorphous phases; the crystalline part makes the polymer more rigid, while the amorphous part is more flexible and allows better chain movement. Ion transport mainly happens in the amorphous regions where the polymer chain movement helps carry the ions. PEO is also flexible, easy to process into thin films, and has moderate thermal stability, which makes it suitable for solid membrane-type electrolytes.

For solid polymer electrolytes, PEO is one of the most popular host polymers because of its strong interaction with salts and its ability to form stable membranes. However, at room temperature, PEO is semi-crystalline, and the crystalline regions slow down ion movement. This causes very low ionic conductivity at room temperature conditions. When the temperature increases, the crystalline parts soften or melt, the polymer chains gain more mobility, and the conductivity improves significantly. This means that pure PEO-based SPEs will work better at elevated temperatures (Chen & Holze, 2024; S. Liu et al., 2023).

The advantages of PEO include good flexibility, strong salt compatibility, easy processing, and the ability to act as both an electrolyte and a separator in a cell. It also has good adhesion to electrodes, which helps reduce interfacial resistance. However, the high crystallinity at room temperature limits its conductivity, and its electrochemical stability window is not very wide, usually up to around 3.8–4.0 V vs Li/Li⁺, which makes it less suitable for high-voltage devices unless it is modified. PEO also has moderate thermal and mechanical stability, so extra support or fillers are often needed for demanding applications.

For example, one study reported that a PEO-based SPE using PEO₂₀-LiDFOB (lithium difluoro(oxalato)borate) showed an ionic conductivity of about 2.46×10^{-6} S/cm at 30 °C (Polu & Rhee, 2016). This value is still considered low for practical room-temperature applications but is typical for unmodified PEO systems because of the high crystallinity that limits ion movement.

2.2.2 - Poly(ethyl methacrylate), PEMA

Poly(ethyl methacrylate) is an amorphous polymer with a flexible polymer chain and polar functional groups that can attract lithium ions from lithium salts. Its structure has less crystallinity compared to many other polymers, which means the polymer chains are more mobile and can provide better pathways for ion movement. PEMA also has good mechanical strength, moderate thermal stability, and good film-forming ability, which makes it suitable for fabricating thin, stable membranes. The adhesion between PEMA and electrode surfaces is also quite good, which helps provide good contact and reduce interfacial resistance.

For solid polymer electrolytes, PEMA is considered a good candidate because its amorphous nature supports ion transport even at room temperature. Unlike PEO, PEMA does not form large crystalline regions that block ion migration, so the ion mobility is generally more stable at lower temperatures. However, pure PEMA still has limited ionic conductivity because the polymer chains alone cannot provide enough continuous ion pathways. This is why it is usually combined with salts, plasticizers, or ceramic fillers to improve conductivity and mechanical strength at the same time (Anuar et al., 2012).

The main advantages of PEMA in SPE systems are its amorphous structure, good mechanical properties, and strong adhesion to electrodes, which help with stable performance and cycling. It is also relatively easy to process into thin films and shows good compatibility with different salts and fillers. On the other hand, the conductivity of pure PEMA is still too low for high-performance devices, and its electrochemical stability window is not as wide as some advanced polymers, which can limit its use in high-voltage systems unless modified. For example, one reported study showed that incorporating 50 wt % LiTFSI into a PEMA matrix achieved an ionic conductivity of around $(1.22 \pm 0.01) \times 10^{-6}$ S/cm at room temperature (Yek et al., 2023). This value shows that while PEMA can dissolve a high amount of lithium salt and form a stable solid membrane, its ion transport is still limited without further modification.

2.2.3 - Poly(vinyl chloride), PVC

Poly(vinyl chloride) is another polymer that can be used as a host material for solid polymer electrolytes. PVC is known for its good mechanical strength, good chemical resistance, and easy processing into thin and stable films. It has a relatively high dielectric constant, which helps in dissolving and dissociating lithium salts to form more free ions for ion conduction.

The polymer itself is also quite stable in a wide range of temperatures and has decent electrochemical stability, which makes it suitable for use in energy storage devices. PVC membranes also have good adhesion to electrode surfaces, which helps reduce interfacial resistance and improves the stability of the electrolyte-electrode interface during cycling.

For SPE applications, PVC shows good potential because it can hold high amounts of lithium salt and maintain a stable structure. The amorphous regions in PVC allow some ion transport, but its ionic conductivity in its pure form is still low, so it usually needs to be modified or combined with plasticizers, co-polymers, or ceramic fillers to enhance its performance. These modifications help to increase chain mobility and create more ion pathways, improving the overall conductivity while maintaining mechanical integrity.

The main advantages of PVC as an SPE host are its mechanical strength, chemical stability, good salt compatibility, and strong adhesion to electrodes. It is also relatively cheap and easy to process, which makes it attractive for low-cost solid electrolyte systems. However, the disadvantages are the low ionic conductivity in pure PVC and the risk of brittleness if not properly modified. Its electrochemical stability window is also limited compared to some advanced polymers, which can restrict its use in high-voltage devices (Ramesh & Arof, 2001). One study reported that a PVC-based SPE containing 80 wt% PVC and 20 wt% LiClO_4 achieved an ionic conductivity of around $8.8 \times 10^{-10} \text{ S/cm}$ at room temperature (Rahman et al., 2008). This low value clearly shows the limitations of pure PVC systems, where the restricted polymer chain mobility and lack of continuous ion pathways greatly hinder ion transport.

2.2.4 - Poly(vinyl alcohol), PVA

Poly(vinyl alcohol) is a polymer that is widely used because of its good film-forming ability, high flexibility, and strong mechanical strength. It is also water-soluble and has good chemical stability, which makes it easy to process into membranes with uniform thickness. PVA contains hydroxyl groups along its backbone, which can form hydrogen bonds with salts or other additives, giving it good compatibility with different ionic compounds. It also has good adhesion to electrodes and reasonable thermal stability, which makes it suitable to be used as a host matrix in polymer electrolytes.

For solid polymer electrolyte applications, PVA is considered feasible because its flexible structure allows easier ion transport when combined with lithium salts or other ionic species. The hydroxyl groups help in salt dissolution and can assist in ion dissociation, but the pure PVA matrix alone usually cannot provide high ionic conductivity because of limited free volume and strong hydrogen bonding that restricts ion mobility. This is why PVA is often blended with other polymers, plasticizers, or fillers to improve its ionic conductivity and thermal stability. It is also commonly cross-linked to create membranes with better mechanical strength and lower solubility in humid conditions, which is useful for long-term stability in devices.

The advantages of PVA in SPEs are its low cost, easy processing, good mechanical strength, and compatibility with many additives. It also has good adhesion properties, which reduce interfacial resistance with electrodes. However, the disadvantages include low intrinsic ionic conductivity and a tendency to absorb moisture, which can sometimes affect stability and performance. The electrochemical stability window of PVA is also limited compared to some other polymers, which can restrict its use in high-voltage applications. One study reported that a PVA(30)–LiClO₄(10)–DMP(60) system, where DMP acts as a plasticizer, achieved an ionic conductivity of around 0.149×10^{-3} S/cm at 302 K (Rajendran, 2004). This result clearly shows how the incorporation of a plasticizer can significantly improve the ionic conductivity of a PVA-based electrolyte compared to pure PVA systems. The plasticizer increases the polymer chain mobility and creates more free volume, which allows ions to move more easily through the polymer matrix.

2.2.5 - Poly(vinylidene fluoride-co-hexafluoropropylene), PVDF-HFP

Poly(vinylidene fluoride-co-hexafluoropropylene) is another polymer that can be used as a host material for solid polymer electrolytes. PVDF-HFP is well known for its high mechanical strength, excellent thermal stability, and strong chemical resistance, which allows it to form thin and flexible membranes with good durability. The presence of hexafluoropropylene units in the copolymer reduces crystallinity compared to pure PVDF, resulting in more amorphous regions that help in ion transport. PVDF-HFP also has a relatively high dielectric constant, which helps in dissolving lithium salts and promoting ion dissociation, thereby providing more charge carriers for conduction.

For SPE applications, PVDF-HFP has shown good potential because the reduced crystallinity allows higher ionic mobility compared to pure PVDF, and the structure can accommodate lithium salt without losing mechanical stability. Modifications are often needed to increase the segmental motion of the polymer chains and provide continuous pathways for lithium-ion transport. The main advantages of PVDF-HFP as an SPE host are its strong mechanical properties, good thermal and electrochemical stability, high dielectric constant, and better amorphous nature compared to pure PVDF. It also offers good film flexibility, which makes it easier to fabricate thin membranes for devices. However, the disadvantages include relatively low-room temperature ionic conductivity, possible interfacial resistance issues, and the need for additives or plasticizers to achieve higher conductivity. In addition, processing PVDF-HFP often involves toxic organic solvents, and uniform filler dispersion can be a challenge in composite systems. These limitations mean that while PVDF-HFP is a promising polymer host, it still requires modification to reach the level needed for efficient solid-state EDLCs.

In one journal, it was reported that the incorporation of ceramic fillers into the PVDF-HFP matrix can further improve the ionic conductivity. For example, a PVDF-HFP/LiTFSI system with a weight ratio of 2:1 and containing 20 wt% of LLZTO showed an ionic conductivity of 4.93×10^{-5} S/cm at 30 °C (Yadav et al., 2023b). This result is much higher compared to a pure PVDF-HFP based electrolyte, indicating that modification is necessary to make PVDF-HFP based electrolyte more feasible in solid-state EDLC applications.

2.2.6 – Chitosan

Chitosan is a natural polymer that comes from the deacetylation of chitin, which is usually found in the shells of shrimp or crabs. It is well known for being biodegradable, non-toxic, and environmentally friendly, which makes it a green option for polymer electrolyte systems. Chitosan has a semi-crystalline structure with amino and hydroxyl functional groups along its backbone. These functional groups allow it to interact well with different lithium salts or fillers and make it possible to form stable films with good mechanical strength. It also shows good adhesion and reasonable thermal stability, which are important properties for making polymer electrolyte membranes.

For solid polymer electrolyte applications, chitosan is quite promising because its polar functional groups help in salt dissolution and ion coordination, which are useful for ionic transport. It can form flexible membranes and is often used in combination with plasticizers, salts, or inorganic fillers to enhance its ionic conductivity. The bio-origin and good film-forming ability make it easy to process, and its compatibility with many additives allows for different composite formulations. However, the pure chitosan matrix usually shows low ionic conductivity because the polymer chains are not mobile enough, and the semi-crystalline regions block smooth ion transport (Hamsan et al., 2020b).

The advantages of chitosan are its eco-friendliness, good mechanical stability, strong film-forming ability, and natural abundance, which also make it cost-effective. It also has good adhesion to electrodes and can reduce interfacial resistance. But the disadvantages include relatively low intrinsic conductivity, a limited electrochemical stability window, and sometimes moisture sensitivity, which may affect long-term device performance. One journal reported that a chitosan (55.6) + LiOAc (44.4) solid polymer electrolyte showed an ionic conductivity of around 10^{-8} S/cm at 302 K (Yahya & Arof, 2003). This result shows that pure chitosan-based electrolytes without any plasticizer or filler have very low ionic conductivity, which limits their direct use in high-performance devices.

2.3 Conductive Lithium Salt

Lithium salt is a key component in solid polymer electrolytes because it provides the mobile lithium ions (Li^+) needed for ionic conduction inside the polymer matrix. When the lithium salt dissolves in the polymer host, it dissociates into Li^+ cations and corresponding anions. The Li^+ ions then move through the polymer chains, usually by segmental motion of the polymer, while the anions remain mostly immobilized in the matrix. This ion transport is what allows the electrolyte to conduct charge between the electrodes, making it essential for the operation of energy storage devices like EDLCs, lithium-ion batteries, and other solid-state systems.

Lithium salts are widely used because lithium has a very small ionic radius and high electrochemical potential, which allows for efficient energy storage and high cell voltages. The choice of lithium salt can also influence the performance of the SPE, such as its ionic conductivity, electrochemical stability, mechanical properties, and compatibility with

electrodes. Common salts like LiTFSI, LiPF₆, or LiClO₄ are often used because they have good dissociation ability in polymer hosts and a wide electrochemical stability window.

In addition to providing Li⁺ ions, lithium salts help improve the overall stability of the electrode–electrolyte interface, reducing resistance and enabling better cycling performance. However, using too much salt can lead to problems such as ion clustering or reduced chain mobility, which can decrease ionic conductivity and flexibility of the membrane. Therefore, an optimal salt concentration is very important to balance conductivity, mechanical strength, and electrochemical stability. Overall, lithium salts are a critical factor in designing efficient and stable solid polymer electrolytes for advanced energy storage devices.

2.3.1 – LiTFSI

LiTFSI (lithium bis(trifluoromethanesulfonyl)imide) is one of the most common lithium salts used in solid polymer electrolytes because it has very good chemical and electrochemical stability, high thermal stability, and excellent dissociation ability in many polymer hosts. The large and delocalized TFSI[−] anion helps the salt dissolve easily in the polymer matrix, which makes it easier for the Li⁺ ions to move and improves ionic conductivity. LiTFSI also has a wide electrochemical stability window, usually above 4.5 V, which makes it suitable for high-voltage energy storage systems. It is less sensitive to moisture compared to some other lithium salts, so it is more stable during processing and handling.

For SPE applications, LiTFSI is very feasible because it provides high ionic conductivity when combined with a good polymer host, such as PEO, PEMA, or other compatible polymers. It can also maintain good stability during long-term cycling, which is important for solid-state devices. However, one drawback is that at very high concentrations, LiTFSI can reduce polymer chain mobility, which lowers ionic conductivity. It also tends to be expensive compared to other lithium salts, and in some cases, the large TFSI[−] anion can lead to interfacial issues with some electrode materials. Even with these limitations, LiTFSI is still one of the most promising lithium salts for SPEs because it provides a good balance of high ionic conductivity, wide voltage stability, and chemical compatibility, making it widely used in research and practical development of advanced energy storage devices.

In one journal, it was also reported that when different amounts of LiTFSI are incorporated into PEMA, the ionic conductivity changes significantly. When the LiTFSI content is increased, the ionic conductivity increases because more lithium ions are available to move through the polymer network (Yek et al., 2023). This shows that the salt concentration plays a big role in determining how well the polymer electrolyte performs.

2.3.2 - LiPF₆

LiPF₆ (lithium hexafluorophosphate) is a very common lithium salt that is widely used in liquid electrolytes and sometimes studied in solid polymer electrolytes. It has good ionic dissociation ability, which helps release Li⁺ ions for conduction, and it supports decent ionic conductivity when combined with a suitable polymer host. LiPF₆ also has good compatibility with many electrode materials, which makes it attractive for different types of energy storage devices. However, LiPF₆ is not very stable in moisture or at higher temperatures because it can decompose and release HF, which is corrosive and harmful to the electrolyte and electrodes.

For SPEs, the use of LiPF₆ is possible but less favourable compared to salts like LiTFSI. It can still provide usable ionic conductivity and can work in systems where proper sealing and dry processing are maintained. The main advantage is that it is cheaper and already well-studied in liquid systems, so adapting it to polymer systems can be easier. But the drawbacks are quite significant, including poorer thermal stability, the risk of HF generation, and a narrower electrochemical stability window compared to LiTFSI.

Because of these issues, LiPF₆ is less preferred in modern SPE research, but it is still explored in some cases where cost and availability are more important than long-term stability and performance. In one journal, it was reported that incorporating different amounts of LiPF₆ into the PVDF polymer matrix shows a clear trend in ionic conductivity, where higher salt content leads to higher ionic conductivity (Chiang et al., 2003). This is because more Li⁺ ions are able to move through the polymer chains, which helps to improve ion transport pathways.

2.3.3 - LiClO₄

LiClO₄ (lithium perchlorate) is one of the older lithium salts studied for solid polymer electrolytes. It has good ionic dissociation, so it can release Li⁺ ions easily and help achieve decent ionic conductivity in many polymer hosts. LiClO₄ is also relatively cheap and easy to handle, which made it popular in earlier research. It has a moderate electrochemical stability window and can work well with common polymers like PEO or PVC. However, LiClO₄ is quite sensitive to moisture and has safety concerns because the perchlorate anion can be reactive and even explosive under certain conditions, especially at high temperatures or when exposed to strong reducing agents.

For SPEs, LiClO₄ can still be used and can give reasonable performance, especially in systems designed for low-cost or experimental setups. It can provide a good level of ionic conductivity when the polymer host has enough flexibility to help ion movement. But the downsides limit its practical use, such as poor thermal stability, safety risks, and sometimes compatibility issues with some electrode materials. So, LiClO₄ is less favoured compared to more stable salts like LiTFSI. Even so, it still appears in some research because of its strong dissociation ability and its value as a low-cost option to test polymer electrolyte performance.

In one journal, it was reported that incorporating LiClO₄ into the PVP polymer matrix shows a clear trend in ionic conductivity based on the weight ratio of LiClO₄ to PVP. The study found that when the ratio of LiClO₄/PVP reached around 1.2, the ionic conductivity achieved the highest value because the amount of Li⁺ ions was enough to create effective ion transport pathways. However, when the ratio went beyond 1.2, the conductivity started to drop (Rodríguez et al., 2013). This result shows that there is an optimal balance of salt and polymer needed to get the best performance, and simply adding more salt does not always mean higher conductivity.

2.4 Additive

Additives are very important components in solid polymer electrolytes because a system with only polymer and lithium salt usually cannot meet all the performance requirements for practical applications. To solve this, many studies add inorganic fillers into the polymer–

salt matrix to improve the electrolyte properties in various aspects. These fillers, often in micro or nano-size, can blend well with the polymer host and create a more stable and functional electrolyte structure. Some of the most common and widely studied additives include barium titanate (BaTiO_3), lithium lanthanum zirconium oxide (LLZTO), zinc oxide (ZnO), and titanium dioxide (TiO_2).

These additives are selected because they are chemically stable, have good compatibility with the polymer matrix, and can tolerate the electrochemical environment inside the device. Researchers often adjust the type, size, and amount of these additives to match the needs of specific energy storage applications like EDLCs, lithium-ion batteries, or hybrid systems. By adding these materials, the polymer electrolyte system becomes more versatile and reliable, making it more promising for future high-performance energy storage devices.

2.4.1 - Barium Titanate

Barium titanate is a well-known ceramic material that has a high dielectric constant and good chemical stability. It is non-toxic and has good thermal stability, which makes it suitable for many electrochemical applications. The crystal structure of BaTiO_3 allows it to interact well with other components in a composite system, and it also shows good mechanical hardness that can help improve the strength of the final membrane. Because of these characteristics, BaTiO_3 has been widely studied as an additive material in solid polymer electrolyte systems.

For SPE applications, BaTiO_3 can blend well with polymer hosts like PEO, PEMA, or PVC together with lithium salts, forming a more stable composite electrolyte membrane. It can help in improving the ionic conductivity and maintaining the mechanical integrity of the electrolyte. The advantage of BaTiO_3 is that it is stable and does not easily degrade during cycling, and it also provides good compatibility with different types of polymers. However, the disadvantage is that if the loading amount is too high, it can cause particle aggregation, which reduces the uniformity of the membrane and may hinder ionic transport. Also, BaTiO_3 itself is not an ionic conductor, so its contribution depends on how well it interacts with the polymer-salt system.

By combining these studies, both filler optimization and polymer selection play an important role in determining the performance of solid polymer electrolytes (SPEs). For example, one study investigated PEO-based SPEs with different sizes and concentrations of BaTiO₃ nanoparticles and found that 8 wt% with a particle size of 5 nm gives the best performance. The ionic conductivity achieved is 2.2×10^{-5} S/cm at 25 °C and increases to 1.9×10^{-3} S/cm at 80 °C (Y. Zhang et al., 2019). Besides, another study used corn starch as a bio-polymer host combined with LiClO₄ salt and BaTiO₃ filler prepared using the solution casting method. The result shows that adding BaTiO₃ improves the conductivity by reducing the crystallinity and increasing the amorphous phase in the polymer structure. The highest conductivity obtained is 1.28×10^{-2} S cm⁻¹ at 75 °C with 10 wt% filler content (Teoh et al., 2015). These results show that the amount of filler and particle size are very important factors, as they help to reduce crystallinity and enhance ion movement, leading to better ionic conductivity.

2.4.2 - Lithium Lanthanum Zirconium Tantalum Oxide

Lithium lanthanum zirconium tantalum oxide is a garnet-type ceramic material that is well known for its high lithium-ion conductivity and good chemical and thermal stability. It has a wide electrochemical stability window and strong mechanical strength, which makes it suitable to be used in advanced energy storage systems. LLZTO is also stable against most lithium salts and polymers, which means it can blend well in composite solid polymer electrolytes. Its crystal structure allows easy lithium-ion movement, making it a very attractive additive for improving the performance of polymer electrolytes.

For SPE application, LLZTO can enhance the overall ionic conductivity of the polymer electrolyte, especially when used in nano or micro-sized particles. It can also improve the mechanical strength of the membrane, making it less likely to deform during cycling. Another advantage of LLZTO is its high thermal and electrochemical stability, which can help the electrolyte withstand higher operating voltages and temperatures. However, LLZTO has some limitations, such as possible agglomeration in the polymer matrix if not well dispersed, and sometimes the interface compatibility with polymer may not be perfect without surface modification. Overall, LLZTO is considered a very promising additive for SPE because it can improve both ionic transport and structural stability, making

the electrolyte more reliable and efficient for energy storage applications like EDLC and other lithium-based devices.

The integration of LLZTO into PVDF-based systems consistently shows significant improvement in electrochemical performance. One study investigated a composite SPE based on PVDF-HFP/LiTFSI with 20 wt% LLZTO, where the ionic conductivity reached about 8.2×10^{-4} S/cm at 60 °C, together with improved lithium-ion transference number and better interface stability (Yadav et al., 2023). These improvements indicate that LLZTO plays an important role in enhancing ion movement while also stabilizing the electrode–electrolyte interface. Besides, another PVDF/LiTFSI system with a 4:1 molar ratio showed that adding 5 wt% LLZTO produced the highest ionic conductivity of 2.4×10^{-4} S cm⁻¹ which is about 2.7 times higher than the filler-free electrolyte membrane. In addition, the electrochemical stability window was expanded to approximately 4.8 V (Zhang et al., 2020). These findings prove that LLZTO additives can effectively improve ionic conductivity and electrochemical stability by promoting more efficient ion transport pathways and enhancing interface compatibility within the polymer electrolyte system.

2.4.3 - Zinc Oxide

Zinc oxide (ZnO) is a ceramic material with good chemical stability, high surface area, and decent thermal stability, which makes it useful as an additive in many electrochemical systems. It also has good mechanical strength and is relatively low cost, making it attractive for polymer electrolyte research. ZnO particles, especially in nano-size, have high surface reactivity that allows them to interact well with polymer chains and lithium salts in the solid polymer electrolyte matrix.

For SPE application, ZnO can help improve the dispersion of the salt in the polymer matrix and enhance the overall structural stability of the membrane. It can also contribute to better mechanical strength, making the membrane less prone to deformation during cycling. Another good point of ZnO is its chemical stability, so it does not easily degrade during operation. However, one drawback is that ZnO itself is not a lithium-ion conductor, so the improvement of ionic conductivity mainly depends on how well it can interact with the polymer-salt system. If the particle size is too large or not uniformly dispersed, it can

lead to agglomeration which reduces membrane uniformity. Overall, ZnO is considered a useful additive in SPE especially when used in small amounts with good dispersion, because it can help improve the stability and durability of the polymer electrolyte without significantly increasing cost.

Research on ZnO-doped systems further proves that filler concentration is an important factor in optimizing ion transport properties. One study investigated ZnO incorporation into a PVC–LiClO₄ based SPE system and found that ionic conductivity is highly dependent on both ZnO concentration and temperature. At room temperature, the highest conductivity of about 3.7×10^{-7} S/cm was achieved at 20 wt% ZnO which is approximately 420 times higher than the filler-free system (Ahmad, Rahman and Su'ait, 2008). Since the glass transition temperature remained nearly unchanged, indicating that the conductivity improvement was mainly caused by changes in surface morphology and better interaction within the polymer–salt matrix which created more effective ion transport pathways. Besides, another study on synthesized nano-composite SPEs showed that conductivity increased as ZnO concentration increased until reaching an optimum value of 3.13×10^{-4} S/cm at 8 wt% ZnO loading. This enhancement is likely because ZnO nanofillers act as solid plasticizers and dissociation promoters, which help increase the amorphous phase of the polymer membrane. In addition, Lewis's acid-base interactions between the ZnO nanofiller and electrolyte components further improve ion dissociation and mobility (Dennis et al., 2022). These findings show that ZnO filler can significantly improve SPE performance, but only at an optimal concentration, where the balance between structural modification and ion transport is maximized.

2.4.4 - Titanium Dioxide

Titanium dioxide (TiO₂) is a ceramic material that is widely used as an additive in polymer electrolytes because of its high chemical stability, good thermal resistance, and strong mechanical properties. It also has a high surface area, especially in its nano-sized form, which allows better interaction with polymer chains and lithium salts in the solid polymer electrolyte matrix. TiO₂ is also relatively inexpensive and easy to process, making it a popular choice for improving electrolyte performance.

SPE application, TiO_2 can help improve the mechanical strength and thermal stability of the membrane, making it more durable during cycling and under different operating conditions. It also helps in reducing crystallinity of some polymer hosts which indirectly enhances the ionic conductivity by creating more amorphous regions for ion transport. Another good thing about TiO_2 is its chemical inertness, so it does not react with most lithium salts or polymer matrices, ensuring good long-term stability. However, like other ceramic additives, TiO_2 itself does not conduct lithium ions, so its benefit on conductivity depends on how well it disperses and interacts in the polymer system. Poor dispersion or large particle agglomeration may reduce the overall effectiveness. Overall, TiO_2 is considered a reliable and cost-effective additive that can enhance the structural and thermal properties of SPE, while also supporting better ionic conductivity when well incorporated.

Research on TiO_2 integration further shows that this filler provides dual advantages in improving both electrochemical performance and safety. One study investigated a hybrid solid polymer electrolyte based on a PVdF-co-HFP/PVA blend with 7.5 wt% TiO_2 , where the ionic conductivity reached $2.69 \times 10^{-3} \text{ S/cm}$ at 30°C which is about 2.5 times higher than the filler-free system (Sasikumar et al., 2021). Besides improving conductivity, this system also achieved a wide electrochemical stability window of 5.4 V and showed better resistance against lithium dendrite growth in Li/LiFePO₄ cells. This indicates that TiO_2 not only enhances ion transport but also contributes to better battery durability and operational safety. Similarly, another study using in situ coated 9 wt% 13 nm TiO_2 fillers in a PEO-based system reported uniform filler distribution within the polymer matrix, resulting in an ionic conductivity of $1.3 \times 10^{-4} \text{ S cm}^{-1}$ at 40°C with the same electrochemical stability window of 5.4 V. The enhanced cell also demonstrated superior cycling stability, achieving up to 550 cycles in full cell configurations (Su et al., 2023). These findings prove that TiO_2 filler is highly effective not only in improving conductivity through structural enhancement and better ion transport, but also in strengthening long-term cycling performance and safety.

2.5 Summary of Review

2.5.1 – Host Polymer Selection

PEMA is considered a promising host polymer for SPEs mainly because of its highly amorphous structure. Unlike semi-crystalline polymers such as PEO which usually require higher temperatures to reduce the limitation caused by crystalline regions, the amorphous structure of PEMA allows the polymer chains to remain more flexible even at room temperature. This flexibility is important because it supports easier ion transport by providing more continuous pathways for lithium ions to move through the segmental motion of the polymer backbone.

Besides its good ion transport potential, PEMA also has strong mechanical and physical properties that are beneficial for device fabrication. It offers good mechanical strength and excellent film-forming ability, allowing stable and thin electrolyte membranes to be produced more easily. In addition, PEMA has strong adhesion toward electrode surfaces which is very important in electrochemical devices such as EDLCs because better contact at the electrolyte–electrode interface helps reduce interfacial resistance and improves cycling stability.

However, PEMA also has several limitations. Although its amorphous nature supports polymer flexibility, pure PEMA itself has very low intrinsic ionic conductivity. This is because the polymer matrix alone does not provide enough charge carriers or efficient ion-conducting pathways for fast ion movement. Therefore, to achieve better electrochemical performance for practical energy storage applications, PEMA usually needs to be modified by adding lithium salts and inorganic fillers. These additives help improve salt dissociation, increase charge carrier concentration, and create more effective ion transport pathways within the polymer electrolyte system.

2.5.2 – Conductive Lithium Salt Selection

LiTFSI is widely considered one of the preferred salts for high-performance solid polymer electrolytes, mainly due to its strong dissociation ability and good structural stability. One

of its key advantages comes from the large and charge-delocalized TFSI⁻ anion. This charge delocalization reduces the lattice energy of the salt, allowing it to dissolve more easily in polymer hosts such as PEMA. As a result, a higher concentration of free mobile ions is released, which is essential for improving ionic conductivity in solid-state electrolyte systems.

In terms of performance stability, LiTFSI also provides good electrochemical and thermal properties. It typically offers a wide electrochemical stability window, often above 4.5 V, making it suitable for high-voltage energy storage applications. In addition, its high thermal decomposition temperature improves safety, allowing the electrolyte to operate under different temperature conditions without significant degradation. This makes LiTFSI a reliable choice for long-term electrochemical device performance.

However, the interaction between LiTFSI and the polymer host still needs to be carefully controlled. Although increasing salt concentration can increase the number of charge carriers, an optimum level is required. This is because the bulky TFSI⁻ anion may cause ion clustering or increase viscosity when present in excess which can reduce polymer chain mobility and slow down ion transport. Therefore, proper concentration tuning is important to balance ionic conductivity and maintain the mechanical flexibility and structural stability of the PEMA-based electrolyte system.

2.5.3 – Ceramic Additive Summary

The incorporation of ceramic additives is an important strategy to overcome the inherent ionic conductivity limitations of SPEs. While the PEMA host polymer and LiTFSI salt provide the basic polymer matrix and ion source, the addition of ceramic fillers such as BaTiO₃, ZnO, TiO₂, and LLZTO can further improve performance through different physical and chemical mechanisms.

Passive additives such as BaTiO₃, ZnO, and TiO₂ mainly improve ionic conductivity indirectly by modifying the polymer matrix structure. BaTiO₃ and ZnO are especially effective in reducing the semi-crystalline regions of the polymer while increasing the amorphous phase, where ion transport is more efficient. In addition, these fillers can also contribute through Lewis acid-base interactions, allowing them to act as solid plasticizers

that improve salt dissociation. Besides conductivity enhancement, TiO_2 is often selected because it can also improve electrochemical stability, with stability windows up to 5.4 V, while enhancing safety performance. TiO_2 nanoparticles have also been shown to improve resistance against lithium dendrite growth and maintain performance even under extreme operating conditions.

In contrast, LLZTO acts as an active filler because it is an ionic conductor by itself. Unlike passive fillers, LLZTO provides additional lithium-ion transport pathways directly through the filler particles. This dual-conduction mechanism, where ions can move through both the polymer phase and ceramic phase, helps improve ionic conductivity, lithium-ion transference number, and interface stability which can refer to Table 2.1.

However, many studies consistently show that filler concentration must be carefully optimized, which can be referred to and compared in Table 2.2.. While the optimum filler loading can create better ion-conducting pathways, excessive filler addition may lead to particle agglomeration which blocks ion transport channels and increases membrane rigidity. As a result, the selection of filler for a PEMA–LiTFSI system should depend on the main performance objective. BaTiO_3 or LLZTO may be more suitable when maximizing ionic conductivity is the priority, while TiO_2 may be a better choice when safety and long-term cycling stability are more important.

Table 2.1 Functional Roles and Mechanisms of Ceramic Additive in Polymer Electrolytes

Additive	Common Functions	Extra / Unique Functions
BaTiO_3	Disturbs polymer crystallinity ($\uparrow$ amorphous content) Provides interfacial ion transport channels- Supports ion hopping via Lewis acid–base interaction	Extreme high dielectric constant
LLZTO		Lithium-ion conducting ceramic Moderate-high dielectric constant
TiO_2		High dielectric constant (rutile) Strong Lewis acid sites (Ti^{4+})
ZnO		Moderate dielectric constant

Table 2.2 Comparative Analysis of Peak Ionic Conductivity for Various Additives

Additive	Polymer / Salt System	Optimal Loading	Conductivity, S/cm	Reference
BaTiO₃	Corn Starch/LiClO ₄	10 wt%	1.28×10^{-2} (at 75 °C)	Teoh et al.
	PEO / LiClO ₄	8 wt%	1.9×10^{-3} (at 80 °C)	Y. Zhang et al.
LLZTO	PVDF-HFP/LiTFSI	20 wt%	8.2×10^{-4} (at 60 °C)	Yadav et al.
	PVDF / LiTFSI	5 wt%	2.4×10^{-4} (at 25 °C)	Zhang et al.
ZnO	NCSPE (Synthetic)	8 wt%	3.13×10^{-4} (at 25 °C)	Dennis et al.
	PVC / LiClO ₄	20 wt%	3.7×10^{-7} (at 25 °C)	Ahmad et al.
TiO₂	PVdF-co-HFP/PVA	7.5 wt%	2.69×10^{-3} (at 30 °C)	Sasikumar et al.
	PEO (in situ)	9 wt%	1.3×10^{-4} (at 40 °C)	Su et al.

2.6 Electrode Fabrication and Characteristics

In an EDLC, the electrode functions as the primary site for energy storage, where electrostatic charge accumulation occurs through the formation of an electric double layer at the electrode–electrolyte interface. A standard EDLC electrode is commonly fabricated as a composite film consisting of activated carbon (AC) as the active material, Super P as the conductive additive, and PVDF as the polymer binder, with N-Methyl-2-pyrrolidone (NMP) serving as the solvent during slurry preparation. The fabrication process begins by dissolving PVDF in NMP to form a viscous binder solution, followed by the homogeneous dispersion of activated carbon and Super P to produce a stable slurry or “ink.” This slurry is then uniformly coated onto a conductive current collector and dried to evaporate the solvent, leaving behind a mechanically stable porous electrode structure. The resulting porous

architecture is essential because it maximizes the interfacial contact area between the electrolyte and the conductive surface, thereby enhancing ion accessibility and charge storage capability, which is shown in Fig 2.5.

The operating mechanism of this electrode is fundamentally based on a non-Faradaic process, where energy storage occurs through physical ion adsorption rather than chemical redox reactions. When an external voltage is applied, electrolyte ions migrate toward oppositely charged electrode surfaces and accumulate within the porous structure of activated carbon, forming an electric double layer. Since no chemical bonds are formed or broken during this process, the charge and discharge mechanism is highly reversible, enabling exceptionally rapid energy transfer and superior cycling durability compared to conventional battery systems. The effectiveness of this electrode system is strongly related to the material properties. Activated carbon provides an exceptionally high specific surface area which directly determines the number of available ion adsorption sites and significantly influences specific capacitance. Super P enhances electrical conductivity by creating conductive pathways that reduce equivalent series resistance, thereby improving power delivery efficiency. PVDF ensures strong mechanical adhesion between the active materials and the current collector, preserving electrode integrity during repeated cycling. Additionally, the evaporation of NMP during drying generates an optimized pore network, where micropores contribute to surface area while mesopores facilitate efficient ion transport. Proper wettability is also crucial, as effective electrolyte penetration throughout the electrode depth ensures full utilization of the active material.

This composite electrode system offers several significant advantages, including high power density due to rapid ion adsorption kinetics, excellent thermal stability, environmental safety associated with carbon-based materials, and an exceptionally long cycle life that can often exceed hundreds of thousands to millions of charges–discharge cycles under optimized conditions. However, certain limitations remain, including lower energy density compared to batteries, self-discharge behaviour over prolonged storage, relatively high processing costs due to the use of high-purity PVDF and NMP, and potential performance degradation if excessive binder content blocks the porous surface of activated carbon. Despite these challenges, EDLC electrodes are widely utilized in numerous applications requiring rapid energy delivery and storage reliability, such as regenerative braking systems in hybrid and electric vehicles, uninterruptible power supply systems for data centres, portable electronic devices requiring fast charging, and industrial energy

recovery systems including cranes and elevators. Through the synergistic combination of AC, Super P, PVDF, and NMP, this electrode design remains a highly effective and commercially relevant solution for high-power energy storage technologies.

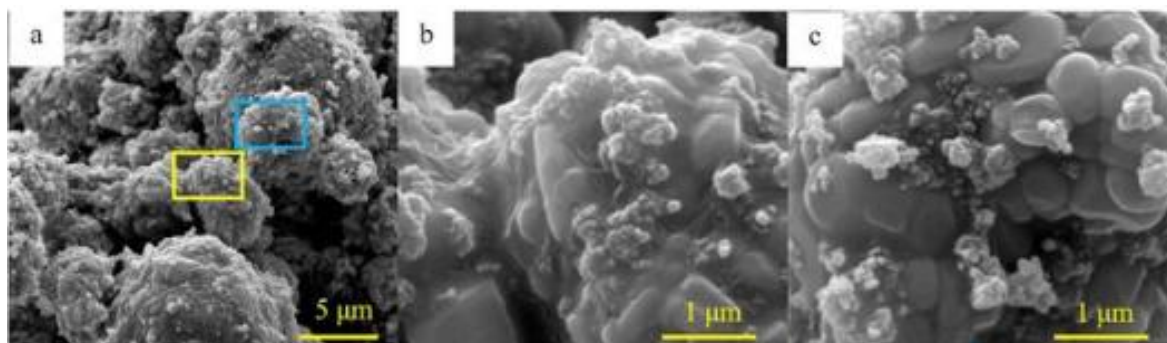


Fig 2.5 SEM images of Electrode (a) The electrode surface, (b) and (c) The regions in yellow and blue rectangles, respectively (Wang et al., 2019).

CHAPTER 3 METHODOLOGY AND WORKPLAN

3.1 Introduction

This chapter explains the research methods used to conduct this study. The necessary processes and information for the overall laboratory work are presented in detail. According to the EDLC fabrication process, the study is divided into four crucial phases. Initially, the first phase focuses on collecting polymer electrolyte characteristic information to determine the optimal ceramic additive composition for achieving the best enhancement in electrical properties. This phase includes polymer electrolyte preparation and testing. The second phase involves electrode coating on the substrate which serves as the preliminary step for the next stage. Following this, the third phase is EDLC fabrication, where functional EDLC specimens are developed. Lastly, the final phase involves EDLC specimen evaluation through various testing procedures. Furthermore, the overall work plan used to conduct this study is also presented.

3.2 Materials

For this SPE research experiment, the main materials that are used include PEMA as the polymer host matrix, LiTFSI as the lithium salt, and BaTiO₃, LLZTO, ZnO, and TiO₂ as ceramic additives to improve the properties of the electrolyte. Acetone is chosen as the solvent because it can effectively dissolve PEMA into a uniform solution which is important for forming a stable polymer electrolyte film (Rodi et al., 2017).

For the electrode side, the main composition is a mixture of activated carbon as the active material, Super P (carbon black) as the conductive agent, and PVDF as the binder. The slurry for the electrode is prepared using 1-methyl-2-pyrrolidone (NMP) as the solvent which helps to create a homogeneous paste that can be coated onto the aluminium current collector. With this combination of materials for both the solid polymer electrolyte and the electrode, the EDLC can be properly fabricated and tested for its ionic conductivity and electrochemical performance.

3.3 Overall Workflow

This project workflow is strategically divided into two main phases which are the theoretical selection phase and the laboratory execution phase, which is shown in Fig 3.1. The first phase focuses on material selection, where a comprehensive literature review is conducted to evaluate the compatibility between polymer matrices and salts. This stage is important to determine the feasibility of forming a SPEs, while also ensuring that the selected materials provide sufficient mechanical properties and that the ceramic additives can deliver measurable performance improvement through supported functional mechanisms.

The second phase involves laboratory workflow where the selected theoretical materials are applied practically through fabrication and testing. This phase mainly focuses on optimizing material composition to achieve better performance than standard reference systems. During the fabrication process, strict quality control is emphasized, including proper electrode coating conditions, accurate thickness control, and prevention of short circuits during EDLC assembly. These controls are necessary to ensure that the fabricated device is properly constructed and capable of delivering reliable electrochemical performance during the final characterization stage.

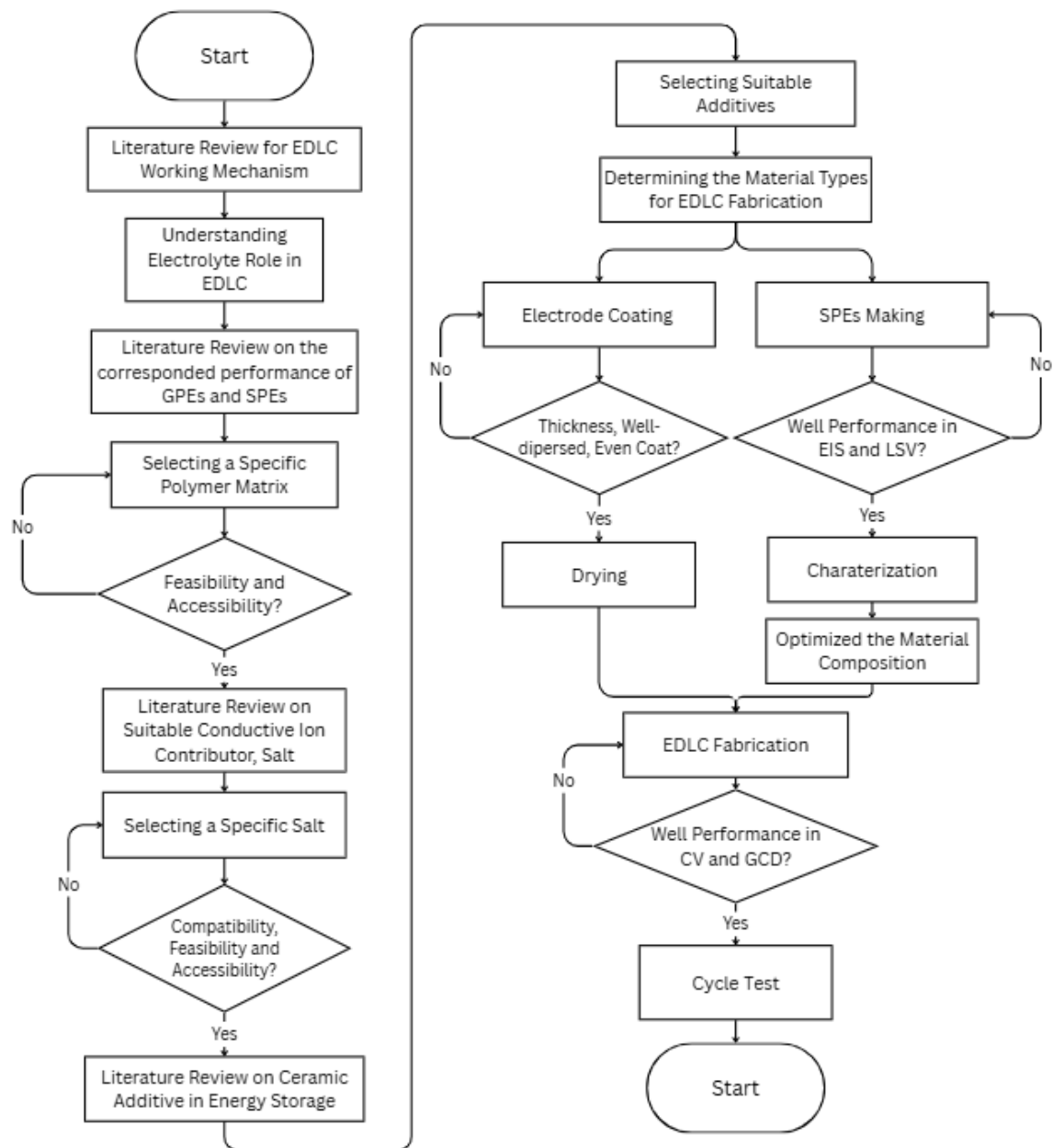


Fig 3.1 Overall Workflow Flow Chart

3.3 Fabrication Process

The experimental design of this project is shown in Figure 3.2 which demonstrates the sequential process from raw material preparation to SPE and EDLC manufacturing and testing.

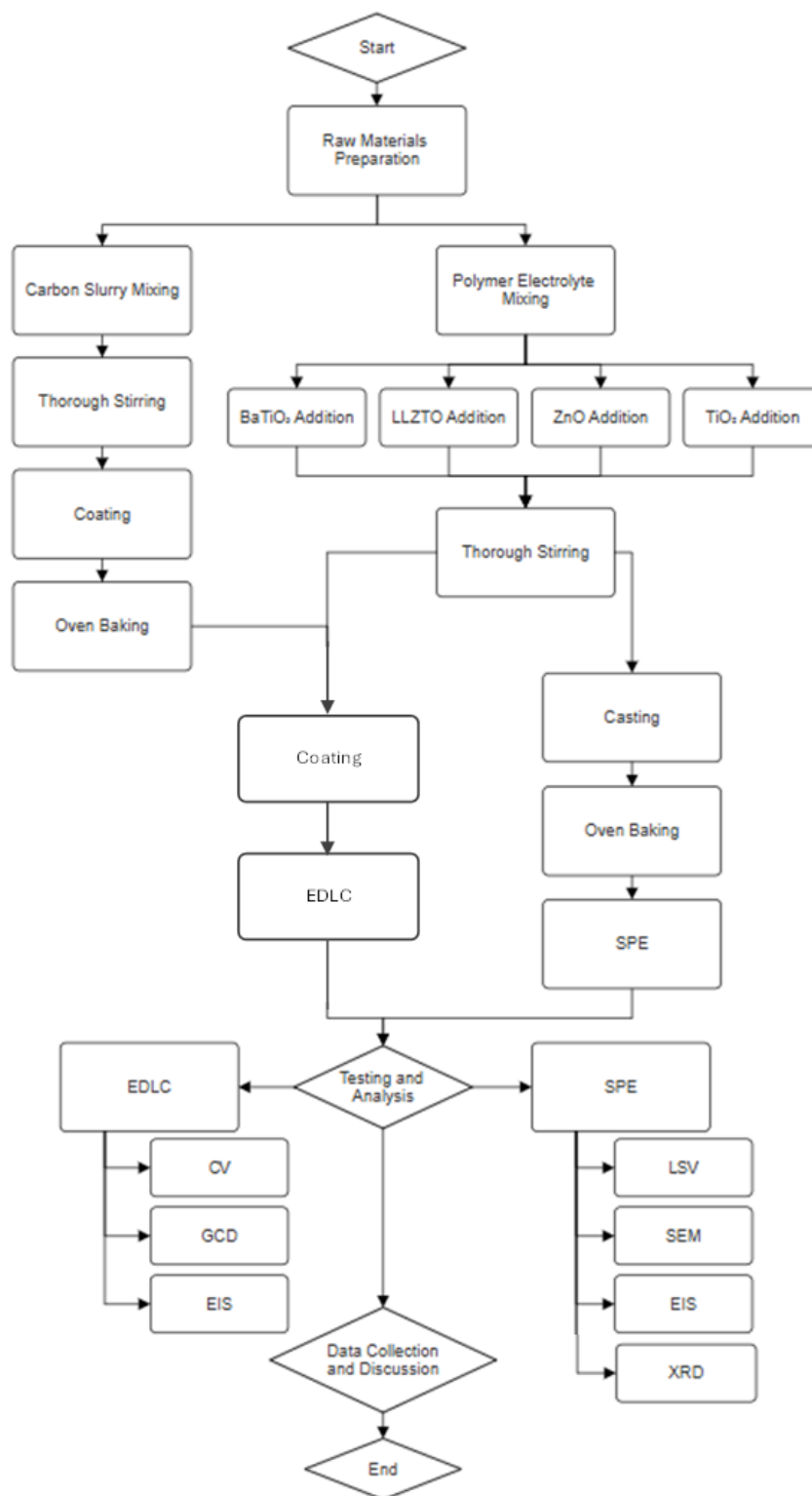


Fig 3.2 Lab Workflow Flow Chart

3.3.1 - Electrode Preparation

The process for electrode preparation started with dissolving 10 wt% of PVDF binder in 5 mL of NMP solvent while heating at 60 °C to ensure proper dissolution. After that, 80 wt% of activated carbon as the active material and 10 wt% of Super P as the conductive additive were slowly added into the solution. The whole mixture was continuously stirred and maintained at 60 °C for about 2 hours to obtain a well-dispersed and homogeneous carbon slurry. Once the slurry was ready, it was carefully applied onto the aluminium current collector using a thin film applicator (Fig. 3.3) and its accessory (Fig. 3.4) to make a uniform coating. The coated electrodes were then placed in an oven and dried at 60 °C for 4 hours to remove the solvent completely and achieve good adhesion of the carbon layer on the current collector. After drying, the electrodes (Fig 3.5) were weighed, and the active material loading was recorded. This step is important to control the consistency of the electrode, as the mass loading directly influences the performance of the EDLC device.

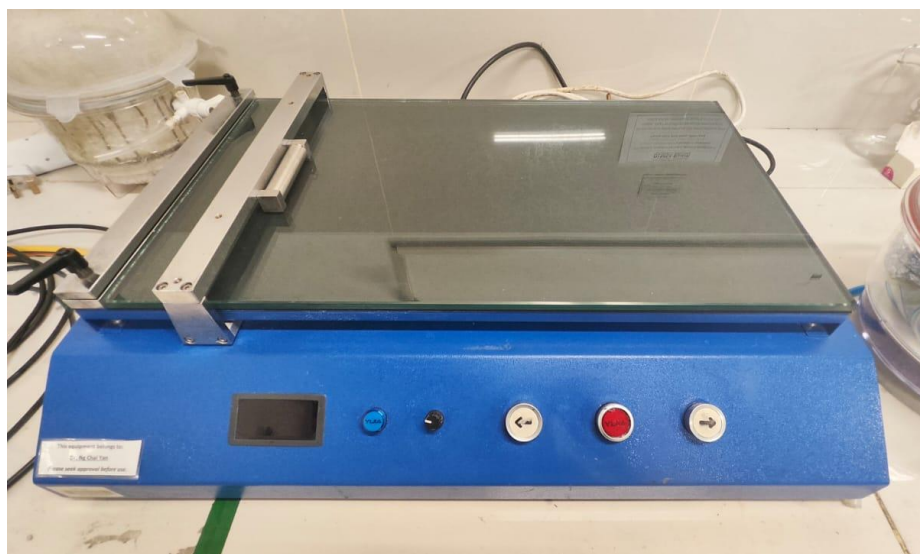


Fig 3.3 Thin Film Applicator



Fig 3.4 Four Side Applicator Accessory

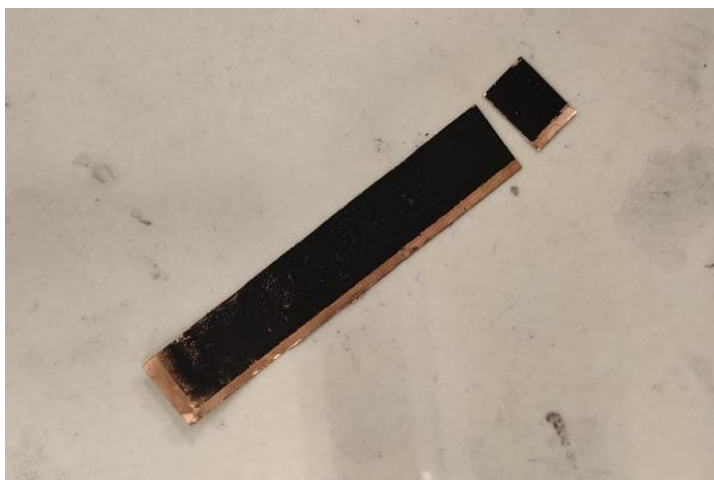


Fig 3.5 Sample of electrode applied activated carbon.

3.2.2 – Solid Polymer Electrolyte Preparation

The solution casting method was applied to prepare the SPE samples, where PEMA was used as the polymer host, LiTFSI as the lithium salt, and BaTiO₃, LLZTO, ZnO, and TiO₂ as additives to improve ionic conductivity. First, PEMA and LiTFSI were mixed in a fixed ratio of 50 wt% and 50 wt%, respectively, and dissolved in acetone solvent at an optimized temperature to form a clear and homogeneous solution. The mixture was continuously stirred for about 1 hours to ensure full dissolution and interaction between the polymer and the salt. After that, different weight percentages of additives, ranging from 0 wt% up to 6 wt% depending on the additive's enhancement, were introduced into the solution, with Table 3.1 showing the specific formulations. Each formulation was further stirred for another 1 hours until a fully complexed and stable solution was obtained. The resulting mixtures were then poured onto a cleaned glass pieces and left to dry at room temperature in the fume hood,

allowing the solvent to completely evaporate. Finally, thin and mechanically stable solid polymer electrolyte films were formed (Fig 3.6 & 3.7), ready for further testing and characterization.

Table 3.1: Formulations of SPE

Sample	Additive, x (wt%)	PEMA-LiTFSI
Ref-SPE	0	
BSPE-x	2, 4, 6	
LSPE-x	1, 2, 3	Fixed Amount, 0.25g
TSPE-x	0.5, 1.0, 1.5	
ZSPE-x	0.5, 1.0, 1.5	

**All samples contain 0.25 g of the PEMA-LiTFSI in a 1:1 ratio*

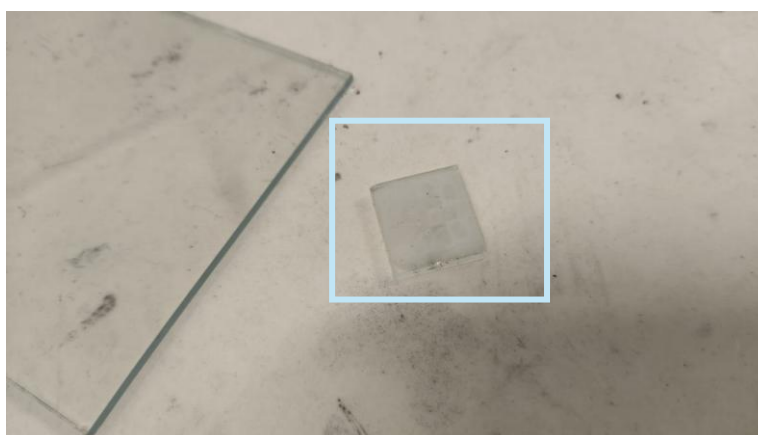


Fig 3.6 SPE thin film samples on glass piece.

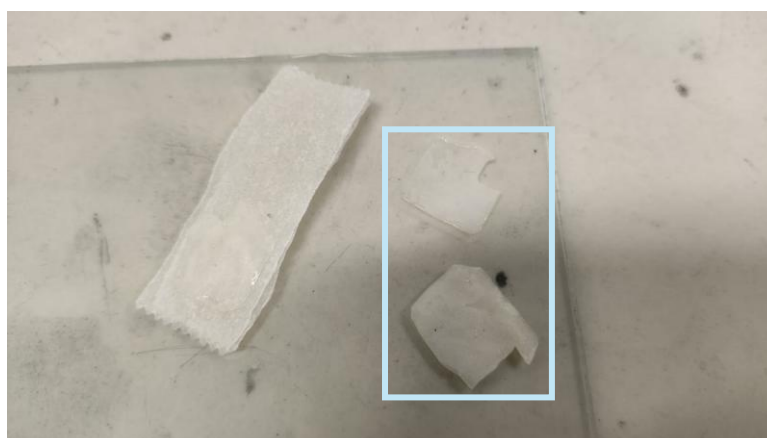


Fig 3.7 Peeled off SPE thin film sample.

3.2.3 – EDLC Fabrication

The process began by cutting the coated aluminium substrates into square pieces slightly larger than $1\text{ cm} \times 1\text{ cm}$. The electrodes were prepared as a pair, with one substrate cut slightly wider than the other to facilitate easier alignment and following testing connection. A fresh electrolyte solution was prepared, and both the anode and cathode (the aluminium substrates coated with the Super P carbon slurry) were fully immersed in the solution. This immersion step ensured that the porous electrode structure was thoroughly wetted, allowing the electrolyte to penetrate the active material.

After an initial drying period of 5 minutes, the smaller electrode was immersed again to ensure a well-wetted electrolyte interface. The two electrodes were then pasted together, face-to-face. During assembly (Fig 3.8), the electrodes were slightly offset to leave exposed side regions of the aluminium substrate, providing a contact point for crocodile clips during electrochemical testing. Finally, the assembled unit (Fig 3.9) was loaded evenly under pressure to ensure a compact structure and to achieve the desired device thickness (Fig 3.10), minimizing internal resistance and maximizing interfacial contact.

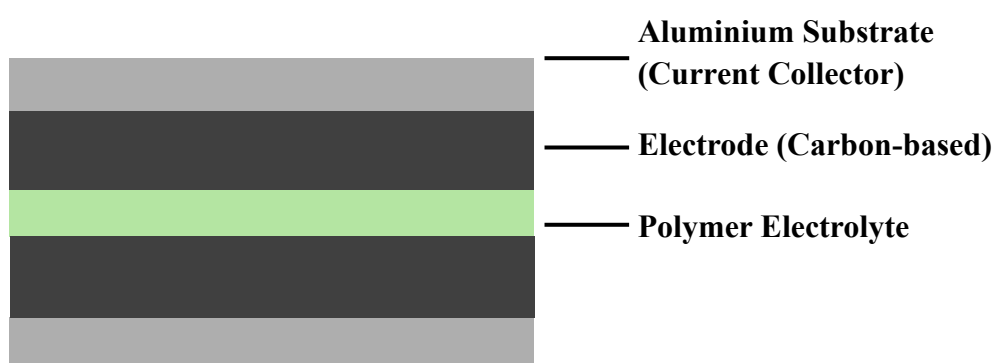


Fig 3.8 Schematic of the fabricated EDLC device

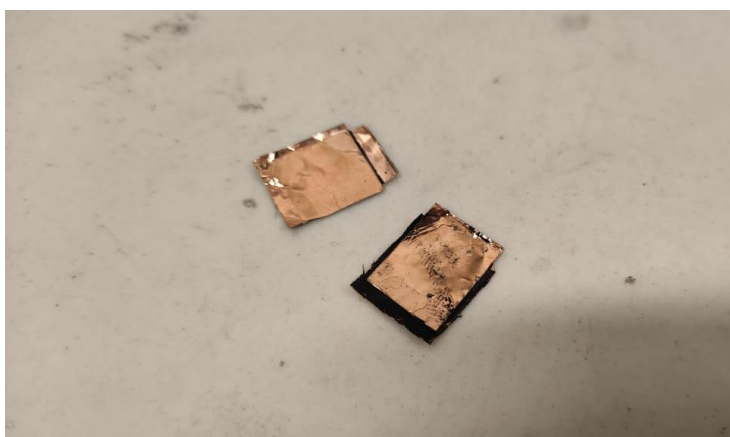


Fig 3.9 Fabricated EDLC device specimens

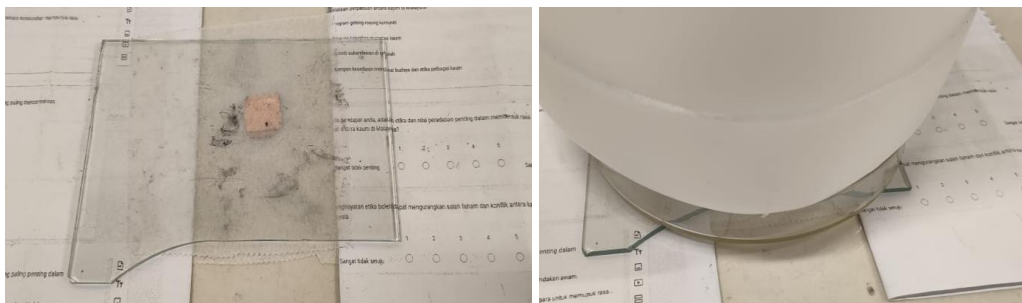


Fig 3.10 Compression applying on EDLC specimens

3.3 Testing Method

For the testing and validation part, the solid polymer electrolyte was characterized using several techniques to confirm its electrochemical and structural properties. Linear sweep voltammetry (LSV) was used to identify the electrochemical stability window of the electrolyte, while electrochemical impedance spectroscopy (EIS) provided the ionic conductivity and resistance behaviour. Besides, the structural information was examined by X-ray diffraction (XRD) to study the crystallinity, scanning electron microscopy (SEM) to observe the surface morphology. Additionally, energy-dispersive X-ray (EDX) spectroscopy was utilized to conduct elemental mapping, allowing for the verification of chemical compositions and the assessment of additive dispersion uniformity within the PEMA matrix.

For the electric double layer capacitor testing, cyclic voltammetry (CV) was applied to analyse the charge storage behaviour, galvanostatic charge–discharge (GCD) was used to evaluate specific capacitance and stability, and GCD was carried out with more cycles to investigate the stability performance of the device.

3.3.1 – Material Characterization

The material characterization phase is important for evaluating the physical and structural integrity of the SPE thin film. By analysing the SPE at a microscopic and atomic level, we know the film's physical properties, such as surface uniformity and molecular arrangement with its eventual electrochemical performance. This stage ensures that the electrolyte possesses the necessary homogeneity and amorphous structure required for efficient ion transport before it is integrated into the final device.

For the objective of XRD testing is to determine the crystallinity and structural arrangement of the SPE thin film, as the degree of crystallinity strongly influences the ionic conductivity. For the procedure, a thin piece of the SPE film was placed on the sample holder and scanned with X-ray radiation over a selected 2θ range (70°). The diffractogram was recorded and the presence of sharp peaks indicated crystalline phases, while broad region suggested amorphous regions presence. The analysis of these patterns provided insight into how the addition of salt and additives affected the overall structure of the polymer electrolyte.

For the objective of SEM testing is to observe the surface morphology of the SPE thin film and to study the distribution of phases such as polymer, salt, and additive. This provides information about the homogeneity and possible defects like pores or cracks that can affect the ionic transport. For the procedure, a small piece of the SPE thin film was cut and mounted on the SEM stub that was coated with a thin layer of conductive material (gold) to reduce charging effect. The sample was then scanned under the electron beam, and the micrographs were collected to analyse the surface features at different magnifications.

For the objective of EDX spectroscopy that in conjunction with SEM analysis is to evaluate the elemental composition and distribution of the synthesized solid polymer electrolyte membranes. This technique was used to confirm the presence of key chemical elements specifically fluorine, and nitrogen from the LiTFSI salt as well as the constituent elements of the ceramic fillers, such as titanium, barium, zinc, or zirconium. By performing elemental mapping, the degree of homogeneity in the dispersion of ceramic additives within the PEMA matrix was assessed. A uniform distribution of these elements is critical, as it indicates a well-mixed composite system without significant particle agglomeration which is essential for providing continuous pathways for efficient ion transport and consistent mechanical properties across the electrolyte membrane.

3.3.2 – Electrochemical Testing

This electrochemical testing phase focuses on evaluating the electrical behavior and charge-storage capabilities of the developed materials and the EDLC device. By employing a suitable of electrochemical techniques, the study transitions from assessing the electrolytic stability and ionic transport of the SPE to measuring the actual efficiency and durability of

the assembled EDLC. These tests are critical for determining if the material interactions established in the characterization phase translate into a high-performing, stable capacitor. All electrochemical measurements, including stability and performance evaluations, are conducted using WonATech's ZIVE SP&PP series potentiostats, with data acquisition and system control managed through the Smart Manager (SM) software interface which are shown in Fig 3.11. Specifically, the SPE is tested using coin cell holders as shown in Fig. 3.12 while the EDLC specimen is connected as illustrated in Fig. 3.13 for testing.



Fig 3.11 Potentiostats and Smart Manager software icon

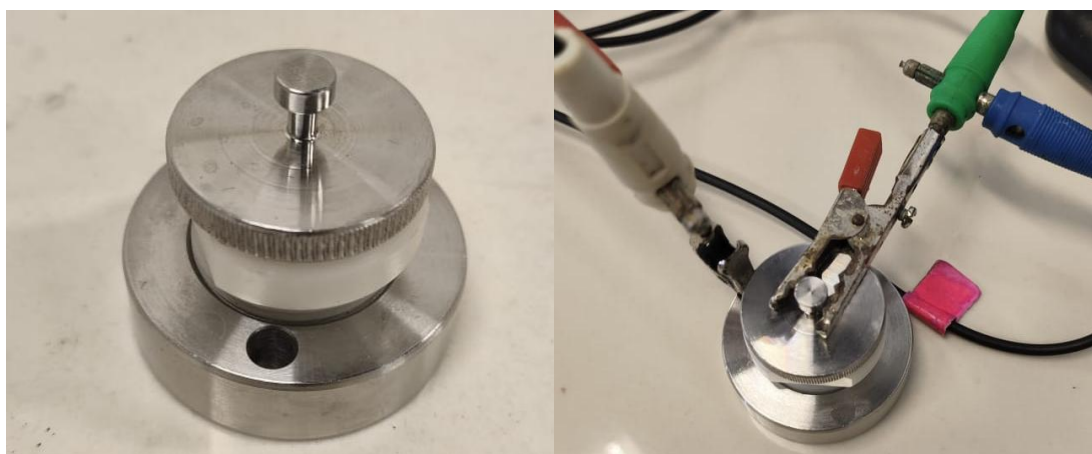


Fig 3.12 Coin cell holders and its connection

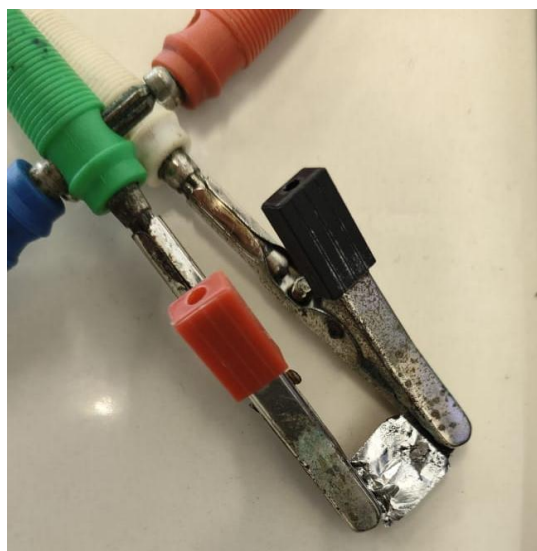


Fig 3.13 EDLC specimen connection

Linear sweep voltammetry

The objective of LSV testing is to determine the electrochemical stability window of the SPE thin film which is important to know the maximum voltage it can withstand before decomposition. For the procedure, the SPE film was assembled in a stainless-steel blocking electrode configuration and connected to the potentiostat. A linear potential sweep was applied at a fixed scan rate, and the current response was monitored (Fig 3.14 a). The onset of a sharp current rise indicated the breakdown potential which defined the stability limit of the electrolyte.

* Technique - Linear sweep voltammetry		
Parameters Information		
ITEM	VALUE	Option
Initial delay	☒ Enable	
-Duration(s)	1:40	
-Stability(V/s)	1.0000e-3	
Deposition	☐ Enable	
-Potential(V)	0.0000e+0	ERef
-Duration(s)	0	
Quiet time(s)	2	
Initial potential(V)	-3.8000e+0	ERef
Final potential(V)	3.8000e+0	ERef
Scan rate(V/s)	100.00e-3	
Sample interval(V)	1.0000e-3	
IR Comp.	None	
PF IR(ohm)	0.0000e+0	
I Range(A)	100mA	☐ Auto

* Technique - Potentiostatic EIS		
Parameters Information		
ITEM	VALUE	Option
Initial delay	☒ Enable	
-Duration(s)	1:40	
-Stability(V/s)	1.0000e-3	
Bias potential(V)	0.0000e+0	Eoc
Amplitude(V)	5.0000e-3	
Initial freq.(Hz)	2.0000e+6	
Middle freq.(Hz)	2.0000e+6	
Final freq.(Hz)	10.000e-3	
Sweep type	Log	
Density	7	
Iteration	1	
Init. I Range(A)	1 A	☒ Auto
Speed	Normal	

Fig 3.14 a) LSV Parameters, and b) EIS Parameters

Electrochemical Impedance Spectroscopy

The objective of EIS testing for both SPE and EDLC is to analyse the resistance and ion transport behaviour inside the system. For the SPE, the test provides the bulk resistance of the electrolyte and allows the calculation of ionic conductivity, while also giving information on interfacial properties between the electrolyte and electrodes.

For the EDLC, EIS is used to study the internal resistance, charge transfer, and capacitive behaviour of the device. In the procedure, the SPE was assembled into coin cells and connected to the potentiostat. A small AC voltage was applied over a wide frequency range (e.g. 2 MHz – 10 mHz), and the impedance response was recorded (Fig 3.14 b). The data were then plotted as Nyquist plots which were analysed to extract the resistance and capacitance characteristics of the respective systems.

The formula for calculating ionic conductivity, σ from EIS data is:

$$\sigma = \frac{t}{R_b \times A} \quad (1)$$

Where, σ is the ionic conductivity (S/cm).

t is the thickness of the SPE film (cm).

R_b is the bulk resistance of the electrolyte (Ω), typically determined from the intercept on the real axis, Z' of the Nyquist plot.

A is the contact area between the electrode and the electrolyte (cm²).

Cyclic Voltammetry

The objective of CV testing for EDLC is to evaluate the charge storage behaviour and to confirm the capacitive nature of the device. It provides information on reversibility, stability, and the shape of the current–voltage curve that indicates double layer formation. For the procedure, the EDLC coin cell was connected to the potentiostat and subjected to a potential sweep within a selected voltage window at different scan rates (e.g., 100, 50, 10, 1 mV/s) which is shown in Fig 3.15 a). The resulting cyclic voltammogram was recorded, and the nearly rectangular shape of the curve reflected the ideal capacitive response, while any distortion or deviation suggested resistive or faradaic contributions.

The formula for calculating specific capacitance, C_{sp} from CV result is:

$$C_{sp} = \frac{\int i dV}{2 \cdot m \cdot v \cdot \Delta V} \quad (2)$$

Where, $\int i dV$ is integrated area of the CV curve (total charge).

m is the mass of the active material.

v is the scan rate (V/s)

ΔV is the potential window (voltage range)

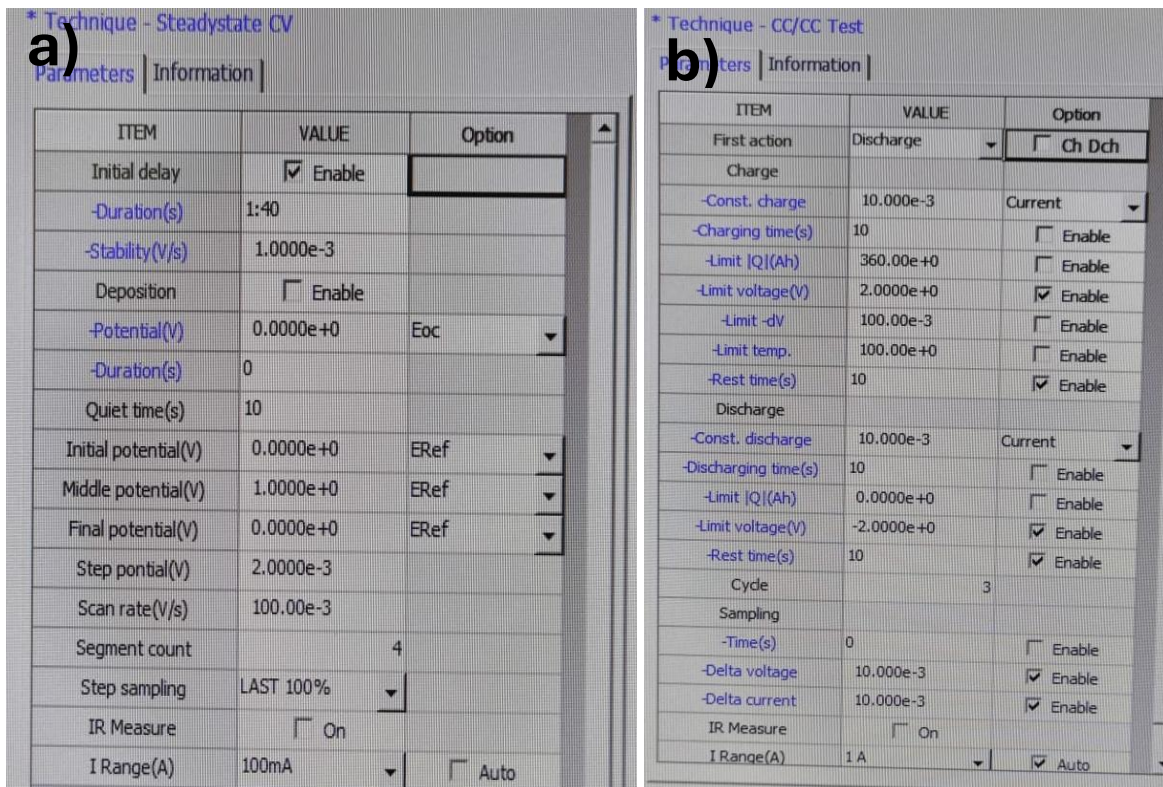


Fig 3.15 a) CV Parameters, and b) GCD Parameters

Galvanostatic Charge/Discharge

The objective of GCD testing for EDLC is to determine the specific capacitance, energy density, power density, and cycle stability of the device. It provides direct information on the charge–discharge characteristics under constant current. For the procedure, the EDLC coin cell was connected to the potentiostat and charged and discharged at different current densities within a fixed voltage range (Fig 3.15 b). The charge–discharge curves were

recorded, where the nearly triangular shape indicated good capacitive behaviour, and any deviation suggested resistive losses or side reactions. From the slope and discharge time, the capacitance and performance parameters of the EDLC were calculated.

The formula for calculating specific capacitance, C_{sp} from GCD result is:

$$C_{sp} = \frac{I \cdot \Delta t}{m \cdot \Delta V} \quad (3)$$

Where, I is the constant charge/discharge current (A).

Δt is the discharge time (s).

m is the mass of the active material.

ΔV is the potential window (voltage range)

GCD Cyclic Stability Testing

The objective of GCD cyclic stability testing is to evaluate the long-term durability and performance retention of the EDLC over repeated use. This test monitors how the specific capacitance drops over a high number of charge-discharge cycles which is critical for determining the practical lifespan of the device. For the procedure, the EDLC specimen was subjected to continuous cycling (**e.g., 500 cycles**) at a constant current density. The discharge capacitance was recorded for each cycle, and the stability was assessed by calculating the percentage of initial capacitance remaining at the end of the test. A gradual drop in capacitance often indicates electrolyte degradation or structural changes in the electrodes, while a high retention percentage confirms the stability and robustness of the system.

The formula for calculating energy density percentage, R from GCD result is:

$$R = \frac{E_{initial} - E_{sp,n^{th} cycle}}{E_{initial}} \times 100\% \quad (4)$$

Where, $E_{initial}$ is the energy density at the initial stage.

$E_{sp,n^{th} cycle}$ is the energy density at the n^{th} cycle

CHAPTER 4 RESULT AND DISCUSSION

4.1 Testing Method

This chapter presents the analysis and discussion of the experimental results obtained throughout the study of PEMA based solid polymer electrolytes. The main objective is to evaluate how the incorporation of different ceramic additives, specifically BaTiO₃, LLZTO, TiO₂, and ZnO, influences the structural, morphological, and electrochemical properties of the electrolyte system. The discussion can be divided into two main sections which are material characterization and electrochemical performance evaluation.

In the first section, material characterization techniques including XRD, SEM, and EDX are applied to examine the phase purity, surface morphology, and elemental distribution of the composite membranes. These analyses provide important structural information for understanding the physical interactions between the PEMA polymer matrix and the inorganic ceramic fillers. Through this characterization, the influence of each additive on membrane structure, crystallinity, and surface features can be identified.

For the second section, it focuses on the electrochemical performance of the fabricated electrolytes when applied in EDLC systems. This includes the evaluation of ionic conductivity using EIS, electrochemical stability through LSV, and charge storage behaviour through CV and GCD analysis. In addition, the long-term durability of the optimized electrolyte system is further examined through cyclic stability testing. By correlating the structural characteristics with the electrochemical response, this chapter aims to determine the most effective additive formulation for improving the overall performance of PEMA based solid polymer electrolytes in high performance energy storage applications.

4.2 Material Characterization

The physical and structural properties of the synthesized SPEs were first investigated to understand the effect of ceramic fillers on the PEMA-LiTFSI matrix. Material characterization is an essential step in this study because the overall electrochemical performance of an EDLC is strongly influenced by the microscopic arrangement and interaction of its internal components. By applying a combination of structural and

morphological characterization techniques, the interaction between the organic polymer host and inorganic ceramic additives can be observed and evaluated systematically.

This section presents the results of XRD analysis which was used to evaluate the crystallinity and phase purity of the composite membranes. Following the structural analysis, SEM and EDX were conducted to examine the surface morphology and verify the elemental composition of the membranes. So, these characterization methods provide a comprehensive understanding of the internal structure of the electrolyte system that in terms of filler dispersion, polymer amorphousness, and their contribution toward the formation of effective ionic conduction pathways.

4.2.1 XRD Analysis

The structural properties and crystalline characteristics of the optimized SPEs were investigated using XRD analysis. To clearly evaluate the structural changes after salt and ceramic filler incorporation, the XRD pattern of pure PEMA was firstly established as the baseline reference (Appendix A f). Based on the obtained diffraction patterns, all samples exhibit a broad hump within the 2θ range of approximately 10° to 25° . This broad feature is the typical characteristic of the amorphous phase of the PEMA host polymer. By comparing with the pure PEMA pattern, it can be confirmed that the polymer matrix remains predominantly in a disordered state after the addition of LiTFSI and ceramic fillers. This amorphous structure is highly important for electrolyte performance because ion transport mainly occurs through the segmental motion of polymer chains within the amorphous region which facilitates lithium-ion mobility.

BSPE-2, LSPE-2, TSPE-1.0, and ZSPE-0.5 were selected for XRD analysis because these compositions represent the optimized electrolyte system with the highest ionic conductivity for each respective ceramic filler. Besides the amorphous PEMA background, several sharp diffraction peaks can also be observed, corresponding to the crystalline ceramic fillers incorporated into each electrolyte system. For the BSPE-2 sample, represented by the orange curve with circle markers, distinct diffraction peaks corresponding to the tetragonal phase of BaTiO_3 are clearly detected, which align well with the pure BaTiO_3 reference pattern provided in Appendix A g) (left). The presence of these sharp peaks confirms that the BaTiO_3 filler successfully retained its crystalline structure

after being incorporated into the PEMA-LiTFSI polymer matrix. Similarly, the other composite electrolyte systems also exhibit their respective characteristic crystalline peaks, where LLZTO is identified in LSPE-2 (referenced in Appendix A g) (right)), TiO_2 in TSPE-1.0 (referenced in Appendix A h) (left)), and ZnO in ZSPE-0.5 (referenced in Appendix A h) (right)). The successful observation of these filler-specific diffraction peaks verifies that the inorganic ceramic additives were effectively incorporated into the SPE system through physical blending.

Furthermore, almost no additional unidentified diffraction peaks are observed in all samples, indicating that no significant chemical reaction occurred between PEMA, LiTFSI, and the ceramic fillers that could otherwise form undesired crystalline impurity phases. Besides that, the absence of sharp crystalline peaks associated with pure LiTFSI suggests that the lithium salt was either fully dissociated or well-complexed within the polymer matrix, which is a favourable condition for effective ion conduction.

Overall, the XRD results confirm that the synthesized electrolytes consist of a predominantly amorphous polymer phase combined with a crystalline ceramic filler phase. Despite the incorporation of additive ceramic fillers, the broad amorphous hump is still retained across all samples, which is considered a positive indicator for enhanced ionic conductivity. This observation demonstrates that the polymer matrix remains sufficiently disordered to support efficient lithium-ion transport while simultaneously benefiting from the structural contribution provided by the ceramic fillers.

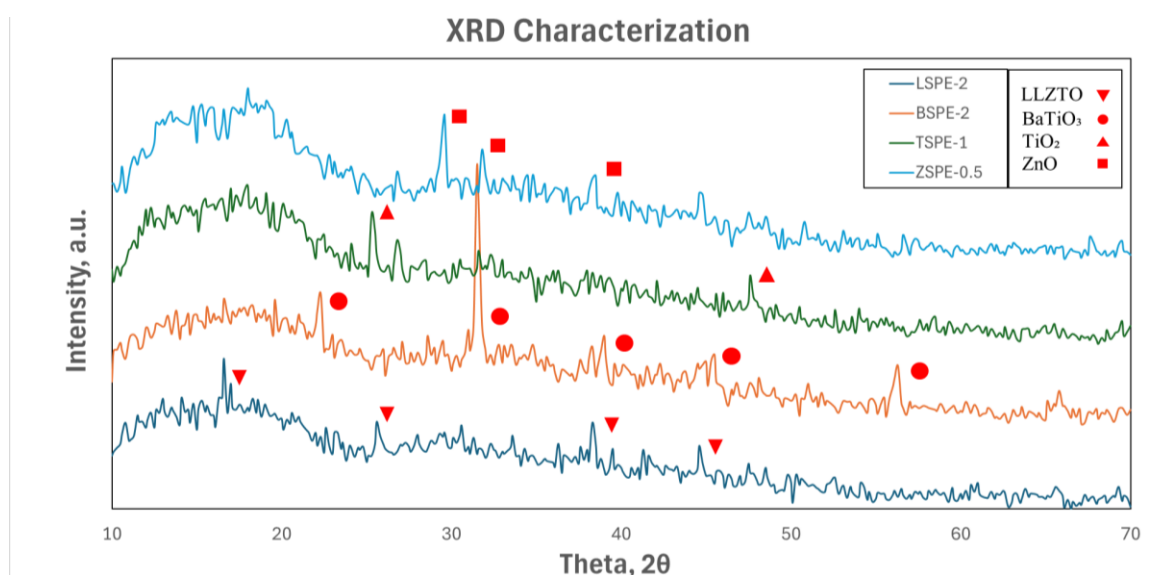


Fig 4.1 XRD Characteristic Result of Various Additives SPE

4.2.2 SEM Morphology Analysis

The BSPE-2 sample was chosen for SEM analysis because it had the best overall performance in both LSV and EIS tests, making it the primary focus sample formulation in this project. The surface morphology of this BSPE-2 sample was characterized to evaluate filler dispersion, polymer structure, and interfacial compatibility within the composite membrane. Based on Fig 4.1(a), the sample surface generally exhibits a relatively uniform morphology with minimal ceramic filler aggregation. At these 2 wt% filler concentrations, the BaTiO₃ particles appear reasonably well distributed throughout the PEMA-LiTFSI matrix, which is important for maintaining larger amorphous polymer regions and establishing more consistent ion conduction pathways. However, as observed in Fig 4.1(b), another region of the same sample shows more noticeable filler clustering. This variation indicates that although the 2 wt% filler loading is generally acceptable, the solution casting process may still produce localized regions with higher particle concentration, possibly due to the settling effect of the relatively dense ceramic particles during solvent evaporation.

The physical characteristics of the PEMA host polymer are also evident from the SEM micrographs. In Figure 4.2(a), the membrane surface is dominated by wrinkle-like structures which indicate the presence of a flexible and ductile polymer matrix. This wrinkled morphology suggests that the membrane is mechanically stable rather than brittle which is beneficial for maintaining effective contact with the electrodes during EDLC assembly and operation. In contrast, Figure 4.2(b) reveals the presence of localized structural defects in the form of small holes or micropores. These imperfections are likely caused by trapped air bubbles during the stirring process or rapid solvent evaporation during membrane drying. Although these micropores represent minor structural defects, their relatively small size suggests that they are unlikely to significantly reduce the overall mechanical integrity of the membrane.

The interfacial interaction between the inorganic filler and organic polymer matrix was further examined through detailed morphological observation. Certain regions, as shown in Figure 4.2(c), display poor wetting behaviour where the polymer matrix does not fully surround the ceramic particles, resulting in microscopic interfacial gaps. These gaps may reduce ion hopping efficiency by creating localized resistance barriers. In comparison, other regions shown in Figure 4.2(d) demonstrate significantly improved wetting, where the

PEMA matrix effectively encapsulates the filler particles. This improved interfacial compatibility at 2 wt% filler concentration is a positive indication of the passive filler mechanism because it suggests that the ceramic additive can effectively disrupt local polymer chain packing while maintaining sufficient polymer-filler interaction which contributes to enhanced ionic conductivity.

Besides these generally positive morphological characteristics, SEM analysis also indicates that the ceramic additives used in this study possess relatively large particle sizes, averaging approximately 20 μm . This micro-scale particle dimension likely limits the total available surface area for interaction with the PEMA polymer chains and LiTFSI salt. Although BSPE-2 demonstrates moderate effectiveness at this filler concentration, the larger particle size may contribute to localized dispersion inconsistency, filler aggregation, and wetting limitations observed in certain regions. It is therefore hypothesized that the use of nano-sized ceramic fillers could significantly improve electrolyte performance. Smaller particles would provide a substantially higher surface-to-volume ratio, allowing more extensive Lewis's acid-base interactions, better polymer chain disruption, and more effective suppression of crystallinity. Such improvements would likely promote a more homogeneous membrane structure with fewer defects and superior ionic conductivity compared to the current micro-sized filler system.

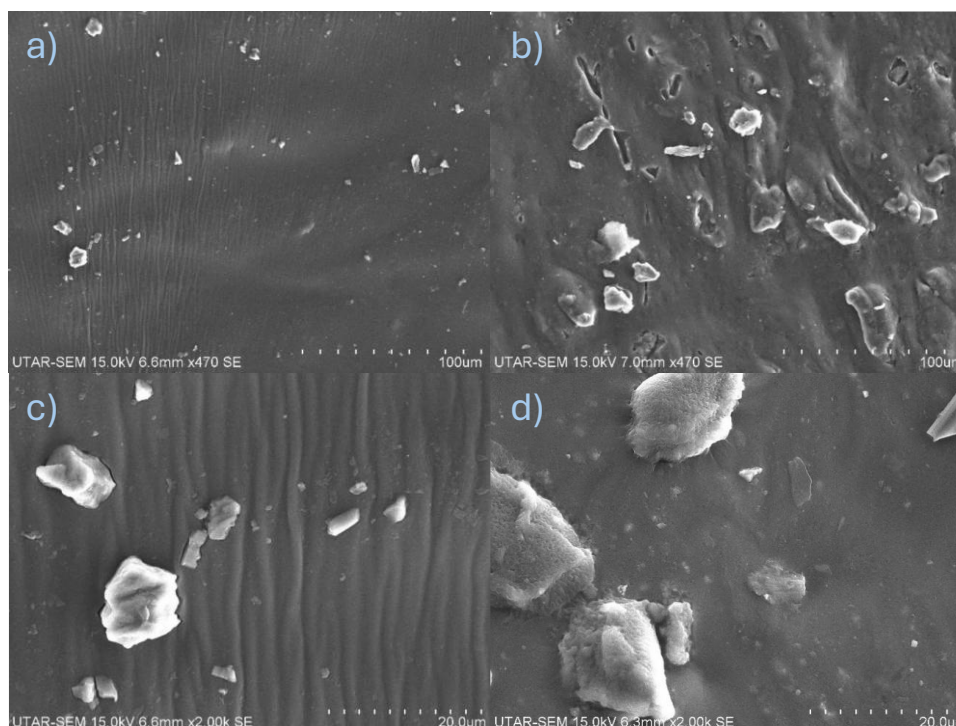


Fig 4.2 SEM Result of BSPE-2 of a), b) Matrix Region, c), d) Filler Particles.

4.2.3 EDX Analysis

To complement the morphological observations obtained from SEM analysis, EDX characterization was conducted on the BSPE-2 sample to verify its elemental composition and identify the chemical nature of the observed dispersed particles. Based on the elemental analysis from Fig 4.3, the primary elements detected throughout the membrane include Carbon (C), Oxygen (O), Fluorine (F), and Sulphur (S). The presence of Carbon and Oxygen is mainly associated with the PEMA $[CH_2C(CH_3)(COOCH_2CH_3)]_n$ host polymer backbone, while F and S confirm the successful incorporation of the LiTFSI ($LiC_2F_6NO_4S_2$) conductive salt within the polymer matrix. It should be noted that EDX analysis is unable to detect Lithium (Li) and Hydrogen (H) due to the inherent instrumental limitation in detecting low atomic number elements, as these elements produce very weak low-energy X-ray signals.

The EDX results also provide important clarification regarding the identity and distribution of the ceramic filler particles dispersed throughout the composite membrane. Spot analysis performed at different regions reveals a significant variation in Barium (Ba) concentration between the polymer matrix region and the visibly distinct filler particle region. In the matrix region, a Ba weight percentage of 8.72% was detected (Fig 4.3), suggesting that smaller fragmented $BaTiO_3$ particles or partial chemical influence from the filler are distributed within the polymer bulk structure. In contrast, the filler particle region exhibits a substantially higher Ba weight percentage of 16.41% which is shown in Fig 4.4. This clear increase in Ba concentration strongly confirms that the larger particulate features observed in the SEM micrographs correspond to $BaTiO_3$ ceramic fillers.

The detection of Ba in both the matrix and filler concentrated regions, although at different intensities, indicates that the $BaTiO_3$ additive is not only present as isolated large particles but also contributes to a broader distribution throughout the composite electrolyte system. This suggests that despite the relatively large micro-sized particle dimension of approximately 20 μm , the ceramic additive still achieves a functional level of dispersion within the PEMA-LiTFSI matrix. Such distribution is beneficial because it supports the passive filler mechanism by promoting localized structural modification of the polymer environment, potentially enhancing ionic transport pathways while maintaining the structural integrity of the membrane.

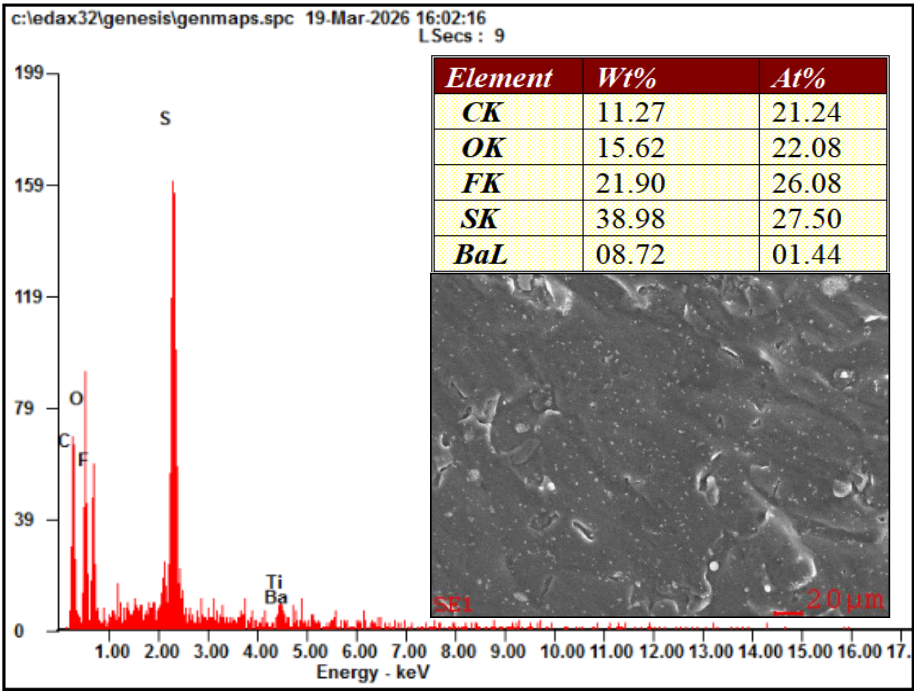


Fig 4.3 EDX Result of BSPE-2 in Matrix Region

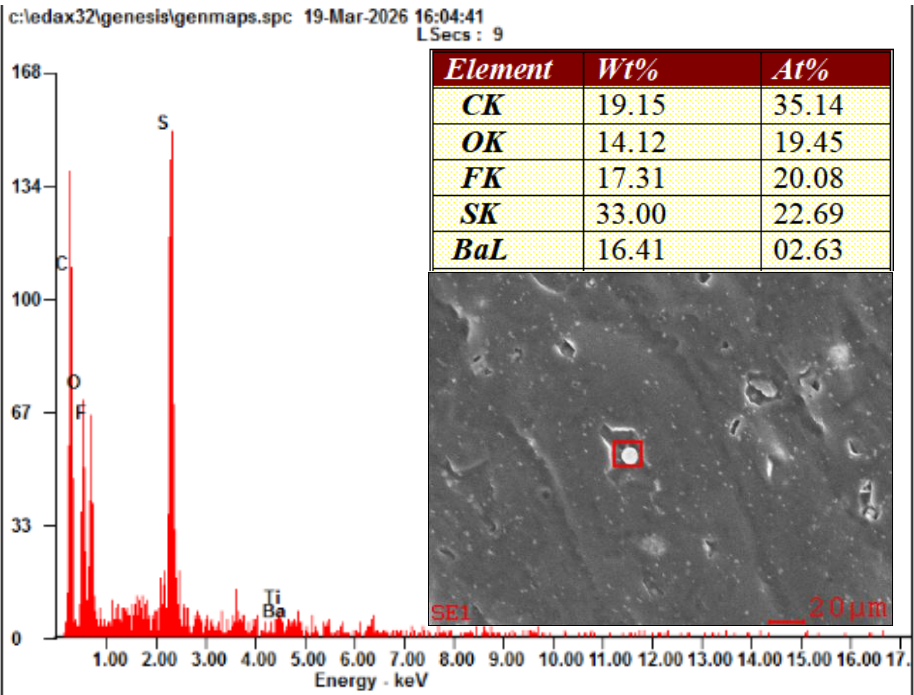


Fig 4.4 EDX Result of BSPE-2 in Filler Particle

4.3 Electrochemical Testing

The electrochemical performance of the prepared SPEs in an energy storage system was evaluated through a series of systematic electrochemical characterization techniques. While material characterization provides essential information on the physical structure of the membranes, electrochemical analysis is necessary to quantify how these structural features, such as polymer amorphousness and filler dispersion, influence functional properties including ion transport, conductivity, and charge storage behaviour. This section focuses on the fundamental electrical response of the electrolytes and their practical performance when incorporated into EDLC systems.

The analysis begins with LSV which is used to identify the electrochemical stability window and assess the operational voltage limits of the electrolytes. This is followed by EIS which is used to determine the ionic conductivity and internal resistance of the different electrolyte formulations. To further investigate the capacitive behaviour, CV and GCD measurements are carried out to evaluate key performance parameters such as specific capacitance, energy density, and power density. Finally, the cyclic stability of the optimized BSPE-2 system is assessed to determine its long-term durability under repeated charge-discharge cycling. Overall, these electrochemical results provide a complete performance profile of the SPE systems and demonstrate their suitability for solid-state energy storage applications.

4.3.1 LSV Stability Window Analysis

The electrochemical stability of the prepared SPEs was evaluated using LSV to determine the voltage limits before electrolyte decomposition. A wide electrochemical stability window is a critical requirement for high energy density EDLC applications, as it enables operation at higher voltages and directly improves the overall energy storage capability.

Based on the comparative potential range results, the incorporation of ceramic fillers is found to significantly enhance the electrochemical stability of the PEMA LiTFSI system, as shown in the final comparison in Fig 4.10. The Ref SPE without any additive exhibits the narrowest stability window of 3.8 V, ranging from 2.2 V to 1.6 V (Fig 4.5). Beyond these

limits, a sharp increase in current is observed, indicating the onset of electrolyte decomposition which may be associated with polymer backbone degradation or LiTFSI breakdown.

To further validate this finding, a comparison was made with the literature reported by Yek, Jun and Liew (2023) which shows a pure PEMA possess a relatively narrow electrochemical stability window of approximately 2.0 V. After the incorporation of 50 wt% LiTFSI, the operational stability to increase to approximately 3.2 V. Although this value shows deviation compared to the experimentally obtained stability window of 3.8 V in the present work, both results consistently demonstrate that the LiTFSI salt can inherently enhance the baseline resistance of the polymer matrix towards early oxidative decomposition.

In contrast, all composite electrolyte systems demonstrate a noticeable improvement in stability. The LSPE system with LLZTO shows an expanded window of 5.2 V, ranging from 2.9 V to 2.3 V (Fig 4.7), while the ZSPE system with ZnO reaches 5.5 V within the range of 3 V to 2.5 V (Fig 4.9). The TSPE system containing TiO₂ exhibits further enhancement, achieving a stability window of 6.0 V from 2.9 V to 3.1 V (Fig 4.8). Among all formulations, the BSPE-2 system with BaTiO₃ presents the most superior performance, delivering the widest electrochemical stability window of 6.2 V, ranging from 3 V to 3.2 V (Fig 4.6).

Based on Park (2003), the molecular mechanism of this significant stability enhancement in the composite electrolytes should be the specific chemical interactions occurring at the filler-polymer interface. It is well-established that the anodic stability limit of solid polymer electrolyte systems is generally limited by the irreversible oxidation of the salt anions at the electrode interface. In the present SPE system, the surface chemistry and functional groups of the inorganic ceramic fillers play a critical role in improving the electrochemical stability. The surface hydroxyl (-OH) groups or highly polarized surface states of the ceramic fillers promote strong localized interactions, such as hydrogen bonding or Lewis's acid-base complexation, with the TFSI⁻ anions from the lithium salt which is shown in Appendix A i) (illustration of Al₂O₃ and PEO-LiClO₄ system). Through these interactions, the salt anions become strongly coordinated and anchored along the ceramic filler surfaces, which effectively immobilizes the anions and reduces their direct exposure towards the inert electrode surfaces.

The outstanding performance of BSPE-2 can be attributed to the high dielectric constant of BaTiO_3 which promotes stronger stabilization of the PEMA LiTFSI matrix by reducing ion pairing and enhancing the dissociation of lithium salts. This improved dielectric environment increases the resistance of the electrolyte against both oxidative and reductive decomposition processes. The extension of the stability window to 6.2 V clearly confirms that the BSPE-2 formulation offers excellent electrochemical robustness and is highly suitable for high performance EDLC applications, providing a safe operational margin well above typical device requirements.

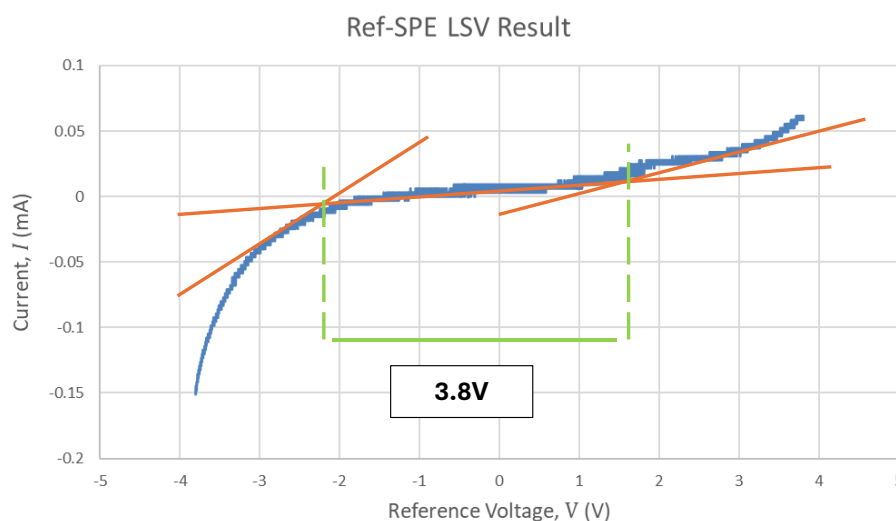


Fig 4.5 LSV Result of Ref-SPE

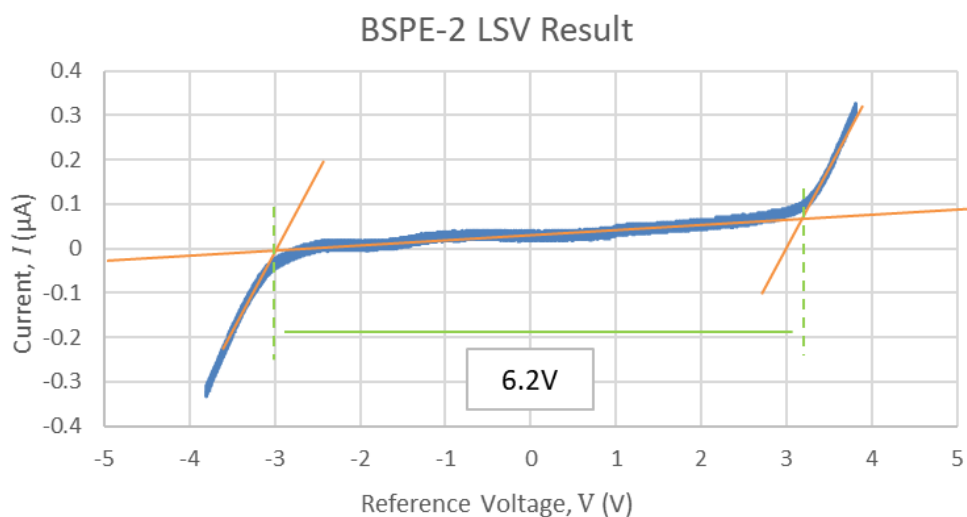


Fig 4.6 LSV Result of BSPE-2

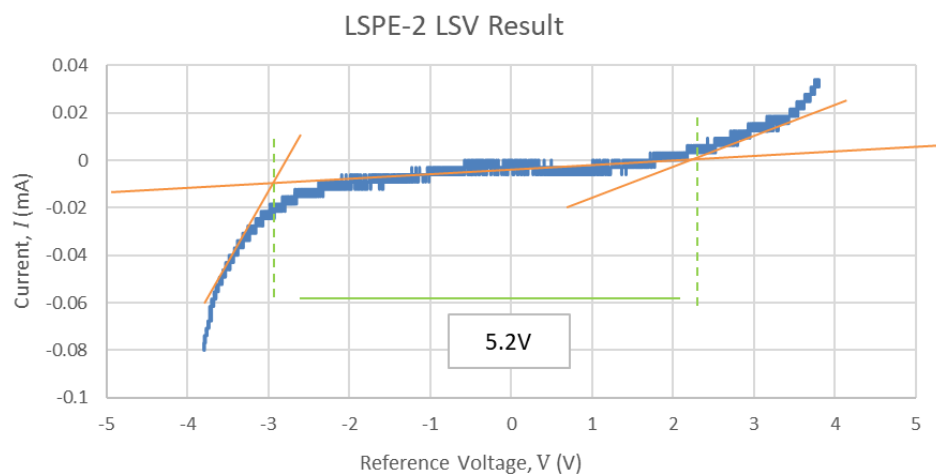


Fig 4.7 LSV Result of LSPE-2

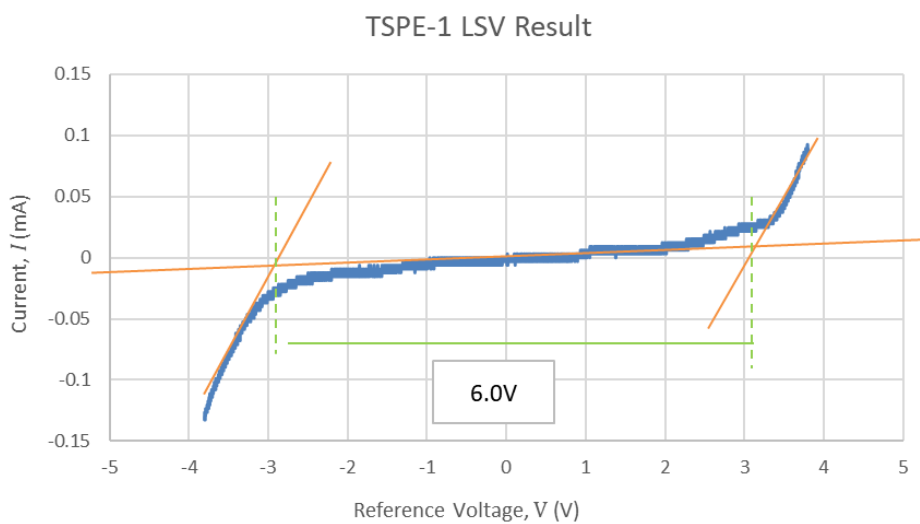


Fig 4.8 LSV Result of TSPE-1

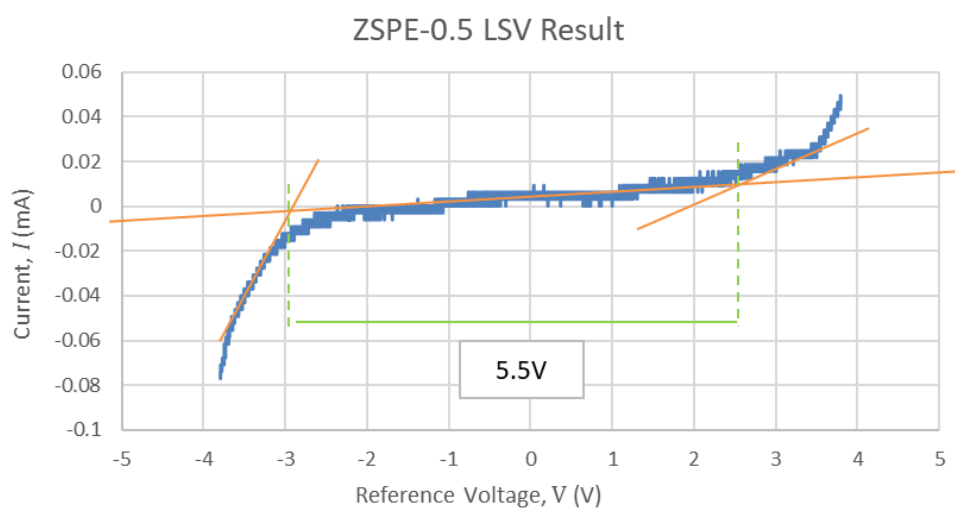


Fig 4.9 LSV Result of ZSPE-0.5

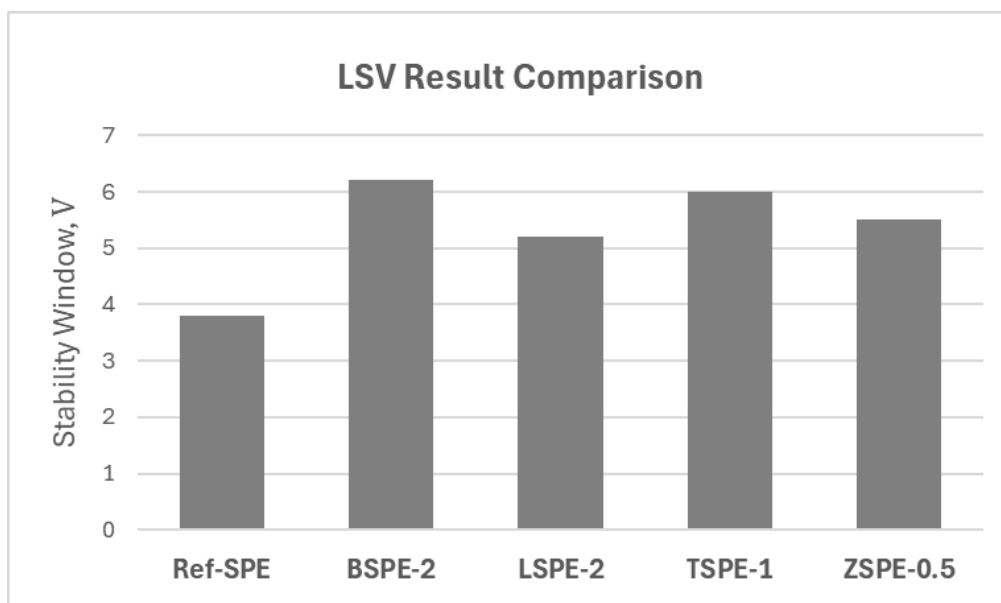


Fig 4.10 LSV Result Comparison Graph

4.3.2 EIS Ionic Conductivity Analysis

To evaluate the ionic conductivity of the prepared SPEs, EIS was conducted at room temperature. Ionic conductivity, σ , is a fundamental parameter for electrolyte systems as it directly influences the internal resistance and power density of the resulting EDLC. In this analysis, the performance of the Ref SPE (Fig 4.11) is compared with the optimal compositions from each ceramic filler system, namely BSPE-2, LSPE-2, TSPE-1.0, and ZSPE-0.5 (Fig 4.12, 4.13, 4.14, and 4.15).

The Ref-SPE consisting of PEMA and 50% LiTFSI exhibits the lowest ionic conductivity of 7.14×10^{-6} S/cm. The incorporation of ceramic fillers significantly improves ionic transport across all composite systems. Among the modified electrolytes, ZSPE-0.5 and TSPE-1 show moderate enhancements, achieving conductivities of 1.58×10^{-5} S/cm and 2.22×10^{-5} S/cm, respectively. The LSPE-2 sample further improves conductivity to 2.90×10^{-5} S/cm, indicating that LLZTO and TiO_2 contribute to suppressing polymer chain recrystallization and promoting a more amorphous structure which facilitates ion migration.

However, the BSPE-2 sample demonstrates the highest ionic conductivity among all tested formulations, reaching 5.28×10^{-5} S/cm. This value represents an improvement of more than one order of magnitude compared to the filler free reference system. The superior performance of BSPE-2 can be attributed to the high dielectric constant of BaTiO_3 which

enhances the dissociation of LiTFSI salt into free charge carriers. In addition, the presence of BaTiO₃ disrupts local polymer chain packing within the PEMA matrix, resulting in increased amorphous regions and more continuous ion transport pathways.

The final comparison bar chart of ionic conductivity is shown in Fig. 4.16 while the detailed properties are shown in Table 4.1, which includes the thickness of the SPE sample, bulk resistance obtained from the EIS plot, fixed area, and the calculated ionic conductivity.

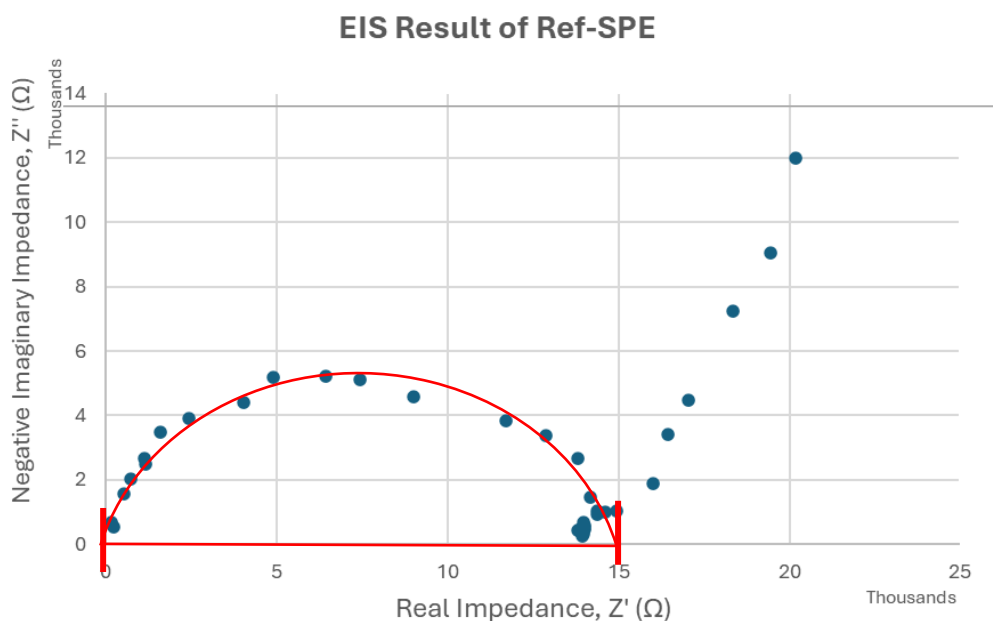


Fig 4.11 EIS Result of Ref-SPE

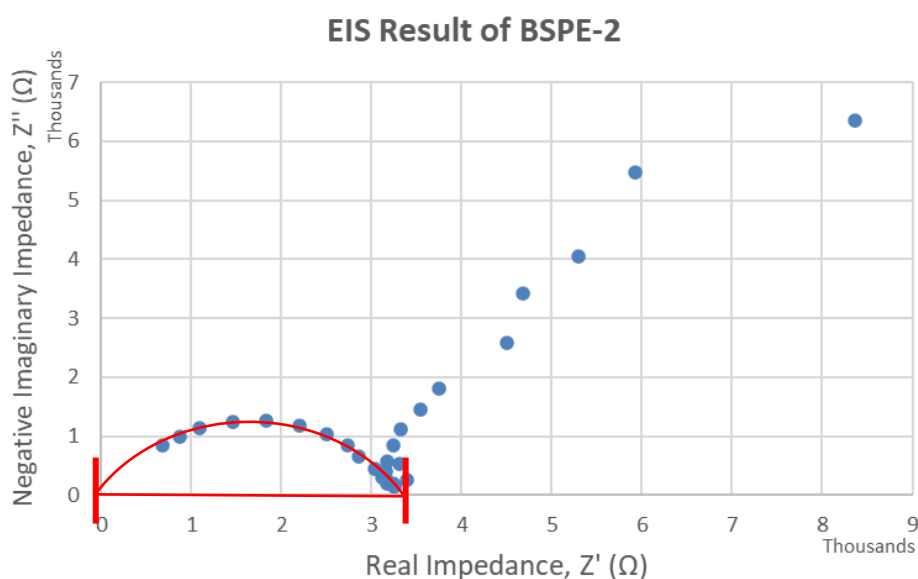


Fig 4.12 EIS Result of BSPE-2

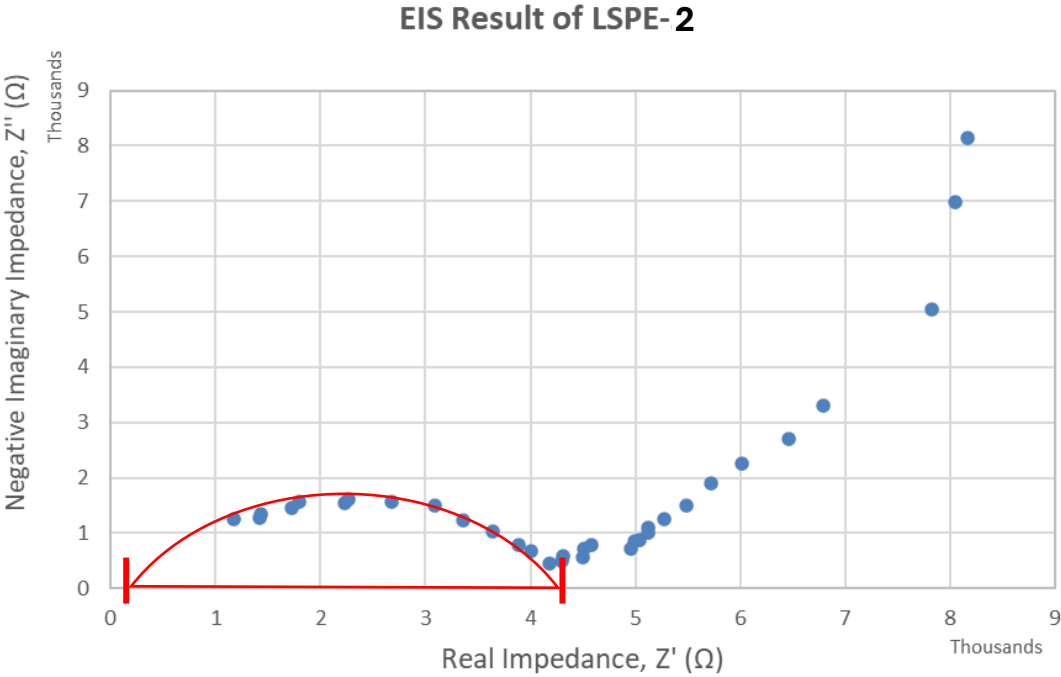


Fig 4.13 EIS Result of LSPE-2

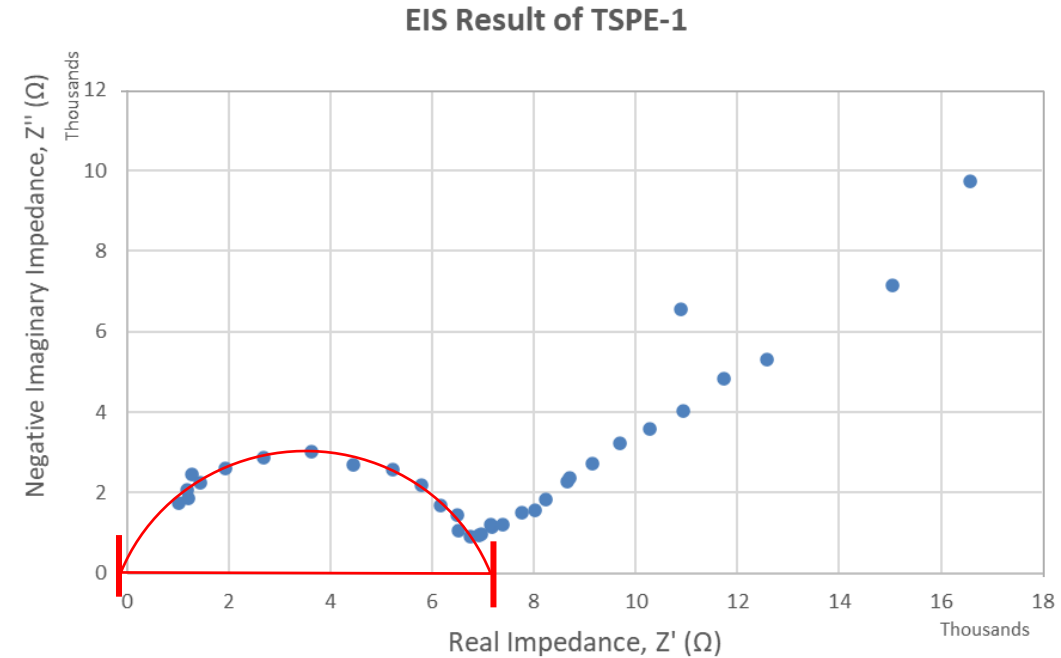


Fig 4.14 EIS Result of TSPE-1

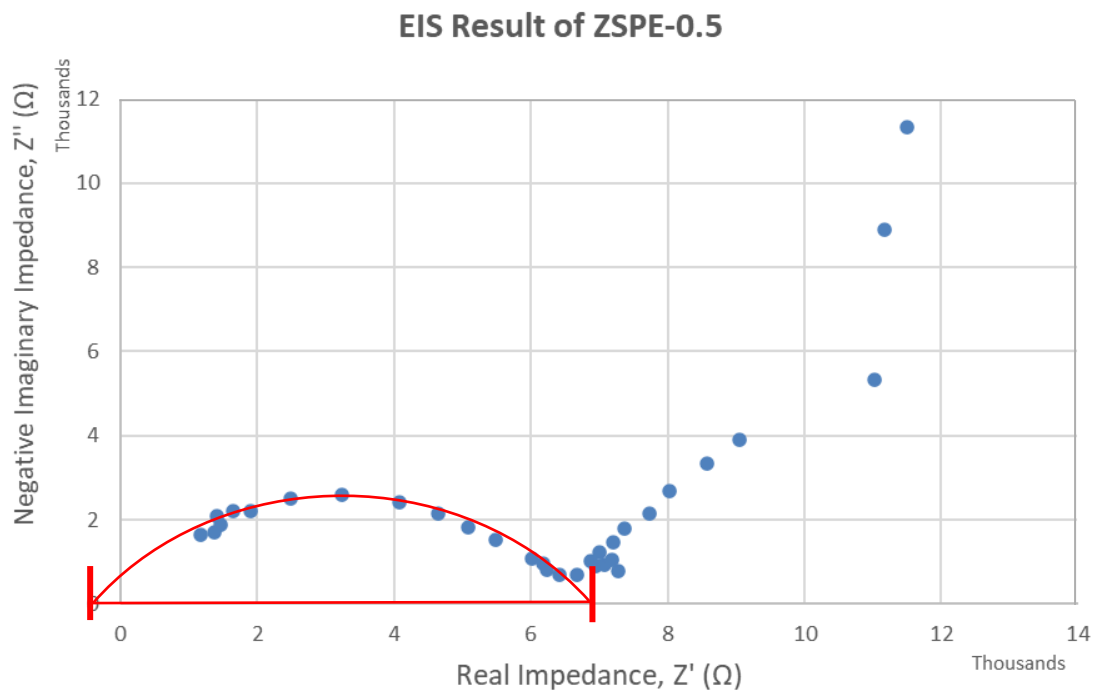


Fig 4.15 EIS Result of ZSPE-0.5

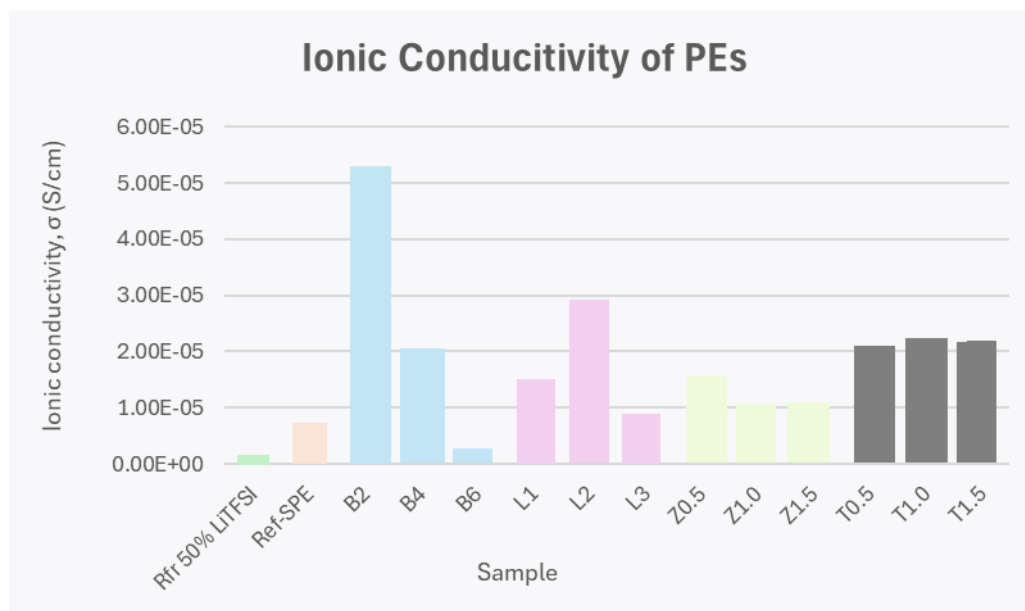


Fig 4.16 Ionic Conductivity of SPEs Thin Film Sample

Table 4.1 Comparative Analysis of Peak Ionic Conductivity for Various Additives

Sample	Thickness, t mm	Area, A cm ²	Bulk Resistance, R_b k Ω	Ionic Conductivity, σ S/cm
Ref-SPE	0.265	0.25	15	7.14×10^{-6}
BSPE-2	0.435		3.3	5.28×10^{-5}
BSPE-4	0.390	0.25	7.7	2.01×10^{-5}
BSPE-6	0.320		51	2.51×10^{-6}
LSPE-1	0.330		8.9	1.49×10^{-5}
LSPE-2	0.290	0.25	4	2.90×10^{-5}
LSPE-3	0.365		17	8.59×10^{-6}
TSPE-0.5	0.315		6	2.10×10^{-5}
TSPE-1.0	0.400	0.25	7.2	2.22×10^{-5}
TSPE-1.5	0.385		7	2.18×10^{-5}
ZSPE-0.5	0.295		7.5	1.58×10^{-5}
ZSPE-1.0	0.505	0.25	19	1.06×10^{-5}
ZSPE-1.5	0.310		11.3	1.10×10^{-5}

4.3.3 CV Specific Capacitance Analysis

The capacitive performance of the EDLC assembled using the optimized BSPE-2 electrolyte was evaluated through CV analysis at various scan rates ranging from 1 mV/s to 100 mV/s to investigate the charge storage mechanism, ion transport behaviour, and overall rate capability of the system. Based on the obtained CV results, a clear relationship between scan rate and voltammetric response is observed, where the enclosed area of the CV curve changes progressively with the applied scan speed.

At the highest scan rate of 100 mV/s, the CV curve shows the smallest enclosed area, indicating the lowest accessible charge storage under rapid polarization conditions. As the scan rate decreases to 50 mV/s and 10 mV/s, the enclosed area gradually increases, reflecting improved charge accumulation capability which are shown in Fig 4.17. The largest CV area is obtained at the slowest scan rate of 1 mV/s (Fig 4.18). However, this

condition also shows a noticeably different current response compared to the higher scan rates. This behaviour is further supported by the measured current range, where scan rates from 100 mV/s to 10 mV/s remain within approximately 0 to 0.035 A, while the 1 mV/s scan rate extends significantly to 0 to 0.082 A, clearly indicating a much higher charge storage contribution under slow ion transport conditions. Overall, this trend confirms that the electrochemical performance of the BSPE-2 based EDLC is strongly dependent on the time available for ion migration and diffusion at the electrode–electrolyte interface.

This variation in CV response can be explained through diffusion-controlled ion transport within the porous activated carbon electrode. At high scan rates such as 100 mV/s, the rapid potential change prevents electrolyte ions from fully penetrating the deeper microporous structure of the electrode. As a result, ion adsorption is mainly limited to the outer surface regions, leading to the formation of a shallow electric double layer and reduced effective surface utilization. Consequently, the CV area decreases, and the apparent capacitance becomes lower. In contrast, at a low scan rate of 1 mV/s, the slower potential sweep provides sufficient time for ions to diffuse into both micropores and mesopores of the activated carbon network. This allows more complete utilization of the internal surface area, resulting in enhanced electric double layer formation and significantly higher charge storage, as evidenced by the larger CV area (Yang, Yiacoumi and Tsouris, 2003).

The distinct change in current response at the lowest scan rate also suggests several internal electrochemical effects within the EDLC system. One key explanation is that diffusion-controlled processes become dominant when sufficient time is available for ion redistribution. At 1 mV/s, ions can approach a near equilibrium state at the electrode surface, meaning the measured current reflects both surface adsorption and deeper ion diffusion throughout the porous structure. This contrasts with high scan rates, where the response is mainly governed by kinetic limitations (Pandolfo and Hollenkamp, 2006). The influence of equivalent series resistance, including the ionic resistance of the BSPE-2 membrane and interfacial contact resistance between electrode and electrolyte, becomes less significant at low scan rates. At high scan rates, equivalent series resistance (ESR) contributes to distorted or slanted CV profiles due to voltage drop and limited charge transfer, whereas at 1 mV/s these resistive effects are minimized, allowing a better capacitive response. Furthermore, the increased current range at low scan rate may also indicate minor pseudocapacitive or Faradaic contributions arising from surface functional groups or localized redox active sites. Although the system is primarily governed by non-Faradaic double layer charging, slower

scan rates allow sufficient time for these secondary processes to contribute more noticeably to the overall response (Hassan and Wollenberger, 2019)(Cougnon, 2023).

Overall, the CV analysis confirms that the optimized BSPE-2 electrolyte provides effective ionic conductivity and stable capacitive behaviour across different operating conditions. However, the rate performance of the EDLC is still strongly affected by diffusion limitations inherent in solid state electrolyte systems, particularly at high scan rates. The superior performance observed at low scan rates demonstrates that BSPE-2 is highly effective when sufficient ion diffusion time is available, while the reduced response at higher scan rates highlights the need for further optimization of ion transport pathways, pore accessibility, and interfacial resistance to improve high-rate performance.

Specific Capacitance

By using the specific capacitance calculation formula and substituting the corresponding values into the formula, the larger electrode contains 0.0182 g of active material mass while the smaller electrode contains 0.0147 g (total 0.0329 g), with a potential difference of 1 V. The results obtained are presented in Table 4.2.

Table 4.2 Specific Capacitance at Various Scan Rates

Scan Rate, mV/s	Enclosed Area, A·V	Specific Capacitance, F/g
100	0.0015	0.23
50	0.0050	1.52
10	0.0100	15.20
1	0.0200	303.00 (unrealistic)

The results show a clear inverse relationship between scan rate and specific capacitance. At the highest scan rate of 100 mV/s, the specific capacitance (C_{sp}) is significantly low at 0.23 F/g. This is mainly due to the limited time available for electrolyte ions in the BSPE-2 system to diffuse into the deeper microporous structure of the activated carbon electrodes, resulting in charge storage being restricted largely to the outer surface region.

As the scan rate decreases to 10 mV/s, the specific capacitance increases to 15.20 F/g. This improvement indicates that slower potential sweeps provide sufficient time for ion diffusion into the internal porous network, enabling more effective electric double layer formation and higher utilization of the available surface area.

However, the value obtained at 1 mV/s (303.00 F/g) is significantly higher and does not follow the expected trend for a typical EDLC system. This unusually large value is likely not representative of pure double layer capacitance. Instead, it is suggested that at this very low scan rate, additional contributions such as parasitic Faradaic reactions or minor electrolyte decomposition may occur. Since the specific capacitance calculation assumes that all measured current is purely capacitive, any slow side reactions can artificially increase the integrated area of the CV curve, leading to an overestimation of the calculated capacitance. Therefore, for a more reliable evaluation of BSPE-2 performance, the results obtained in the range of 10 mV/s to 100 mV/s are more representative of the actual device behaviour in practical operating conditions.

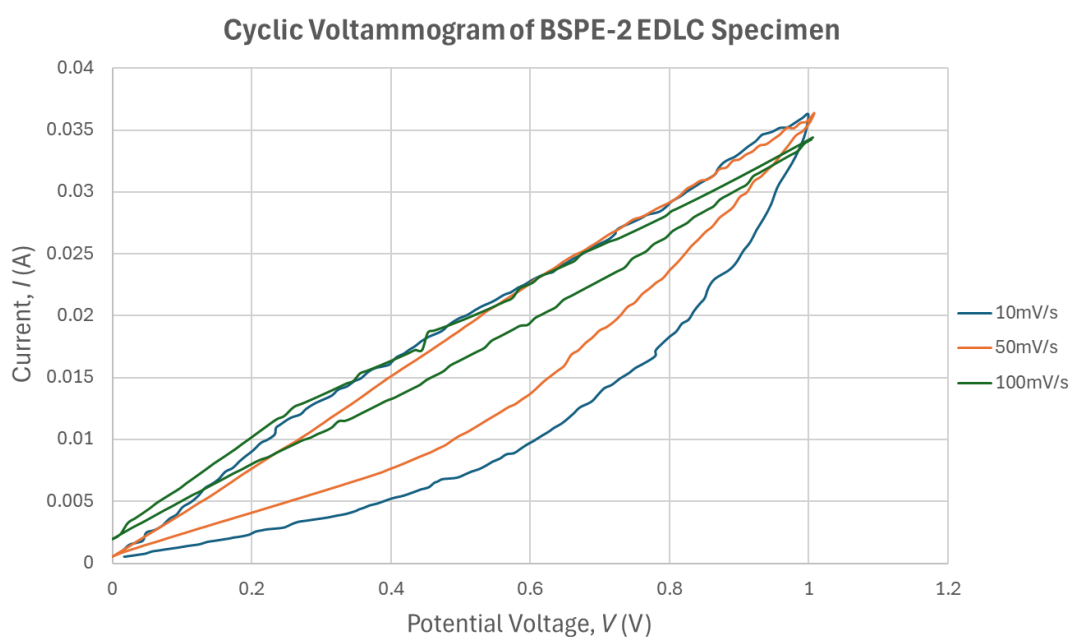


Fig 4.17 CV Result of Difference Scan Rate of BSPE-2 EDLC Specimen

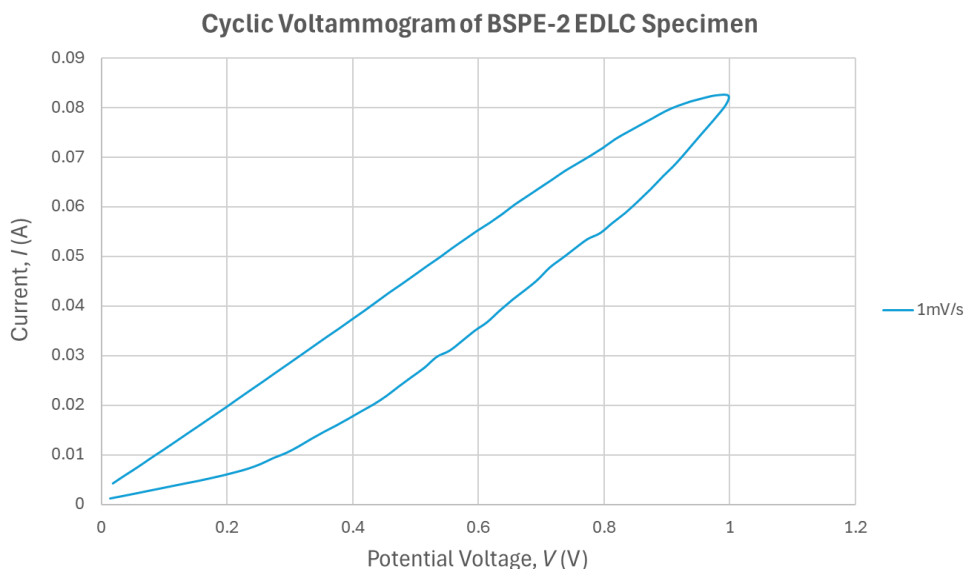


Fig 4.18 CV Result of 1mV/s Scan Rate of BSPE-2 EDLC Specimen

4.3.4 GCD Electrochemical Performance Analysis

Following the EIS analysis, the energy storage performance of the EDLC assembled with the optimized BSPE-2 electrolyte was further evaluated using Galvanostatic Charge Discharge (GCD) measurements. The resulting GCD profiles exhibit a well-defined quasi triangular shape, which is a typical characteristic of ideal capacitive behaviour which is shown in Fig 4.19. The nearly linear discharge slope indicates that the charge storage mechanism is mainly governed by the physical adsorption and desorption of ions at the electrode electrolyte interface, confirming that the system operates predominantly through a stable electric double layer mechanism. Although the curves show good symmetry between charge and discharge processes, a small initial voltage drop, commonly known as the IR drop, is observed at the beginning of the discharge curve. This IR drop is attributed to equivalent series resistance which arises from the intrinsic resistance of the PEMA-LiTFSI-BaTiO₃ composite electrolyte as well as the interfacial resistance between the electrolyte membrane and the activated carbon electrodes.

From the discharge curves, the calculated specific capacitance of the device is **11.02 F/g**. This value is consistent with the results obtained from CV analysis at moderate scan rates, indicating that the BSPE-2 electrolyte effectively facilitates ion transport within the porous electrode structure under constant current operation. In addition, the device achieves

an energy density of **0.462 Wh/kg** and a power density of **83.14 W/kg**. These values demonstrate a balanced electrochemical performance, where both energy storage capability and power delivery efficiency are maintained within a practical operating range. In the referenced study of PEMA with 40 wt% LiTFSI system (Yek, Jun and Liew, 2023), the energy density and power density were limited to only 22.2 mW kg⁻¹ and 14.0 W kg⁻¹, respectively. The poor electrochemical performance was mainly attributed to high interfacial resistance and low bulk ionic conductivity at the electrode-electrolyte interface. In contrast, the BSPE-2 system developed in the present work demonstrates a significant performance improvement, achieving an energy density more than twenty times higher together with a power density nearly six times greater than the reported baseline system.

This improvement originates from the enhanced bulk ion transport behaviour within the electrolyte matrix which indirectly improves the specific capacitance performance. Although specific capacitance mainly occurs at the electrode-electrolyte interface, its performance is still strongly influenced by the resistance of the electrolyte medium. The high ionic conductivity achieved by the BSPE-2 membrane helps minimize the internal ESR, then reducing the initial internal resistance drop during discharge. The improved ionic mobility enables lithium ions to penetrate more efficiently into the microporous structure of the activated carbon electrodes, allowing better utilization of the available surface area for electric double-layer formation (Suen, J.W. *et al.*, 2023).

Besides that, the expanded electrochemical stability window of 6.2 V achieved by the BSPE-2 electrolyte also contributes significantly towards the enhancement of the overall energy and power performance. Based on the energy density relationship:

$$E = \frac{1}{2} CV^2 \quad (5)$$

the energy density increases proportionally with the square of the operating voltage. Therefore, the ability of the BaTiO₃-stabilized electrolyte system to withstand higher operating potentials without oxidative decomposition allows the EDLC device to operate over a wider voltage range, which significantly enhances the energy storage capability of the system.

Overall, the excellent electrochemical performance of the BSPE-2 system can be attributed to the synergistic effect between the expanded electrochemical stability window and the enhanced ionic conductivity. The wider stability window increases the allowable

operating voltage, while the improved ionic conductivity enhances accessible capacitance and reduces internal resistance within the EDLC system.

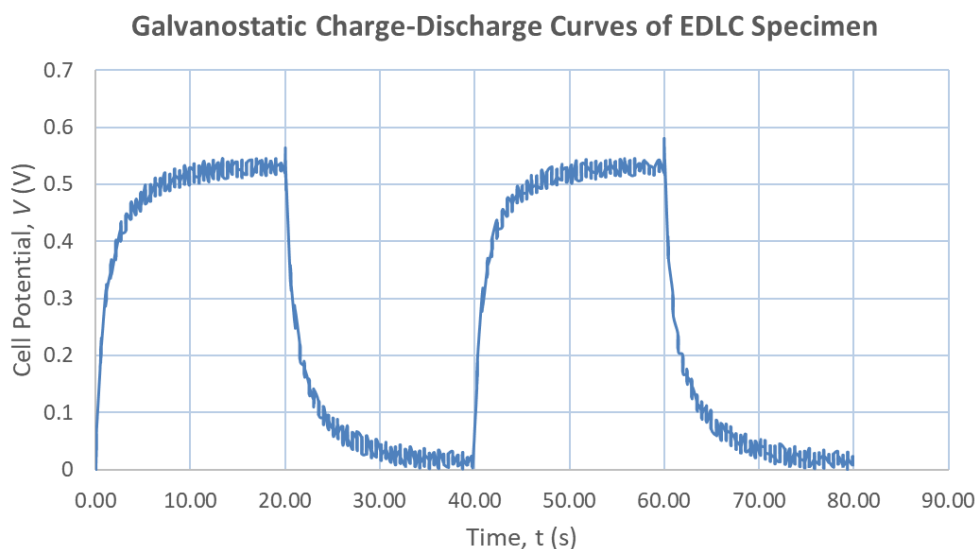


Fig 4.19 GCD Result of BSPE-2 EDLC Specimen

4.3.5 Cycle Stability Test Analysis

To evaluate the long-term durability of the BSPE-2 based EDLC, a cyclic stability test was carried out over 500 charge discharge cycles. The results indicate a notable limitation in the operational lifespan of the device. During the initial 200 cycles, the energy density remains relatively stable at around 0.55 Wh/kg, suggesting that the electrolyte electrode interface is initially stable and capable of sustaining repeated charge storage without significant degradation. However, after surpassing the 200-cycle mark, a clear and continuous decline in performance is observed. By the end of the 500th cycle, the energy density decreases significantly to approximately 0.245 Wh/kg, corresponding to a reduction of about 55.5%, which is shown in Fig 4.20. A comparison was made against a reference system consisting of PEMA with 40 wt% LiTFSI (Yek, Jun and Liew, 2023). That reference system showed exceptionally poor durability, with its specific capacitance deteriorating by 57.5% within just the first 10 cycles. The literature attributed this rapid decay to the formation of ion aggregates that blocked the carbon pores and obstructed ion accumulation at the interface.

By comparison, the BSPE-2 system exhibits a better trend which maintains a stable energy density for the first 200 cycles before declining. This extended result proves that the 2 wt% BaTiO₃ filler successfully delays early-stage ion pairing compared to the reference system.

However, standard liquid-electrolyte EDLCs typically exhibit excellent capacity retention, often maintaining over 90% performance across thousands of cycles due to fluidic ion diffusion (Queirós, G.P. *et al.* 2026). The 55.5% drop observed here after 500 cycles indicates unique solid-state challenges. Because this drop occurs much later and more gradually than the reference literature, it is likely caused by a dynamic build-up of localized ion polarization and concentration gradients rather than permanent material breakdown.

This pronounced drop in performance indicates poor long term cycling stability for the current BSPE-2 formulation. The degradation behaviour can be attributed to several possible mechanisms. One likely factor is the presence of micro sized BaTiO₃ particles which may lead to mechanical instability within the PEMA matrix during repeated cycling. Over time, the continuous expansion and contraction of the electrode structure during charge and discharge may induce localized stress, causing partial detachment of filler particles or the formation of micro cracks within the electrolyte membrane. These structural defects can gradually disrupt ion transport pathways and increase internal resistance. In addition, the performance decay may also be influenced by slow interfacial changes such as the accumulation of resistive decomposition products or partial loss of electrolyte integrity due to residual solvent effects.

Overall, the cyclic stability results highlight a clear limitation in the long-term durability of the current system. Although BSPE-2 demonstrates good initial electrochemical performance, its structural and interfacial stability under prolonged cycling is insufficient for practical long-term applications. This suggests that further optimization is necessary, particularly using nano sized ceramic fillers or improved filler polymer interfacial bonding to enhance mechanical stability and maintain consistent ionic transport pathways throughout extended cycling operation.

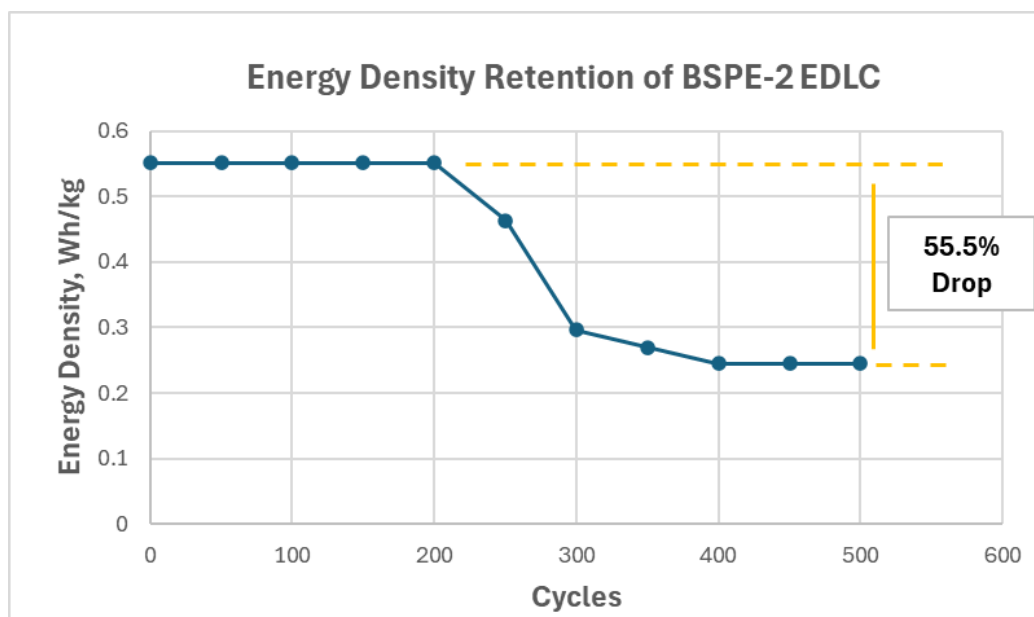


Fig 4.20 Cyclic Stability and Energy Density Retention of BSPE-2 EDLC over 500 Cycles

4.4 Summary

In summary, the characterization and testing of the PEMA based SPEs demonstrate that the incorporation of ceramic fillers, particularly BaTiO₃, significantly modifies both the structural and electrochemical behaviour of the system. The material analysis confirms that the polymer matrix remains largely amorphous which is beneficial for ion transport; however, the use of micro sized fillers introduces localized dispersion inconsistencies and wetting limitations at the filler polymer interface.

From an electrochemical perspective, the BSPE-2 formulation shows the best overall performance among all samples, achieving the highest ionic conductivity of 5.28×10^{-5} S/cm and the widest electrochemical stability window of 6.2 V. When applied in an EDLC configuration, this electrolyte supports a specific capacitance of 11.02 F/g with a stable quasi triangular charge discharge profile, indicating effective electric double layer formation. However, despite these promising initial results, the observed 55.5 percent energy density degradation over 500 cycles reveals a significant limitation in long term cycling stability. This degradation is most likely associated with the relatively large particle size of the ceramic fillers which may induce interfacial stress, poor mechanical cohesion, and progressive deterioration of ion transport pathways during repeated cycling.

Overall, these findings clearly demonstrate a strong relationship between filler characteristics and overall device performance, highlighting that while BaTiO₃ effectively enhances conductivity and stability in the short term, its micro scale morphology limits long term durability. This provides a clear direction for future optimization, particularly using nano sized fillers and improved interfacial engineering to enhance both electrochemical performance and cycling stability.

CHAPTER 5 CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The primary objective of this research was to develop and optimize a high-performance SPE for EDLC applications by investigating the effects of different ceramic additives on a PEMA-LiTFSI host matrix. Through a systematic evaluation of both structural and electrochemical properties, it was found that BaTiO₃ at 2 wt%, designated as BSPE-2, represents the most effective formulation among all tested candidates. This study successfully achieved its intended goals by demonstrating that the incorporation of BaTiO₃ significantly improves electrolyte performance compared to LLZTO, TiO₂, and ZnO based systems.

Material characterization provided important insights into the relationship between membrane structure and electrochemical functionality. XRD analysis confirmed that all electrolyte systems maintain a predominantly amorphous structure which is essential for efficient ion transport through polymer segmental motion. However, SEM and EDX results revealed a key limitation associated with filler morphology, where the micro sized BaTiO₃ particles, averaging approximately 20 μm , lead to localized dispersion inconsistencies and wetting issues within the PEMA matrix. Despite these structural limitations, the BSPE-2 electrolyte achieved a significantly improved ionic conductivity of $5.28 \times 10^{-5} \text{ S/cm}$ which is more than an order of magnitude higher than the filler free reference system. In addition, the electrochemical stability window was expanded to 6.2 V, indicating strong potential for safe high voltage operation in energy storage applications.

When applied in an EDLC system, the optimized electrolyte demonstrated a specific capacitance of 11.02 F/g and a power density of 83.14 W/kg, with quasi triangular GCD profiles confirming stable electric double layer behaviour. However, the cyclic stability test revealed a major limitation in long term performance, with a 55.5 percent reduction in energy density after 500 cycles. This degradation suggests that although BaTiO₃ enhances ionic conductivity and voltage stability, the large particle size introduces mechanical stress and interfacial resistance within the membrane during repeated cycling, ultimately affecting durability.

In conclusion, this work demonstrates that BaTiO₃ is an effective ceramic additive for improving the electrochemical performance of PEMA based SPEs, particularly in terms of conductivity and stability window. However, for practical and commercial level applications, further improvement is required, especially using nano sized fillers and enhanced polymer filler interfacial engineering, to improve mechanical stability and long-term cycling reliability in solid state energy storage systems.

5.2 Recommendation of Future Work

To further improve the performance and practical viability of PEMA based SPEs, several key strategies should be considered in future work to address the limitations identified in this study. The most important direction is the replacement of micro sized ceramic fillers with nano sized particles. By reducing the particle size to the nanoscale, the surface to volume ratio would increase significantly, enabling stronger Lewis's acid base interactions with the polymer chains. This improvement would also help eliminate the interfacial wetting issues and localized agglomeration observed in the BSPE-2 morphology, leading to a more homogeneous electrolyte structure and improved ion transport pathways.

Besides, the fabrication process for both the electrolyte membrane and the EDLC assembly should be further refined to improve reproducibility and data reliability. Techniques such as high energy ball milling or probe ultrasonication should be introduced to replace manual stirring, ensuring a more uniform dispersion of ceramic fillers within the PEMA-LiTFSI matrix. At the same time, developing and adopting a suitable coating method would allow for better control over electrolyte thickness, producing thinner and more uniform electrolyte films. Reducing the thickness of the SPE layer is particularly important as it can lower bulk resistance, reduce IR drop during discharge, and ultimately enhance power density.

Beyond physical processing improvements, the chemical formulation of the electrolyte can also be further optimized. The incorporation of solid plasticizers or non-volatile additives could transform the system into a quasi-solid or gel like electrolyte, increasing the free volume within the polymer matrix. This would enhance polymer segmental motion and improve the ability of the electrolyte to accommodate repeated mechanical strain caused by electrode expansion and contraction during cycling, thereby helping to mitigate the long-term energy density degradation observed in this study.

Furthermore, future work should include temperature dependent conductivity studies over a wider range, such as 200 °C to 800 °C, to better understand ion transport behaviour under different operating conditions. There is also strong potential in exploring multi filler synergistic systems, where different ceramic additives are combined to take advantage of complementary properties, for example using BaTiO₃ for dielectric stabilization together with LLZTO for enhanced lithium-ion conduction pathways. Lastly, alternative copolymer hosts such as Poly(MMA-co-EMA) may be investigated to engineer a more mechanically robust yet highly amorphous matrix, improving both durability and long-term cycling stability for advanced solid state energy storage applications.

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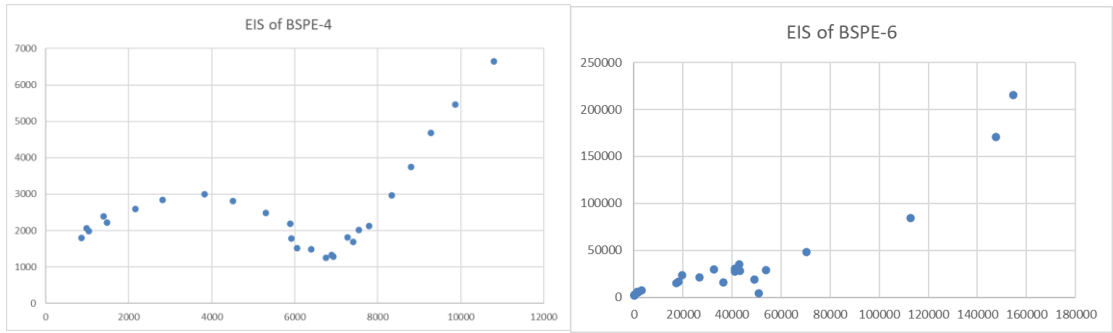
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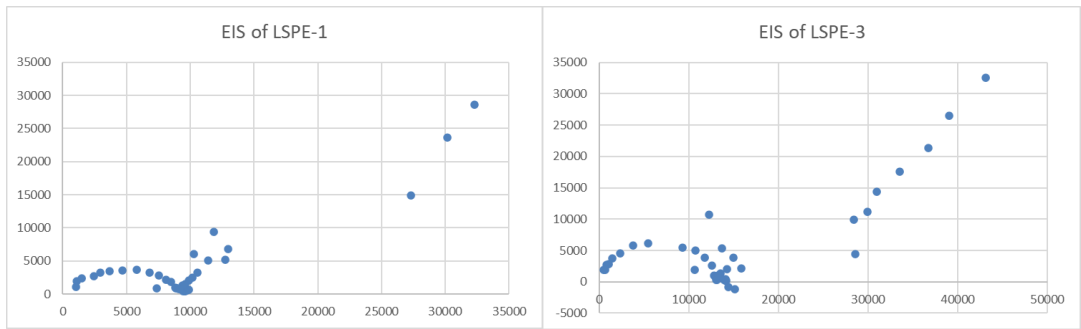
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APPENDICES

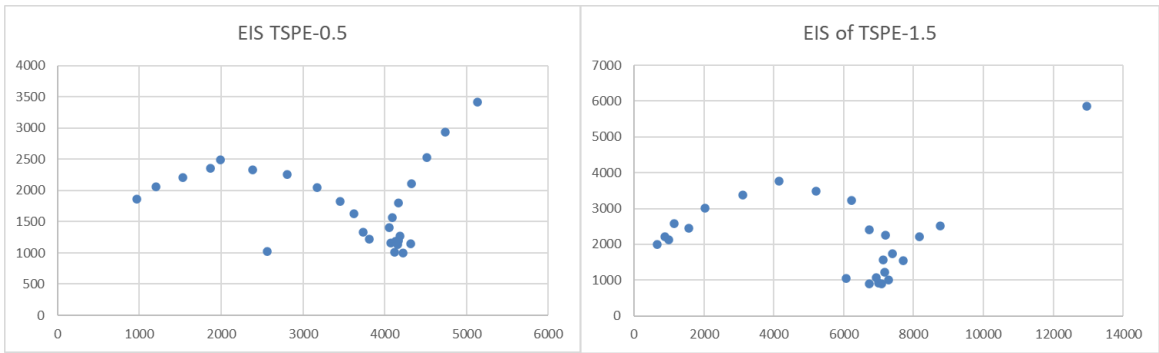
APPENDIX A: EIS Result of Remaining Composition SPE



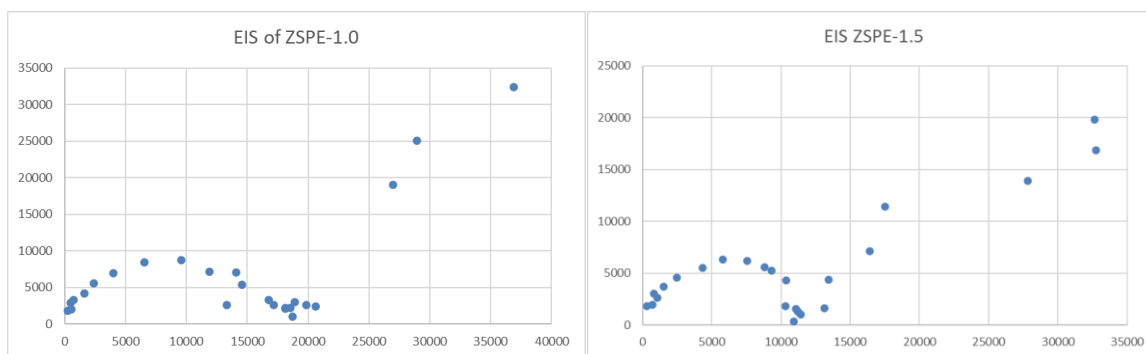
a) EIS of BSPE-4 (left) and BSPE-6 (right)



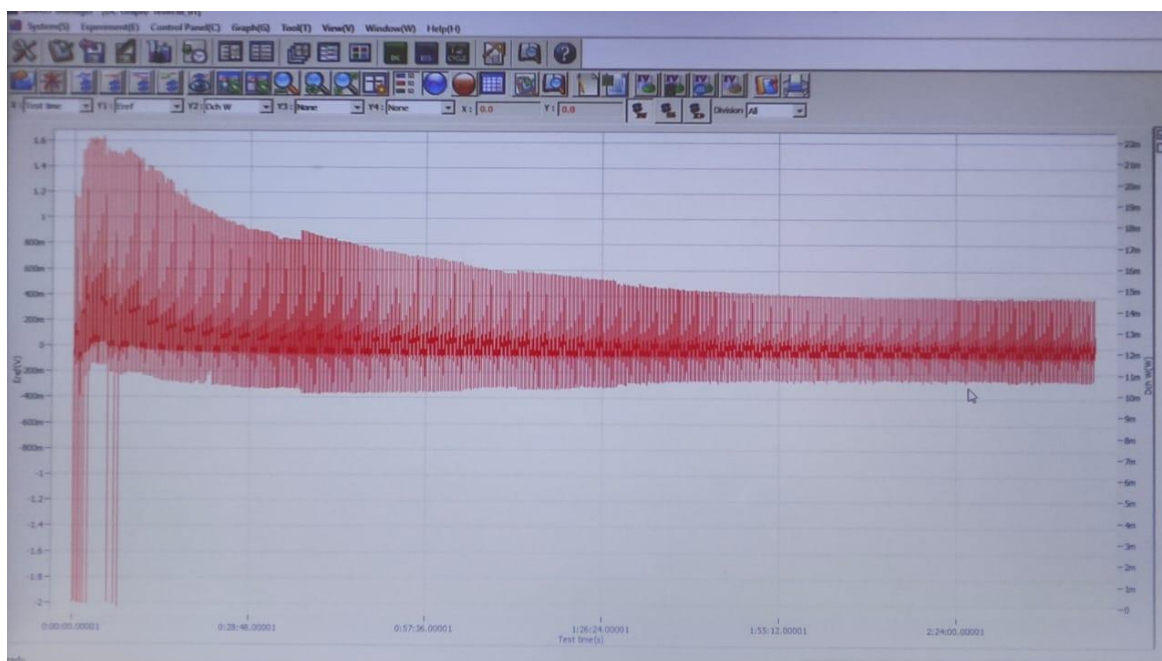
b) EIS of LSPE-1 (left) and LSPE-3 (right)



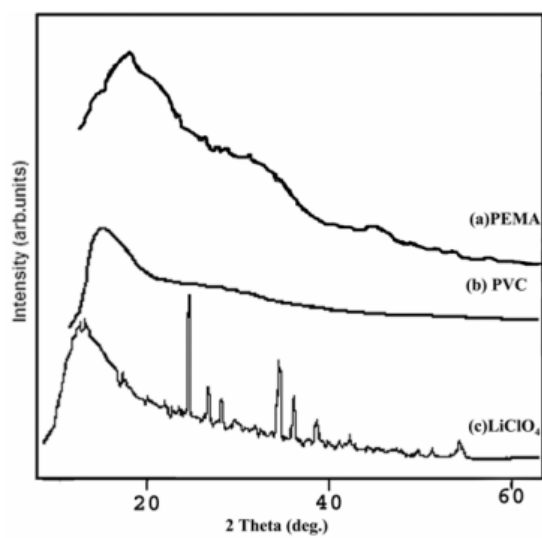
c) EIS of TSPE-0.5 (left) and TSPE-1.5 (right)



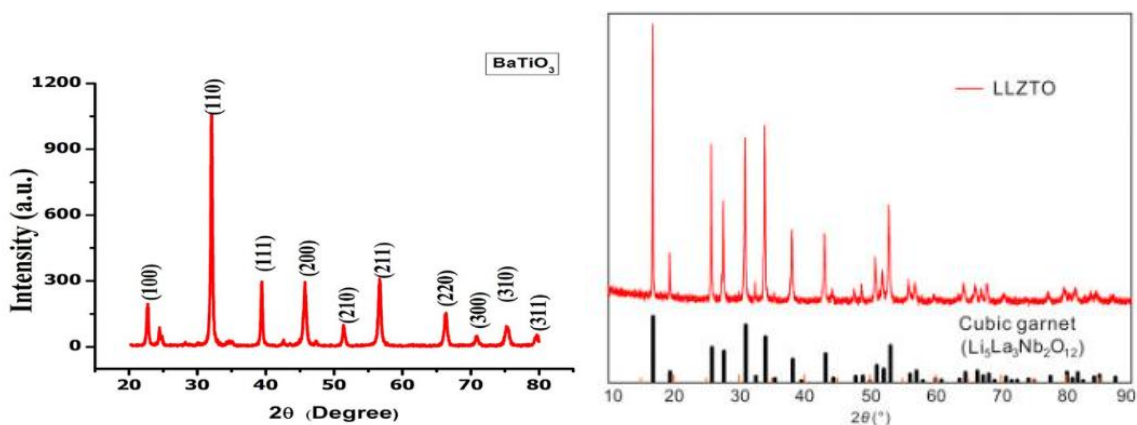
d) EIS of ZSPE-1.0 (left) and ZSPE-1.5 (right)



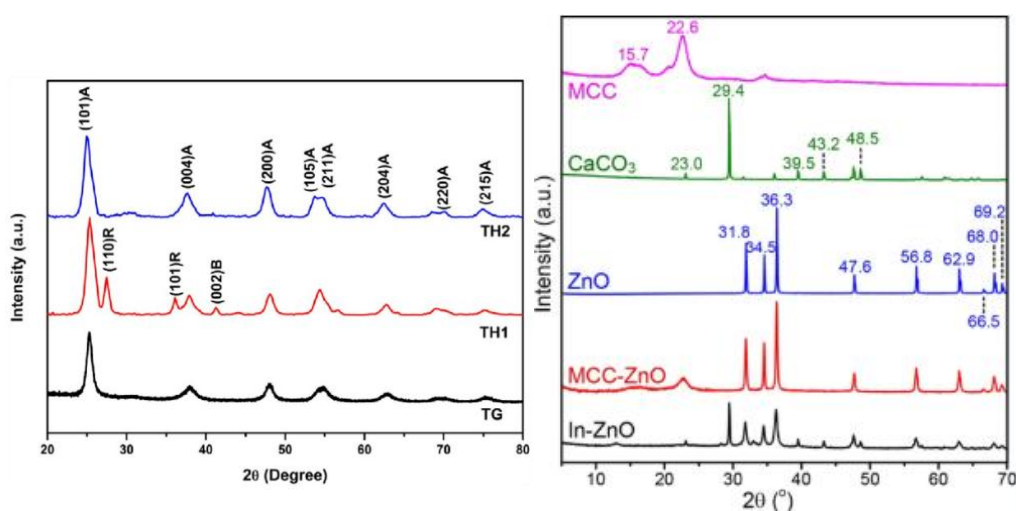
e) 500 Cycle Test of BSPE-2



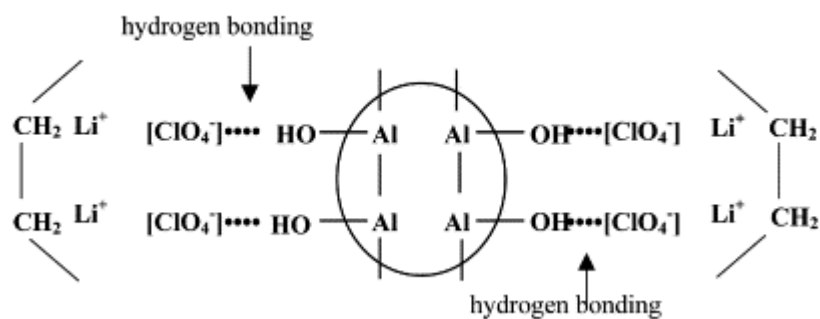
f) XRD Pattern of PEMA



g) XRD Pattern of BaTiO_3 (left) and LLZTO (right)



h) XRD Pattern of TiO_2 (left) and ZnO (right)



i) Pictorial model of the surface interaction between Al_2O_3 inorganic filler and PEO- LiClO_4 electrolyte complex