Study and Analyze the Effect of Inorganic Filler on Ionic Conductivity in Polyethylene Oxide (PEO) Composite Polymer Electrolyte.

By

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2023

Study and Analyze the Effect of Inorganic Filler on Ionic Conductivity in Polyethylene Oxide (PEO) Composite Polymer Electrolyte.

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H-12, Islamabad, Pakistan
September, 2023

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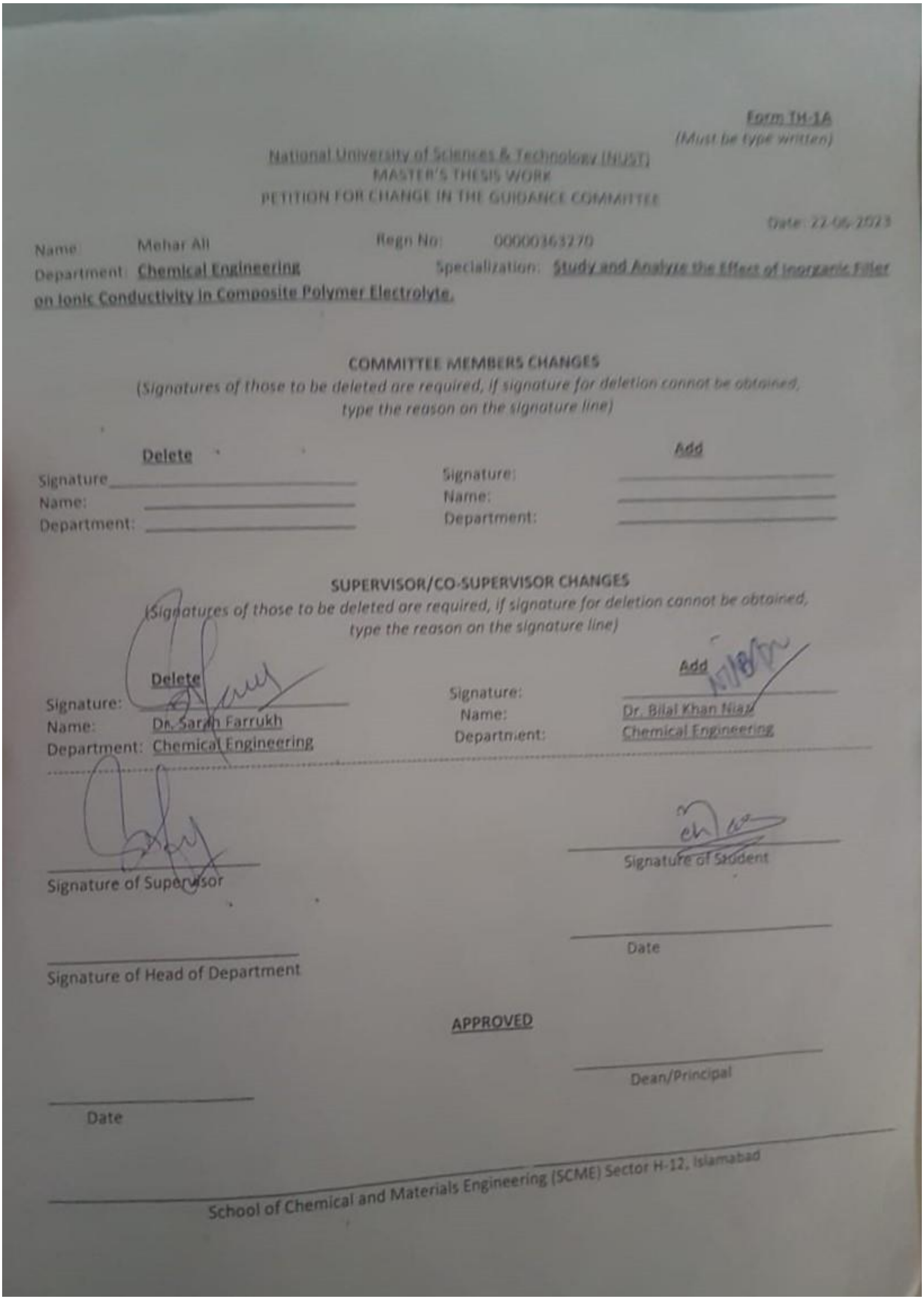

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Presented on: **19 Oct 2023** at: **1430 hrs in SCME Seminar Hall**

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Dedication

By the grace of Almighty Allah, who is the most Beneficent and the most merciful

This research is dedicated to my parents, who have always been my source of guidance and support.

To my supervisor who shared his knowledge, gave advice, and encouraged me to fulfill my tasks.

And to all my fellows, with whom I worked with and shared good memories.

Acknowledgements

All praises to Almighty Allah, without His will nothing can happen, who favored us with the capacity to think and made us anxious to investigate this entire universe. Incalculable greetings upon the Holy Prophet Hazrat Muhammad (PBUH), the reason for the creation of the universe and wellspring of information and blessing for whole humankind.

From the core of my heart, I am thankful to my research supervisor, Dr. Muhammad Bilal Khan Niazi for his unwavering technical and moral support and enlightening me with a research vision and pushing me for excellence. His quest for perfection and excellence had been a source of inspiration and driving force. It is his consistent and encouragement that empowered me to achieve the onerous milestone.

I extend my sincere gratitude towards my guidance and committee members, Dr. Erum Pervaiz, Dr. Tayyaba Noor and Dr. Ghulam Ali for guiding and supporting me in my research course. It would not have been possible without them. I express my gratitude for Dr. Muhammad Bilal Khan Niazi for sharing his knowledge and experience regarding research work.

I am thankful of My Seniors who shared their knowledge regarding experimental techniques, and they motivated me in this entire research work. Without any doubt, SCME’s supporting staff coordinated with me while I was working on different equipment’s.

I am highly obligated to my Parents and Siblings for their never-ending love. Thanks for believing in me, wanting the best for me, and inspiring me to follow my passion. To my friends and colleagues, thank you for your support, advice, and encouragement.

Mehar Ali

Abstract

This work is mainly focused on achieving energy challenges that can arise in future. Solid electrolyte which is used in secondary battery is an attractive technology to meet future energy demands as renewable energy resources. Solid electrolyte is next generation technology comparing to liquid electrolytes because of its easy handling easy processing and having flexible structure. The motive of current research work is to make such solid electrolyte material for secondary battery, PEO based composite polymer electrolytes were made to analyze the effect on conductivity of ions in solid polymer electrolyte by the incorporation of nano-filler. Characteristics of samples that were made with polyethylene oxide host polymer characterized with various techniques like XRD analysis it was observed that PEO:Lithium Triflate with 10:1 ratio showed two peaks at 23.3° and 19.06° which is corresponding to crystalline phase of the PEO, FTIR analysis identified presence of groups that are -OH, -CH, C=O and Ti-O at 3500cm^{-1}, 2970 cm^{-1}, 1642 cm^{-1}, 640 cm^{-1} respectively, SEM confirms the morphology of the samples and EIS conducted to obtain ionic conductivity of CPEs, maximum ionic conductivity was calculated 2.08x10^{-1} mS/cm without any filler. TiO_2 nano-filler was utilized to make composites. It is observed that with increasing TiO_2 in the host polymer with fixed amount of PEO and salt there is significant decrease in the crystallinity of the composite films comparing to pure PEO while increasing amorphous region in the CPEs which is responsible for the conduction of ions. The PEO and salt complex film has exhibited an increased conductivity which is around five times greater in magnitude than that of the pure polymer.

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Acronym and Abbreviations

PEO	Polyethylene Oxide
CPE	Composite Polymer Electrolyte
SPE	Solid Polymer Electrolyte
DI Water	Deionized water
FTIR	Fourier Transform Infrared Radiation
SEM	Scanning Electron Microscope
XRD	X-ray diffraction
EIS	Electrochemical Impedance Spectroscopy
Avg FT	Average Film Thickness
TPU	Thermoplastic Polyurethane
HIPS	High Impact Polystyrene
PEGDMA	Poly(ethylene glycol) dimethacrylate
PEGMA	Poly(ethylene glycol) methyl ether methacrylate
TFA	Trifluoroacetic acid
PEI	Polyethylenimine
LiI	Lithium Iodide
EC	Ethylene Carbonate
PPO	Polypropylene Oxide
PVC	Poly (vinyl chloride)
PEMA	Poly (ethyl methacrylate)
SSLIBs	Solid-State Lithium-Ion Batteries

Chapter 1

Introduction

1.1 Background

The global population is increasing, especially in developing countries. This population growth, combined with advancements in technology, has resulted in a higher demand for electricity. As time goes on, this demand for energy is expected to continue rising. By the middle of the century, it is estimated that the world may require twice as much energy as it currently does. By the end of the century, this energy demand could potentially triple. This forecast underscores the importance of implementing sustainable and efficient energy solutions to meet the increasing energy demands of the future [1]. With the rise in energy consumption and decrease in the availability of fossil fuels, a growing focus on researching renewable energy storage solutions and their utilization [2]. Lithium-ion Solid-state rechargeable batteries are considering as an alternative solution for addressing energy density and safety challenges associated with conventional lithium-ion batteries. These batteries employ solid electrolytes in place of flammable liquid electrolytes, inherently enhancing their safety [3-7]. Metallic conductors are commonly employed as electrodes in batteries. However, an alternative approach introduced the utilization of conductive polymers as electrode materials, marking an early suggestion in battery technology. The adoption of conductive polymers offers several advantages compared to traditional metals. These advantages include reduced weight, cost-effectiveness, enhanced recyclability, and lower toxicity levels [8].

Conductive polymers are a class of organic polymers known for their ability to conduct electricity through ion migration. In terms of transport properties, polymer electrolyte membranes exhibit similarities to liquid ionic solutions. The unique characteristic of conductive polymers lies in their capacity to blend the properties of both metals and organic compounds [9].These materials combine the high electrical conductivity typical of metals with the mechanical properties characteristic of polymers. The mechanical traits of polymers encompass attributes such as flexibility, elasticity, malleability, and toughness. The introduction of polymer electrolytes can be traced back to their initial development by Fenton in 1973, and their technological significance was fully recognized in 1980. In terms of ionic conductivity, poly(ethylene oxide)-based solid electrolytes exhibit very low values, typically around 10-8 S cm-1 at room temperature. The polymer in this system serves as a solid solvent, eliminating the need for any organic liquids [10]. The cycling performance of this dry solid polymer electrolyte proved to be unsatisfactory when paired with a lithium metal electrode. When it comes to polymer electrolytes, one prevalent category is polymer composites. Polymer composites represent a macroscopic union of two or more materials with well-defined interfaces. Typically, polymer composites consist of fibers or particles embedded within a matrix material. The inclusion of fillers in these composites offers several advantages, including enhanced fire/flame resistance, improved thermal and electrical conductivity, as well as cost-effective benefits [11]. The lightweight and high-strength properties of polymer composites make them valuable in applications within the automotive and aerospace industries. Polymer composites find use in various sectors, including transportation, aerospace, sports, construction, and many others.

Polymer composites are created by introducing insoluble and electrochemically inert fillers into polymer matrices. Common inert fillers include Al2O3, TiO2, SiO2, and ZrO2. These composite materials fall into the category of either composite ceramic electrolytes or composite polymer electrolytes. The addition of fillers enhances stability at the electrode interface and increases ionic conductivity, particularly at lower temperatures. Some examples of polymer hosts that have been developed and characterized for this purpose include polyethylene oxide, poly(methyl methacrylate), and poly(vinyl chloride). Solid electrolytes that exhibit very low activation energy for ionic transport at temperatures significantly below their melting points, negligible electronic conductivity, and high ionic conductivity are often referred to as fast ion conductors [12]. Solid electrolytes are categorized based on the conducting species they support, such as Li+, Na+, or Ag+ ions. Li+ ion solid conductors, in particular, find applications in high-energy-density batteries due to their lightweight nature and high electrochemical potential. Various methods have been employed to achieve solid electrolytes with high ionic conductivity at room temperature. These methods include (i) dispersing insoluble, insulating particles like Al2O3 or SiO2 into ionic matrices and (ii) forming complexes between polymers and metal salts.

Lithium and sodium share similar physicochemical properties, but lithium is considerably more expensive than sodium. The softness of sodium metal plays a crucial role in ensuring good contact with components in solid-state ionic devices, such as batteries, during charging and discharging processes.

Organic materials capable of conducting electricity under different conditions are referred to as organic semiconductors. Their electrical conductivity behavior falls between that of metals and non-conductive materials. Unlike ionic conduction, which relies on ions, electrical conduction in conductive materials is purely electronic [13]. Graphite serves as an example of an organic conductor, and its electrical conduction can be likened to that of a semiconductor.

When comparing organic polymers to semiconductors and metals, it becomes evident that organic polymers are relatively poor conductors of electricity. This distinction arises from the fact that electrical conductivity in metals and semiconductors results from the presence of delocalized electrons. In the case of organic polymers, large energy gaps exist between conduction bands, leading to the localization of the most energetic electrons.

In 1977, it was discovered that polyacetylene exhibits metallic conductivity. Polymers that display both the electrical and optical properties of metals while retaining the mechanical properties of polymers are referred to as synthetic metals or intrinsically conductive polymers.

Leading examples of conducting polymers with significant technological applications include polyaniline, polypyrrole, and derivatives of polythiophene. Ionic-conducting polymer electrolytes are utilized in electrochromic displays and batteries, although their conductivity values tend to be relatively low [14]. The relatively lower conductivity observed in ionically conducting polymer electrolytes may be attributed to the strong ion pairing between cations and polymer-bound anions.

To enhance the conductivity of conductive polymers, various carbon fillers such as carbon black, graphite, and carbon fibers can be incorporated. These resulting conductive materials offer several advantages, including reduced weight, adaptability to specific application requirements, and resistance to corrosion.

The intrinsic conductivity of pure polymers typically falls within the range of 10^{-14} to 10^{-17} S cm^{-1}. Specific properties of polymer materials can be achieved by incorporating an appropriate amount of conductive fillers. Polymer composites' conductivity has been improved by introducing conductive fillers like metals (e.g., aluminum, copper, and nickel) or carbon. Carbon fibers enhance both electrical and thermal conductivity, while carbon black primarily enhances electrical conductivity and has no significant impact on thermal conductivity.

Conducting polymers can be categorized into four main classes.

A wide range of ionically conducting polymers has been developed, and these materials find numerous applications. Ionic-conducting polymers exhibit lower conductivity because the ionic conduction mechanism involves the dissociation of oppositely charged ions and the migration of these ions between coordination sites. This ion migration is often associated with the segmental motion of polymeric chains [15]. The overall conductivity of conducting polymers is influenced by the transportation of electrons within and between polymer chains.

Highly ionic conductive solid polymer electrolytes have been developed for potential applications in various electrochemical devices, including high-energy-density batteries, chemical sensors, and electrochromic devices. One of the earliest and most extensively studied polymer electrolytes is based on polyethylene oxide (PEO). However, practical applications of PEO-based polyelectrolytes at room temperature are limited due to the coordination of cations with oxygen atoms in the crystalline phase of PEO and the high melting point of this crystalline phase, resulting in very low ionic conductivity.

To address these issues, the mechanical strength of polymer electrolytes can be enhanced by employing PVC/PMMA blend electrolytes. Polyvinyl chloride (PVC), a readily available and cost-effective polymer, exhibits good compatibility with various plasticizers such as ethylene carbonate (EC), propylene carbonate (PC), and dibutyl phthalate (DBP) [16]. The plasticized PVC is extensively used in the form of films, sheets, flooring and wallboard due to its good mechanical strength [17-19].

1.2 Conducting Polymers

1.2.1 Types of Conducting Polymers

1.2.1.1 Polyacrylonitrile **(**PAN**)**

PAN is a promising material for this application because it is relatively inexpensive has good mechanical properties and can be easily processed into films. However, PAN has a low ionic conductivity on its own so it is often necessary to add plasticizers or other additives to improve the conductivity of the electrolyte.

Osman and colleagues talks about creating PAN-based polymer electrolytes softened with ethylene carbonate (EC) and propylene carbonate (PC). Babu and team focus on PAN-based polymer electrolytes that include polyvinyl chloride (PVC) as a mix.

Research on solid electrolytes made from PAN (Polyacrylonitrile) for lithium-ion batteries is in the early stages but there has been notable advancement in recent years. PAN shows promise as a material for these electrolytes and we need more research to enhance its ionic conductivity and electrochemical performance.

1.2.1.2 Polyethylene Oxide (PEO)

polyethylene oxide (PEO) is a popular polymer studied for solid electrolytes because it can dissolve lithium salts and has strong mechanical features. However, PEO doesn't conduct ions well at room temperature making it less useful in real-life applications.

Tarascon and Armand's provided an overview of the latest advancements in using PEO for solid electrolytes in lithium-ion batteries. Bouchet and colleagues have worked on developing PEO-based solid electrolytes that are cross-linked enhancing how well they conduct ions. Murugan and team have explored PEO-based solid electrolytes that contain LLZO with a garnet structure improving their conductivity.

PEO shows great promise as a material for making solid electrolytes in lithium-ion batteries. Researchers have made significant strides in improving the ion conduction and electrochemical performance of PEO-based solid electrolytes. However further research is needed to create PEO-based electrolytes suitable for widespread commercial use.

1.2.1.3 Polyvinylidene fluoride-hexafluoropropylene (PVdF-HFP)

Poly (vinylidene fluoride-hexafluoropropylene) (PVdF-HFP) is a polymer that many scientists are researching for making solid electrolytes. It's attractive because it's stable in different conditions both chemically and with heat and it's strong. PVdF-HFP also allows ions to move better than PEO at room temperature.

1.2.1.4 Poly (ethylene carbonate) (PEC)

Poly(ethylene carbonate) (PEC) is a polymer that holds great potential for making solid electrolytes in lithium-ion batteries. This is because it allows lithium ions to move easily is stable in different conditions and can handle heat well. However PEC doesn't conduct ions very well at room temperature which makes it less useful for real-life applications.

A major difficulty with solid electrolytes made from PEC is their cost. PEC is a relatively expensive material making it less viable for commercial use. Researchers are striving to find ways to produce PEC at a lower cost.

Another issue with solid electrolytes based on PEC is their mechanical properties. PEC is relatively soft which can pose challenges during processing and assembly into batteries. Researchers are working to devise new methods to enhance the mechanical properties of solid electrolytes based on PEC.

1.2.1.5 Polyacetylene (PA)

Polyaniline (PA) is a material that shows great promise for creating solid electrolytes in lithium-ion batteries. This is because it allows lithium ions to move easily is stable in different conditions and can handle heat well. However PA doesn't conduct ions very well at room temperature which makes it less useful for practical applications.

1.2.1.6 Polypropylene oxide (PPO)

Poly (propylene oxide) (PPO) holds promise as a material for creating solid electrolytes in lithium-ion batteries because it has good strength and can handle heat well. However PPO doesn't conduct ions very well at room temperature which limits how it can be used practically.

A significant issue with solid electrolytes based on PPO is that they don't conduct ions well at room temperature. Scientists are trying different methods to improve how well these solid electrolytes conduct ions like adding plasticizers and ceramic fillers.

Another challenge is making sure that solid electrolytes based on PPO can work well with all the other parts of a lithium-ion battery like the electrodes and separator.

1.2.1.7 Polyaniline (PANI)

Polyaniline (PANI) is a special kind of polymer that scientists are looking into as a possible material for solid electrolytes in lithium-ion batteries. It offers various benefits compared to other polymer electrolytes like being strong resistant to heat and stable during electrochemical processes. PANI can also conduct ions better than other polymer electrolytes at room temperature.

However PANI also has some downsides like not dissolving easily in common liquids and wearing down over time. To deal with these issues researchers have come up with different approaches such as:

- Adding special substances to PANI: Adding certain substances like acids to PANI can help it dissolve better and conduct ions more effectively.

- Mixing PANI with other polymers: Mixing PANI with other polymers such as polyethylene oxide (PEO) can make it dissolve better and make it stronger.
- Changing the way PANI is made: Scientists have also altered the way PANI is built making it even better. For example, modifying PANI by connecting its molecules can make it stronger and better at conducting ions.

Solid electrolytes based on PANI have the potential to enhance the safety and performance of lithium-ion batteries. However more research is necessary to create PANI-based solid electrolytes that conduct ions better work well with all the parts of a lithium-ion battery and last a long time.

1.3 Stability of Conductive Polymers

Some special polymers that can conduct electricity may break down over time even in an environment without oxygen and moisture. This happens because there's a chemical reaction that can't be undone between certain charged parts of the conductive polymer. This can occur when the dopant a substance that helps with conductivity is lost. The loss of this dopant happens because the charged parts are not stable especially when the polymer structure changes its shape.

1.4 Limitations of Conductive Polymers

Conductive polymers are seen as working well alongside silicon and metal devices rather than being in direct competition with them. These polymer materials don't conduct electricity in the same way as metals or semiconductors do. In fact, the speed at which electrical signals travel through silicon chips is faster than in conductive polymers [20].

However conductive polymers have their own advantages. They can stretch a lot and can be shaped easily. On the flip side they also have downsides. While they're better than silicon-based devices in terms of flexibility they're not as strong as metals. Polymers can be easily damaged through scratching because they are very soft. To solve this scratching issue researchers are trying to create new polymers that are more resistant to scratching.

When it comes to conducting electricity polymeric materials do it in one or two directions unlike metals which conduct in all three directions. This is because of how the polymer's structure is either in a straight line or in a flat plane. This directional conductivity in conductive polymers might be advantageous in some cases resisting conductivity in certain directions. However, in some situations it could also be a drawback.

1.5 Types of Salts used in Solid Electrolyte

Solid electrolytes made from polymers are a crucial part of storing energy in devices like lithium-ion batteries and supercapacitors. They play a key role in moving ions between the positive and negative sides and they have advantages in terms of safety and flexibility compared to the typical liquid electrolytes. The performance of these polymer solid electrolytes is greatly affected by the salts chosen for them. Below are some typical salts used in these types of electrolytes:

1.5.1 Lithium salts

In lithium-ion batteries solid electrolytes made with lithium are very popular. They often use different lithium salts like lithium perchlorate (LiClO4) lithium hexafluorophosphate (LiPF6) lithium trifluoromethanesulfonate (LiTFSI) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). These salts help lithium ions move within the solid polymer structure.

1.5.2 Sodium salts

Sodium-based polymer electrolytes are being explored as alternatives to lithium-based ones due to the abundance of sodium. Sodium salts like sodium perchlorate (NaClO4) and sodium hexafluorophosphate (NaPF6) can be used in sodium-ion batteries.

1.5.3 Potassium salts

Potassium-based polymer electrolytes are less common but are being studied for use in potassium-ion batteries. Potassium hexafluorophosphate (KPF6) and potassium bis(trifluoro-methane-sulfonyl)-imide (KTFSI) are examples.

1.5.4 Silver salts

In solid-state silver-ion batteries you can use silver salts like silver triflate (AgTf) in the polymer electrolytes.

1.5.5 Ammonium salts

Ammonium-based salts like ammonium hexafluorophosphate (NH4PF6) and ammonium trifluoro-methane-sulfonate (NH4Tf) can be used in solid-state electrolytes for certain applications.

1.5.6 Magnesium salts

In solid-state magnesium-ion batteries magnesium salts like magnesium perchlorate (Mg(ClO4)2) and magnesium hexafluorophosphate (MgPF6) are investigated for use in polymer electrolytes.

1.5.7 Phosphonium salts

Phosphonium-based salts such as tri-hexyl(tetradecyl)phosphonium bis(trifluoro-methane-sulfonyl)-imide (P14666TFSI) have been studied for their potential in polymer electrolytes.

1.5.8 Imidazolium salts

Some organic polymer electrolytes use salts that have imidazolium as their base like 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF4).

Choosing the right salt depends on what you want to use it for how well it conducts ions whether it goes well with the polymer and how safe it is. Scientists are always trying to create new combinations of salts and polymers to make energy storage devices work better and be safer.

1.6 Plasticizers

Plasticizers are often added to polymer solid electrolytes to enhance their flexibility reduce brittleness and improve ionic conductivity. However it's important to choose plasticizers carefully to ensure they do not negatively affect the overall performance and stability of the solid electrolyte. Here are some possible plasticizers that can be used in polymer solid electrolytes for energy storage devices:

1.6.1 Polyethylene glycol (PEG)

PEG is a common plasticizer used in polymer electrolytes. It can improve the flexibility of the polymer matrix and enhance ion transport properties. Different molecular weights of PEG can be selected based on the desired properties.

1.6.2 Propylene carbonate (PC)

PC a commonly used plastic softener is frequently added to polymer electrolytes particularly in lithium-ion batteries. It serves a dual purpose of increasing flexibility and improving the connection between the polymer electrolyte and the electrode materials.

1.6.3 Ethylene carbonate (EC)

Another softener called EC which is based on carbonates is utilized in solid polymer electrolytes especially for lithium-ion batteries. It helps boost how well ions move (ionic conductivity) and the movement of lithium ions (lithium-ion transference number).

1.6.4 Dimethyl carbonate (DMC)

DMC a low-viscosity softener based on carbonates can enhance how well polymer electrolytes perform by making them better at conducting ions and more flexible.

1.6.5 Ionic liquids

Some liquid salts known as ionic liquids can also act as softeners. They don't just make the material more flexible but also help it conduct ions better.

1.6.6 Phosphonium-based plasticizers

Certain compounds based on phosphonium can be used as softeners in solid polymer electrolytes. For instance a compound called tri-hexyl(tetradecyl)phosphonium bis(trifluoro-methane-sulfonyl)imide (P14666TFSI) has been studied for how well it softens the material.

1.6.7 Lithium salts as plasticizer

In some situations lithium salts themselves can act as softeners while also aiding in ion movement. However using them as softeners might be limited due to worries about how well they mix with the polymer structure.

1.6.8 Esters

Certain esters like tributyl phosphate (TBP) or trimethyl phosphate (TMP) can work as softeners in polymer electrolytes especially in lithium-ion batteries.

Softeners serve multiple crucial roles in solid polymer electrolytes used for energy storage devices:

1.7 Role of Plasticizers in Solid Electrolyte

1.7.1 Enhancing Flexibility and Mechanical Properties

The main job of plasticizers is to make the polymer electrolyte more flexible and robust. They do this by lowering the glass transition temperature (Tg) of the polymer material making the solid electrolyte more bendy and less likely to break. This flexibility is crucial because it helps the solid electrolyte handle stress and changes in shape during charging discharging or temperature changes without breaking or coming apart.

1.7.2 Improving Ionic Conductivity

Plasticizers can make the solid electrolyte conduct ions better. They help the ions (like lithium ions in lithium-ion batteries) move more easily within the polymer material.

This improved movement of ions lowers the resistance inside the material and makes ion transportation more effective. That in turn improves how well the energy storage device works and how fast it charges and discharges.

1.7.3 Reducing Interfacial Resistance

Certain plasticizers like propylene carbonate (PC) or ethylene carbonate (EC) can make sure that the solid electrolyte sticks well and connects properly with the electrode materials. This means ions can move more smoothly between the electrode and the electrolyte making the device perform better overall.

1.7.4 Enhancing Electrode-Electrolyte Compatibility

Some plasticizers can help the solid electrolyte match well with the electrodes in terms of how strong they are and how they behave chemically. This match-up reduces pressure at the spots where the electrodes and electrolyte meet lowering the risk of the electrode getting damaged and making the device more stable for a longer time.

1.7.5 Maintaining Ionic Liquid Properties

In certain cases plasticizers can have parts that act like liquid with ions within the solid electrolyte. This helps increase ion movement and allows the device to work in a broader range of temperatures.

1.7.6 Adjusting Tg and Phase Behavior

Plasticizers allow us to manage the glass transition temperature (Tg) and how the solid electrolyte changes its structure. By adjusting the Tg the solid electrolyte can be made to work well in specific temperature conditions making it suitable for different uses.

1.7.7 Increasing Safety

Carefully chosen plasticizers can enhance safety in energy storage devices. For example they can help lower the risk of harmful reactions starting at high temperatures making the device safer to use.

It's important to pick the right plasticizer based on the specific polymer used in the solid electrolyte what properties you need (like flexibility and ion movement) and how well it fits with the other parts of the energy storage device. Also we need to be careful about how much plasticizer we use to avoid overdoing it.

1.8 Types of nano Fillers used in Solid Electrolyte

Incorporating tiny particles of inorganic materials into polymer solid electrolytes can make them better in many ways. These particles can be like very small pieces of ceramics or metals. When added to the electrolyte they can improve how well ions move make it stronger handle heat better and work well in chemical reactions. Let's look at some common tiny inorganic particles added to polymer solid electrolytes:

1.8.1 Nano-sized ceramic particles

Tiny ceramic particles like alumina ($Al2O3$) silica ($SiO2$) zirconia ($ZrO2$) and titania ($TiO2$) can be added to the polymer. They make it easier for ions to move and make it stronger.

1.8.2 Lithium salts and lithium-containing nanoparticles

Tiny particles made of materials that help lithium ions move like lithium aluminum titanium phosphate (LATP) lithium lanthanum titanate (LLTO) or lithium garnets (e.g. $Li7La3Zr2O12$ LLZO) can be used to make the solid polymer electrolytes conduct lithium ions better.

1.8.3 Carbon-based materials

Tiny particles made of carbon materials like graphene carbon nanotubes (CNTs) or carbon black can be added to make the electrolyte conduct electricity better and make it stronger. They can also make the whole thing work better in chemical reactions.

1.8.4 Metal nanoparticles

Tiny particles made of metals like silver (Ag) copper (Cu) or nickel (Ni) can be added to make it conduct electricity better and make it connect better with the electrodes.

1.8.5 Metal oxide nanoparticles

Tiny particles made of metal oxides like tin dioxide ($SnO2$) titanium dioxide ($TiO2$) or zinc oxide (ZnO) can be added to make the electrolyte conduct ions better make it stronger and handle heat better.

1.8.6 Sulfide nanoparticles

Some solid-state electrolytes for lithium batteries have tiny sulfide particles (e.g. $Li2S$) added to make ions move better especially when it's not very hot.

1.8.7 Nanoporous materials

Tiny materials with lots of small holes like zeolites or metal-organic frameworks (MOFs) can be used to catch and release ions. This helps ions move better in the solid electrolyte making it work well.

1.8.8 Clay nanoparticles

Tiny clay particles can be added to make the polymer stronger and more flexible. They can also help ions movement.

1.8.9 Hydroxide and carbonate-based nanoparticles

Tiny particles from things like magnesium hydroxide (Mg(OH)2) or lithium carbonate (Li2CO3) can be added to make ions move better and make the solid electrolyte work better.

1.8.10 Polymer-grafted nanoparticles

Adding tiny inorganic particles or nanoparticles into polymer solid electrolytes helps in many ways depending on what kind of tiny particles and properties we want for the solid electrolyte.

1.9 Role of nano Fillers in Solid Electrolyte

Incorporating inorganic fillers or nanoparticles into polymer solid electrolytes serves several important functions depending on the type of filler and the specific properties desired for the composite electrolyte. Here are the main functions of these inorganic fillers in polymer solid electrolytes:

1.9.1 Enhanced Ionic Conductivity

Many tiny inorganic particles like ceramic nanoparticles and metal oxides can create paths for ions to move inside the solid electrolyte. This helps ions move better and makes the solid electrolyte work well.

1.9.2 Improved Electrochemical Performance

By making ions move better these tiny particles can make batteries and supercapacitors work better. They can make the charging and discharging faster and make the device more powerful.

1.9.3 Reinforcement

These tiny inorganic particles can make the polymer solid electrolyte much stronger and keep its shape. They act like reinforcements making sure it doesn't break easily during use or when it gets hot and cold.

1.9.4 Enhanced Interface Properties

Certain tiny inorganic particles especially those with a lot of surface area like nanoparticles can make the connection between the solid electrolyte and electrode materials work better. This can make the device work better overall by making it more efficient.

1.9.5 Reduced Swelling and Leakage

Some tiny inorganic particles can help stop the solid electrolyte from swelling too much or changing its shape too much. This is important to keep the device stable and safe. They can also reduce the risk of the electrolyte leaking.

1.9.6 Thermal Stability

Tiny inorganic particles can make the solid electrolyte able to handle high temperatures better. They can make it more resistant to getting too hot which helps keep the device safe.

1.9.7 Glass Transition Temperature (Tg)

Adding certain particles can make the solid electrolyte change its behavior when it gets hot or cold. This helps to match how it works with the temperature it's in making it better for different situations.

1.9.8 Preventing Dendrite Formation

In lithium-ion batteries certain tiny particles can stop harmful growth that can cause short circuits and safety problems. They can act like barriers to this harmful growth or make the connection between the electrolyte and electrode stronger and safer.

1.9.9 Improving Cyclability

By making the solid electrolyte stronger and making the connection between parts better tiny inorganic particles can make the device last longer and work better for a longer time. This is good for how many times you can use it and how well it works overall.

1.9.10 Enhanced Safety

Inorganic fillers can make energy storage devices safer by reducing the chances of them getting too hot or breaking. They help to keep the solid electrolyte strong even when it's working in tough conditions.

Choosing the right inorganic filler depends on what you want for your application. Scientists and engineers carefully pick and improve these fillers to make sure the composite solid electrolyte works better stays stable and is safe.

Choosing the best inorganic filler or tiny particle depends on what the application needs and what properties you want in the composite solid electrolyte. It's important to choose the right type size and amount of filler carefully to make the solid electrolyte work better without breaking.

The choice of the tiny filler depends on different things like what properties you want for the composite solid electrolyte how much it costs and how easy it is to prepare. Composite solid electrolytes with these tiny fillers have shown to work very well in solid lithium-ion batteries. Scientists found that adding 10% TiO2 made the conductivity much better reaching a value of 4.89 × 10-2 mS cm-1 at normal temperature. Adding 50% ethylene carbonate plasticizers increased the conductivity even more to 1.59 × 10-1 mS cm-1 at room temperature. Adding both TiO2 and ethylene carbonate made the solid material less structured and more flexible. These changes made the conductivity better. Scientists also looked at how the electrolyte reacts to heat and found that adding TiO2 and EC made the material more flexible and less structured. This means the material's molecules can move around more easily. The better conductivity happened because of some special bonds and better movement of ions and molecules in the material [21].

1.10 Structural Properties of Polymer Electrolytes

Ionically conducting polymer is made by dissolving a salt in a polymer. In these polymer electrolyte systems ions move between specific sites. This movement happens because the polymer's parts can move. The main polymer should have spots where electrons are given to make bonds with positive ions the right spacing for making bonds with ions and easy movement of polymer parts.

Polyethylene oxide is a good polymer for solid polymer electrolytes. Different salts can dissolve in polyethylene oxide but lithium and sodium salts are the best. When the temperature goes above a certain point the conductivity of the polymer electrolyte gets better because the polymer's parts can move more and ions can move more [22].

Polymer electrolytes are good because they're solid devices and don't need seals. They come in different shapes and can replace liquid electrolytes in batteries. The structure of the polymer should let the charges move easily through it. A special kind of polymer called a conjugated polymer works well because the electrons can move along the polymer backbone. Polyacetylene is a good conductive polymer because of its simple structure and how it acts with electricity.

Most normal polymers don't have the right charge carriers but we can add them by changing the polymer a bit either by adding or taking away some electrons. Changing a nonconductive polymer into a conductive one isn't easy but band theory can help us understand what's happening. According to this theory how well a material conducts electricity depends on its electronic structure. Electrons can only move in certain energy levels and there's a gap between the highest and lowest levels. In normal polymers this gap is big but in conjugated polymers it's much smaller. Changing how many electrons are in these bands can make a nonconductive polymer conductive.

1.11 Transport Mechanism and Chain Flexibility

The movement of electrical charge in the polymer happens when the polymer chains move more at higher temperatures especially above a certain temperature called the glass transition temperature. When the polymer has charged particles and a fixed amount of salt how well the charge moves (called ionic conductivity) is linked to how easily these charged particles can move [23]. In polymer electrolytes adding certain types of substances called plasticizers can boost ionic conductivity especially at low temperatures. These plasticizers can be liquids like specific types of polyethylene glycols or certain organic solvents or they can be solid particles like tiny ceramic or nanoparticles. Adding liquid plasticizers can make the ionic conductivity better but it may not work well with lithium electrodes used in lithium batteries and can affect the strength of the material.

Adding ceramic particles to polymer electrolytes can also be helpful. It can increase ionic conductivity by creating small disordered areas because of the large surface area of the ceramic particles. It also makes the material stronger by creating a network with the particles and it can make the polymer electrolyte work better with lithium electrodes. Usually having more disordered areas in polymer electrolytes makes ionic conductivity better. However, some polymer electrolytes surprise us. In some cases, crystalline polymer electrolytes (with an ordered structure) can conduct ions better than amorphous ones (with a disordered structure). For example, a crystalline polymer electrolyte called PEO-LiSbF6 can have higher ionic conductivity than its amorphous counterparts.

The way temperature affects how well the ions move in these special polymer electrolyte materials can't be explained just by using a certain equation. When we look closely at the structure of these crystalline materials, we see that lithium ions are surrounded by oxygen atoms from the polymer chains forming tunnel-like structures. The negatively charged parts of the polymer electrolytes stay outside these tunnels and aren't coordinated with the positively charged ions. The positive ions can move freely inside these tunnels which makes the ionic conductivity better. The ionic conductivity in the typical polymer electrolytes is much lower (1-3 orders of magnitude) compared to polymer electrolytes that have crystalline ceramic particles [24]. Even plastic crystalline materials have high ionic conductivity because lithium can move. That's why the ionic conductivity in crystalline polymer electrolytes can be higher than in amorphous ones because the ordered structures leave spaces (vacancies) in their patterns.

1.12 Charge Transportation

We still don't completely understand how charges move through conductive polymers. The challenge is figuring out the exact path these charged particles take through conductive polymers.

Conductive polymers have a mix of disorderly (amorphous) and ordered (crystalline) parts giving them a complex structure. We think charges move along and between the chains of the polymer materials. They might also move through the complicated borders formed by multiple phases. Understanding how electrical charges move in this system involves looking at factors like temperature magnetism current frequency and doping. There are different theories about how the charges move but the most important one involves charges hopping or tunneling between specific spots. The electrical conductivity in conductive polymers is related to temperature—when its higher conductivity is better.

1.13 Factors Affecting Ionic Conductivity

The ability of ions to move within solid electrolytes known as ionic conductivity is really important for how well energy storage and conversion devices work. Devices like solid-state batteries fuel cells and supercapacitors all depend on this movement of ions. There are several things that can affect how easily ions can move in solid electrolytes and it's important to understand these things to make these devices work the best they can. Here are some important factors:

1.13.1 Temperature

When it's hotter ions can move more easily so the ionic conductivity increases. This is because the ions have more energy to move around the solid electrolyte. But if it gets too hot bad reactions can happen or the solid electrolyte can break down. So there's a temperature range that's just right for the best ionic conductivity.

1.13.2 Crystal Structure

The way the crystals are arranged in the solid electrolyte affects how well ions can move. Some arrangements like perovskite or garnet provide clear paths for ions to move through. If there are empty spaces or defects in the crystal arrangement it can also help ions move more easily.

1.13.3 Chemical Composition

The types of materials used and what they're made of are really important. Different materials can help or slow down how ions move. For instance, adding certain other substances can help ions move better within the solid electrolyte. Picking the right mix of materials is crucial to make the movement of ions as efficient as possible.

1.13.4 Grain Boundaries

The borders between individual crystal grains known as grain boundaries in a polycrystalline solid electrolyte can affect how ions move. Depending on how they are structured and if they have defects these grain boundaries can either help or hinder the movement of ions. Finding ways to lessen the impact of grain boundaries can make ion movement better improving overall conductivity.

1.13.5 Microstructure

The way the solid electrolyte is put together including things like how big the grains are if there are tiny holes (porosity) and if there are extra materials mixed in can affect how ions move. Smaller grains fewer holes and a consistent setup can make ions move more easily.

1.13.6 Pressure

Putting a lot of pressure on some solid electrolytes can change how the crystals are arranged and make it easier for ions to move. But this doesn't work for every solid electrolyte it depends on what it's made of.

1.13.7 Humidity

For certain solid electrolytes like those made of polymers they can take in moisture from the air. This moisture can help ions move around acting like a helper. But too much moisture can be a problem and cause bad reactions or break down the solid electrolyte.

1.13.8 Doping

Putting in tiny amounts of special substances called dopants or other extras into the solid electrolyte can make a big difference in how ions move. The right choices can create more helpers for the ions or change how the crystals are arranged making movement easier.

1.13.9 Chemical Stability

The solid electrolyte needs to stay strong and not change too much over time for the device to work well for a long time. If the solid electrolyte reacts with other parts of the device like the electrodes it can slow down the ion movement and make the device not work as well.

1.13.10Electrode-Electrolyte Interface

The connection between the solid electrolyte and the electrodes can impact how ions move. If there's a lot of resistance at this connection ions might have a hard time moving making the device not work as well.

Getting the right balance to make ions move well in solid electrolytes is pretty tricky. Scientists keep trying out different materials ways to make them and techniques to make ions move better. This helps create better and safer ways to store and use energy.

In materials like conductive polymers how ions move depends on how the chains or sheets are structured and connected. Sometimes adding or removing tiny particles in these materials can change how easily ions can move. The way these materials conduct electricity can also change based on how many special sites are there that don't have enough or have too many electrons [25].

When we mix certain particles like Al2O3 Fe2O3 SiO2 ZrO2 into other materials that conduct ions (like LiI AgCl) the ability of these materials to let ions move can get a lot better. We call these mixed materials 'composite solid electrolytes.' These can be used in devices like cell phones. However sometimes these materials can't be used in certain types of batteries or display devices because they don't conduct ions well enough. We can make them stronger and better at conducting ions by adding certain substances or by mixing in tiny particles [26, 27].

1.14 Solid Electrolytes

Solid electrolytes are really important in different devices that use chemicals to make energy. They help ions move and unlike liquids that do the same job these are in a solid form. These solid electrolytes have many good points compared to liquids. One big thing is safety. Unlike liquids that can catch fire and be dangerous these solids don't. They also don't leak or get too hot too quickly. This makes them great for lithium-ion batteries which have had safety worries because of the liquid inside.

Another good thing about these solid electrolytes is they can work well in very hot or very cold places. They stay stable in high and low temperatures which makes them good for using in things like space tools or cars in really cold areas.

Solid electrolytes show a lot of promise for making new kinds of batteries that can store a lot of energy. We often use lithium-ion batteries in our phones and electric cars but they can only store so much energy because they have a liquid inside that can catch fire. Solid-state lithium-ion batteries use a solid instead of a liquid and this change can make them store a lot more energy. That means our batteries can last longer and work even better.

Solid electrolytes also have benefits when it comes to how strong and flexible, they are. We can make them to be tough and not break easily which is really important for making batteries that last a long time and always work.

These solid electrolytes come in different forms like ceramics plastics and mixtures of materials. Each type has its own special properties and works well for different things. For example, ceramic solid electrolytes are good at letting ions move around but they aren't very flexible. On the other hand, plastic solid electrolytes like polyethylene oxide (PEO) or polyvinylidene fluoride-hexafluoropropylene (PVdF-HFP) can bend and flex so we can use them in batteries that need to be flexible.

Using solid electrolytes is a big step forward in the world of batteries and storing energy. They are safer can work in lots of different temperatures and can store a ton of energy. This makes them a really important part of making better and safer batteries as well as fuel cells and other energy devices. As we keep studying and creating new things with solid electrolytes, we could change the way we store energy and open up new possibilities for our phones cars renewable energy and more. Solid electrolytes in solid-state batteries come in three main types

1.14.1 Inorganic Solid Electrolytes

Inorganic solid electrolytes (ISEs) are a type of solid materials used as electrolytes in different energy storage gadgets like solid-state batteries and fuel cells. These electrolytes are mainly made of inorganic materials like oxides sulfides and halides. They have unique features because of their crystalline or glassy nature and have the potential to advance energy storage technology.

However, ISEs have their challenges. One notable drawback is their ionic conductivity which is relatively low at normal temperatures. This affects the energy and power density of energy storage devices especially solid-state lithium-ion batteries that use these materials. Research is ongoing to enhance the ionic conductivity of ISEs through methods like doping or nano structuring to boost their performance.

Another challenge is the complexity and cost of making ISEs. Creating high-quality inorganic solid electrolytes can be a difficult and expensive process affecting the overall cost of energy storage devices. Researchers are striving to develop more cost-effective production methods to make technologies based on ISEs more affordable.

Moreover, ISEs are prone to being brittle which means they can crack or break under mechanical stress. This brittleness can harm the structure of energy storage devices reducing their strength and lifespan. Strategies are being explored to enhance the mechanical properties of ISEs and tackle this problem.

Additionally, the connection between inorganic solid electrolytes and the electrodes in energy storage devices can be challenging. High resistance at this connection can impede the smooth movement of ions affecting the overall performance of the device. Researchers are working on techniques to create better interfaces and improve ion movement at these important boundaries.

Although ISEs show promise for advancing energy storage technology they do have challenges like low ionic conductivity at normal temperatures manufacturing complexity and cost brittleness and resistance at interfaces. Continuous research and development aim to tackle these issues and unlock the complete potential of ISEs leading to safer more efficient and longer-lasting energy storage solutions for various applications.

1.14.2 Solid Polymer Electrolytes

Solid polymer electrolytes (SPEs) are a specific type of polymers that contain salts within them. These materials are valued for being easy to work with and for reducing resistance at the point where the electrode meets the electrolyte in devices like batteries and fuel cells. However, their usefulness can be limited because they don't conduct ions very well at regular temperatures.

In SPEs the polymer part provides the structure and flexibility and the addition of salts usually lithium salts boost their ability to conduct ions. This combination of polymer and salt allows for creating flexible safe and non-flammable alternatives to traditional liquid electrolytes.

Still a big challenge with SPEs is that they don't conduct ions very well at normal temperatures. While they do show promise for moving ions their typical conductivity which ranges from 10-5 to 10-2 mS/cm might not be enough for energy storage applications that require quick charging and discharging or high power.

Researchers are actively working to overcome this limitation using different methods. These methods include choosing the right salts and their amounts changing the structure of the polymer to create better paths for ions and experimenting with adding other substances or tiny materials to improve conductivity.

Even with these challenges solid polymer electrolytes have the potential to transform energy storage technology. They can offer better safety flexibility in design and the possibility of being used in solid-state batteries. As ongoing research continues to address the ion conductivity problem SPEs are set to play a vital role in advancing high-performance solid-state energy storage solutions for various uses.

1.14.3 Composite Solid Electrolytes

Composite solid electrolytes are a big step forward in energy storage devices. They bring together different materials to create a mix of properties that tackle the problems of regular solid electrolytes. These composites use a mix of materials to boost how ions move how stable they are and how safe they can be. Let's explore what these composites are their benefits and where they can be used.

Composite solid electrolytes are a kind of solid material that blends different materials to make one useful structure. Usually, they have a polymer base mixed with inorganic materials like ceramics tiny particles or other conductive bits. This mix helps ions move better while keeping the material strong.

1.15 Benefits of Composite Solid Electrolytes

1.15.1 Enhanced Ionic Conductivity

One of the main advantages of composite solid electrolytes is how well ions can move through them. Adding conductive bits like ceramic particles or polymer mixes creates pathways for ions to travel faster. This is great for high-power and high-energy devices.

1.15.2 Mechanical Stability

Composite solid electrolytes are usually tougher than pure polymer or ceramic ones. The mix of materials can make the polymer part stronger reducing the chances of cracks or breaks when the device is used or exposed to different temperatures. This toughness means these materials last longer.

1.15.3 Enhanced Safety

Using composite solid electrolytes makes energy storage devices safer. They don't catch fire easily compared to traditional liquid electrolytes. This is a huge plus as it lowers the risk of accidents like fires or explosions in batteries.

1.15.4 Compatibility with Multiple Electrode Materials

Composite solid electrolytes can be made to work well with different electrode materials like lithium or sodium. This makes them versatile and usable in a lot of energy storage devices from common lithium-ion batteries to newer sodium-ion or solid-state batteries.

1.16 Potential Applications of Composite Solid Electrolytes

1.16.1 Solid-State Lithium-Ion Batteries

Composite solid electrolytes hold great potential for solid-state lithium-ion batteries. These batteries use a solid electrolyte instead of a liquid one which makes them safer and more efficient. By using composite solid electrolytes, we can make solid-state lithium-ion batteries perform even better and be safer to use.

1.16.2 Solid-State Sodium-Ion Batteries

Sodium-ion batteries are becoming a popular alternative to lithium-ion batteries because sodium is abundant and potentially cheaper. Using composite solid electrolytes can make the sodium-ion electrolytes conduct ions better. This improvement is essential for making high-performing solid-state sodium-ion batteries.

1.16.3 Supercapacitors

Supercapacitors store energy and release it quickly when needed. By using composite solid electrolytes in supercapacitors, we can increase how much energy they can store and how fast they can release it. This makes them great for situations where quickly storing and using energy is crucial.

1.16.4 Fuel Cells

Composite solid electrolytes find uses in fuel cells too. They can improve how well the electrolyte materials conduct ions especially in solid oxide fuel cells. These improvements make fuel cells work better and stay stable for longer

Composite solid electrolytes are a big step forward in energy storage devices. By combining different materials to create a mix of useful features they improve how well ions move how stable the materials are and how safe they can be. These composites can be used in solid-state batteries supercapacitors and fuel cells making these energy storage technologies more powerful long-lasting and safer to use. As we keep researching and improving these composites, they hold great potential to shape the future of how we store energy

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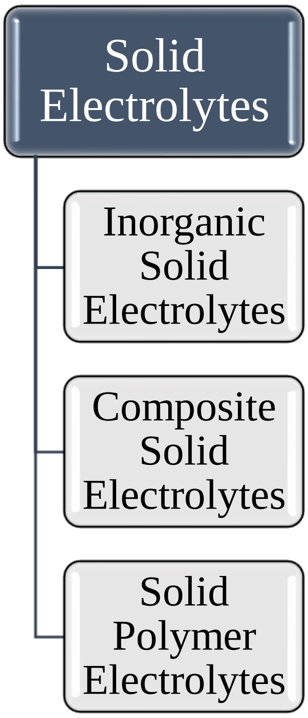

Figure 1 Major different types of solid electrolytes

1.17 Composite Polymer Electrolytes in Lithium-Ion Solid Batteries

Composite polymer electrolytes (CPEs) are a very promising type of material for making lithium-ion solid-state batteries better. These electrolyte composites are made up of a mix of a polymer material and inorganic fillers. This mix makes them better at conducting ions stronger and able to handle high temperatures without problems. One big advantage of CPEs is that they can replace the liquid electrolytes used in older lithium-ion batteries which can catch fire or evaporate easily making them risky. On the other hand, CPEs are safe because they don't catch fire or evaporate easily [3].

CPEs can significantly improve the performance of solid-state lithium-ion batteries (SSLIBs). Higher ionic conductivity in CPEs means the batteries can be charged and used more quickly and they can store more energy [28]. CPEs with strong mechanical properties can prevent the growth of lithium dendrites which can cause short circuits and make the battery fail [29]. CPEs that can handle high temperatures well allow the battery to work well even when it's hot [30]. Even though CPEs are still being developed they have the potential to revolutionize the lithium-ion battery industry. With CPEs we can make SSLIBs that store more energy last longer and are safer. This makes SSLIBs a great choice for electric cars systems that store energy and portable devices like phones and laptops.

Here are some examples of how we could use CPEs in SSLIBs:

- Electric vehicles: SSLIBs with CPEs could power electric cars for longer distances and charge them faster [31].
- Energy storage: SSLIBs with Composite Polymer Electrolytes (CPEs) could store energy generated from sources like solar panels and wind turbines [32].
- Portable electronics: SSLIBs with CPEs could power laptops smartphones and other portable devices making their batteries last longer [33].

Apart from these uses CPEs could also be very useful in other areas like aerospace marine and medical devices. CPEs are a really promising kind of material for solid-state lithium-ion batteries. They have the potential to make these batteries safer better and last longer. This makes SSLIBs a great choice for many different uses [34].

1.18 Preparation Methods for Composite Polymer Electrolytes

Composite polymer electrolytes (CPEs) are a great fit for solid-state energy storage and conversion devices like batteries and fuel cells. They're made by mixing a polymer material with inorganic fillers ionic salts or other substances to improve its ability to conduct electricity while still staying flexible [35].

1.18.1 Solution Casting

One common way to make composite polymer electrolytes (CPEs) is using a method called "solution casting." In this process we dissolve a chosen polymer in a suitable liquid and then mix it with inorganic fillers or ionic salts. This mix of polymer and other stuff is spread onto a flat surface making a thin film or sheet. As the liquid evaporates it leaves a solid CPE where the polymer has inorganic fillers spread evenly through it. This method lets us control how the fillers are spread how thick the CPE is and what it's made of.

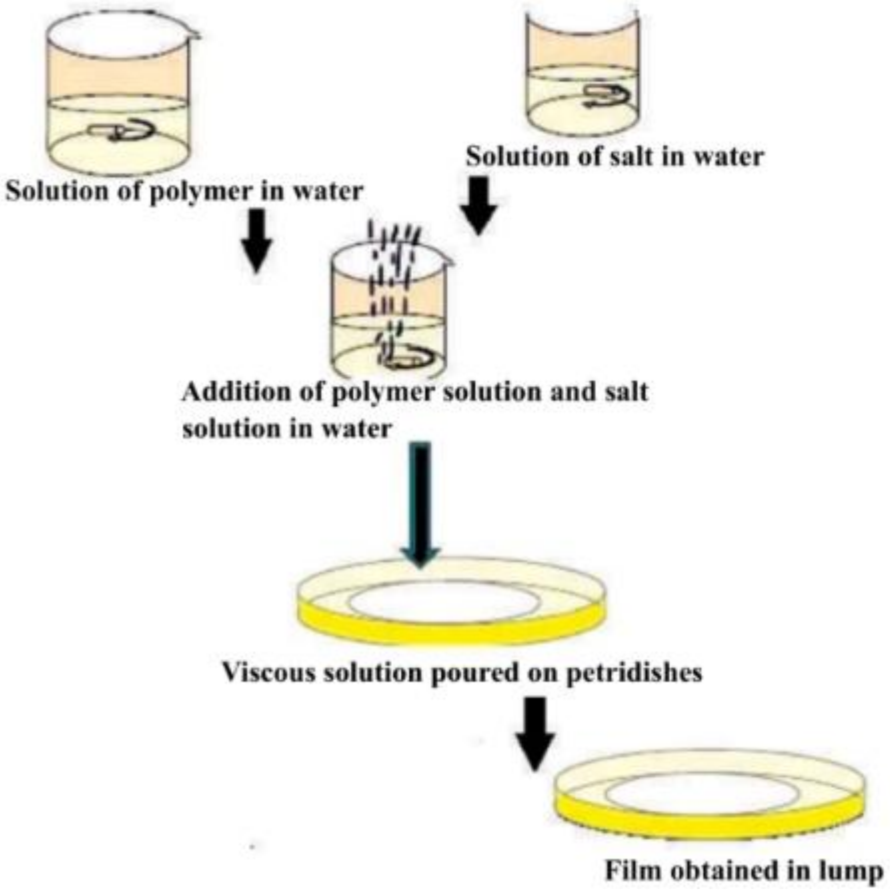

Figure 2 Synthesis of nanocomposite polymer electrolyte films by Solution Casting [36].

The resulting CPE combines the bendiness of the polymer with better ionic flow making it great for various energy storage and conversion gadgets like batteries and supercapacitors. The way we make it solution casting allows us to make CPEs with certain traits for different needs.

1.18.2 Melt Blending

Another method we use to make this material is called "melt blending." It's a common way to create a mix of things especially combining a type of plastic with other stuff like minerals:

1.18.2.1 Polymer Selection

To start we pick a type of plastic to use as the main material. Plastics are large molecules made of repeating parts. Some can melt when heated and then solidify when cooled and those are the kinds we like for this method

1.18.2.2 Inorganic Filler Selection

Then we choose what to mix with this plastic. These aren't the usual materials based on carbon and hydrogen like plastics are. Instead they're often minerals or non-organic things. Some examples are tiny pieces of glass silica clay or bits of metal. What we choose depends on what we want the mix to be like – strong stiff good at handling heat and so on.

1.18.2.3 Mixing in Molten State

Next, we heat the chosen plastic until it becomes like a gooey liquid. Then we add the other chosen materials into this melted plastic. We mix it up really well either by stirring it a lot or using a special process called extrusion. We want the other materials to be spread out evenly in the melted plastic to get a mix that's consistent.

1.18.2.4 Cooling and Solidification

Once we've mixed everything up well, we let it cool down. As it cools it turns solid again with the other materials now trapped in the plastic. We can cool it in molds shape it by pushing it out through a special shape or flatten it with rollers.

1.18.2.5 Forming the Composite

After it's cooled and solidified it's a blend – a mix of plastic and the other materials. The extra materials are spread out inside the plastic making it stronger stiffer or better in different ways compared to plain plastic. The specific qualities it has – like how strong it is or how well it conducts heat – depend on what we mixed in and how much of it we used.

1.18.2.6 Additional Processing

Depending on what we want to use it for and what we want it to be like we might do more things to it. This could be cutting it shaping it or treating it in some way to make it just right for what we need.

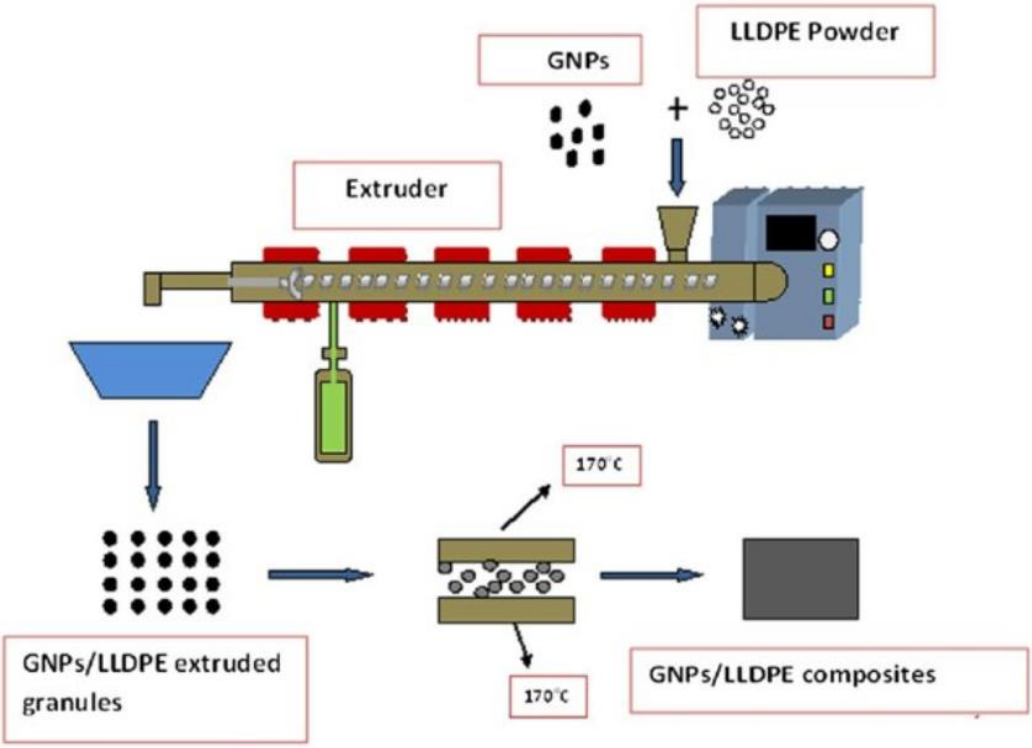

Figure 3 Schematic diagram of melt mix processing of GNPs/LLDPE nanocomposites [37].

The method involves making a polymer all gooey by heating it up then adding special powders into the gooey stuff. When it cools down and becomes solid again, we get a blend of the polymer and the powders. This blend has the good parts of both the polymer and the powders. Lots of different industries use this method to create just the right material they need for their specific jobs [38].

1.18.3 In-Situ Polymerization

Making materials inside something is called "in-situ polymerization." We do this by directly turning small building blocks into a bigger material inside a certain place instead of making the material first and then putting it there.

In-situ polymerization is a great way to make all sorts of materials with special qualities. For instance, it helps us make materials that are strong stiff and can handle heat better. It also helps us make materials that have lots of tiny holes and a large surface area which is useful for some jobs like cleaning things.

Here's how we usually do it: we put the small building blocks (called "monomers") where we want the new material. Then we add something that makes these building blocks start linking together kind of like how legos stick to each other. This starting process is called "initiation" and it can be started using heat light or other types of energy.

Once the building blocks start linking together, they make long chains like a string of beads. Eventually these chains fill up the empty spaces where we put the building blocks and we get a solid material.

This way of making materials inside something helps us create materials with just the right properties we want. Many industries like aerospace cars electronics and medicine use this technique to make the materials they need.

Here are some examples of how we use in-situ polymerization:

1.18.3.1 Polymer composites

We use in-situ polymerization to make blends that are super strong stiff and can handle heat well. For example, we mix tiny carbon structures into a liquid building block and when they link together, we get a super strong blend that we can use for many things.

1.18.3.2 Porous materials

In-situ polymerization helps us make materials that have lots of holes and a large surface area. For example, we mix a type of plastic building block with something that creates holes and we get a material full of tiny holes. This can be used for jobs like cleaning stuff or helping reactions happen.

1.18.3.3 Medical devices

In medicine we use in-situ polymerization to make special stuff for our bodies. For instance, we can turn a liquid building block into a gel right inside our bodies. This gel can help grow tissues or deliver medicine exactly where it's needed.

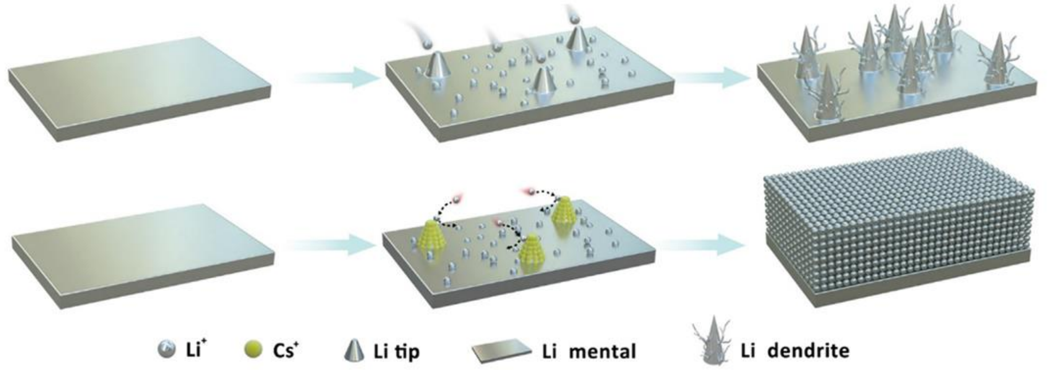

Figure 4 Schematic illustration for Li deposition process [39].

In-situ polymerization might sound complicated but it's a strong tool to create materials with cool properties that we want.

1.18.4 Solvent-Free Mixing

Mixing without using liquids is also called "solvent-free mixing." It's a way to make special materials without using liquids like water. Here's how we do it for making special materials with both a polymer and powders inside:

1.18.4.1 Components:

In making these special materials we need some main ingredients: the main solid or semi-solid stuff (we call it the "polymer matrix") some tiny powders (we call them "inorganic fillers") and maybe other extra things like salts.

1.18.4.2 Mechanical Mixing:

The big part of this method is mixing everything together very well using machines. We use machines like ball mills which are like big mixers that spin really fast or move a lot. These machines mix the polymer and the powders so they're all spread out evenly.

1.18.4.3 Controlled Process:

We have to be careful while mixing. We need to mix in a way that all the powders get spread out really well in the polymer. We can control how we mix by changing things like how long we mix and how fast the mixer moves.

So by using this method we can make materials that have both the polymer and the powders mixed perfectly. It's like baking a cake and making sure all the ingredients are mixed just right

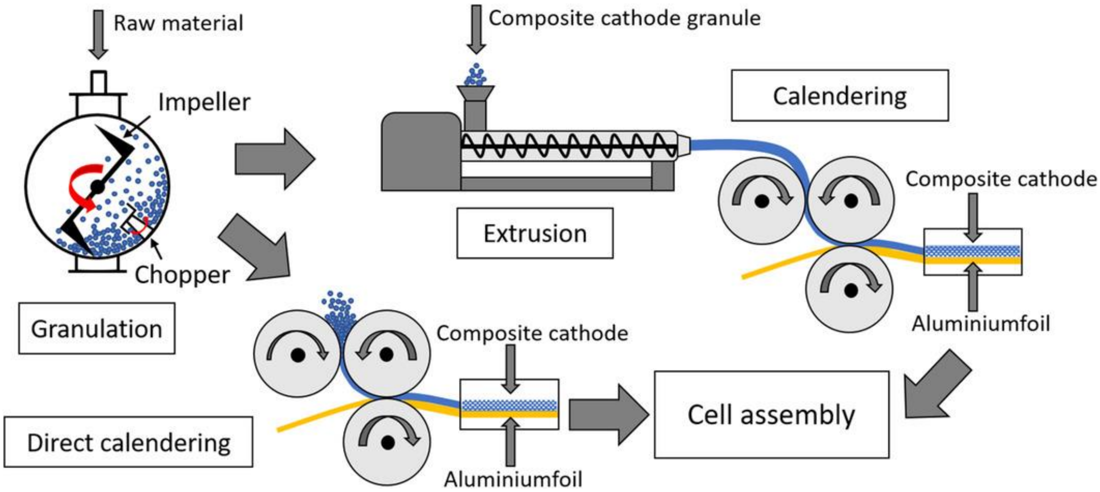

Figure 5 Solvent-free scalable process chain for manufacturing of solid-state cathodes [40].

Mixing without using liquids called solvent-free mixing is a way to create special materials like composite polymer electrolytes (CPEs) for really cool energy storage. It involves blending solid or semi-solid parts like a polymer matrix and tiny particles (inorganic fillers). We mix these without needing any liquid substances. This way we have control over how the particles are spread resulting in CPEs that conduct ions better and are stronger.

1.18.5 Electrospinning

Electrospinning is an awesome method to make composite polymer electrolytes (CPEs) in the form of ultra-thin fibers almost like tiny threads. It's super useful for creating CPEs that work better for many things especially in the advanced energy storage and electronics world. Let's break down how electrospinning works for CPEs:

1.18.5.1 Components:

When making CPEs with electrospinning we need a few main things: the main polymer stuff something that helps ions move (like lithium salts for batteries) and tiny particles like super tiny bits of stuff. The main polymer stuff is really important for shaping these ultra-thin fibers.

1.18.5.2 Preparation of Electrospinning Solution:

To kick off the electrospinning process we prepare a mix of the polymer stuff the ions-mover and the tiny particles. This mix should be just the right thickness and should let electricity move through it smoothly for electrospinning to work well. We need to get the right balance of how much of the polymer is there what kind of stuff helps it dissolve or melt and how much of the tiny particles we include.

1.18.5.3 Electrospinning Setup:

The setup for electrospinning usually has a special pump that carefully releases the mix a tiny tool (like a needle or nozzle) that holds the mix something that gives a high voltage zap and a surface that collects the ultra-thin fibers as they're made. The mix goes into the tiny tool and the collector is placed at a distance.

1.18.5.4 Electrospinning Process:

Now when we zap the mix with high voltage something amazing happens! The mix gets charged up and it's so charged that it pushes out tiny fibers from the tool toward the collector. These fibers are so thin like really really thin threads. It's like magic but its science doing some super cool stuff.

1.18.5.5 Nanofiber Formation:

As the tiny fiber travels through the air towards a collector two things happen: the liquid evaporates and the fiber stretches. The liquid part disappears leaving behind tiny solid fibers made of the polymer stuff the ions-mover and the really small bits. The stretching and movement of the fiber during its flight make these fibers extremely thin usually in the nanometer size range.

1.18.5.6 Composite Structure:

When we do this special spinning the really small bits or tiny particles are spread out evenly inside the tiny fibers because we included them in the spinning mix. This creates a special structure where the tiny bits are mixed into the polymer stuff in a really tiny way.

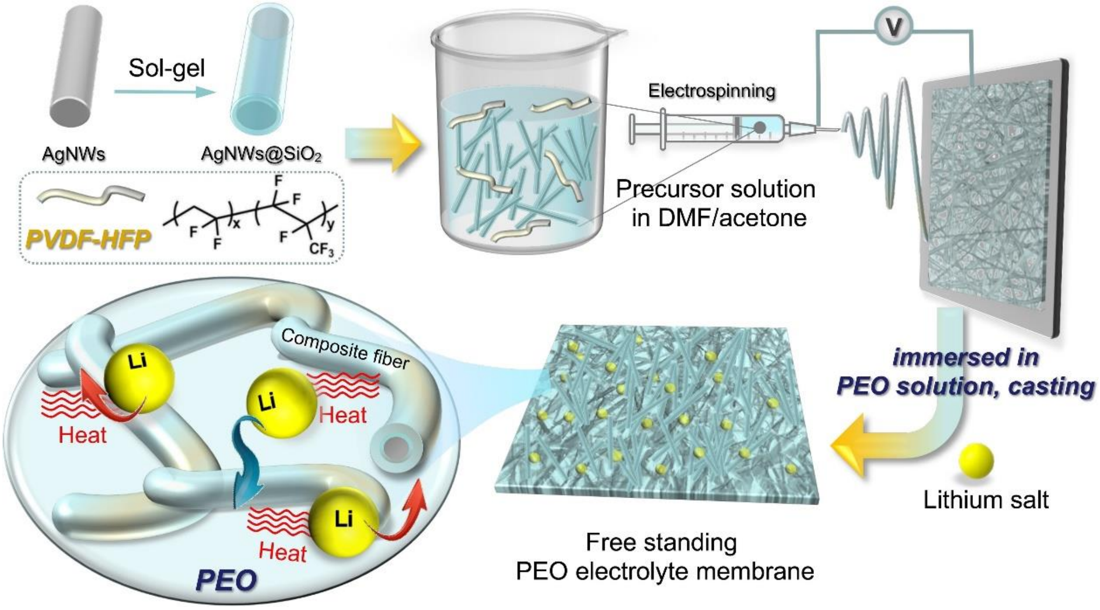

Figure 6 Schematic illustration of AgNWs@SiO2 and PVDF-HFP/AgNWs@SiO2/PEO/LiTFSI SPEs [41].

Electrospinning is a helpful method to create composite polymer electrolytes with nanofibrous structures. It lets us mix inorganic fillers and really small particles into the polymer material in a controlled way resulting in these special materials with improved properties for different electrochemical uses.

1.18.6 Tape Casting

Tape casting is a way of making thin flat and bendy sheets or tapes of these special materials called composite polymer electrolytes (CPEs). This method helps us create solid electrolyte materials that are super precise and the same thickness throughout. Here's how we do it:

1.18.6.1 Components:

To make these special sheets we mix the polymer material the ions-mover (like lithium salts for batteries) and the really small particles into a mix that looks like a liquid.

1.18.6.2 Tape Casting Setup:

To make the sheets we use a special machine called a tape caster. This machine has important parts like a thing called a doctor blade a moving surface (like a smooth glass or steel) and a way to spread the liquid mix.

1.18.6.3 Preparation of Slurry:

First, we mix the polymer the ions-mover and the tiny particles with a liquid to make a nice even mix.

1.18.6.4 Casting Process:

We pour this mix onto the moving surface using a special system. The doctor blade helps spread the mix evenly and control how thick the tape becomes.

1.18.6.5 Solvent Evaporation:

After we spread the mix, the liquid part starts to go away and what's left becomes a solid sheet made of the polymer ions-mover and tiny particles. The thickness of the sheet is decided by how far apart the doctor blade is from the surface.

1.18.6.6 Drying and Solidification:

After we make the sheet, we let it dry and become really solid. We do this by putting it in a place with a specific temperature and humidity. During this time all the liquid goes away leaving a solid and flexible CPE sheet.

1.18.6.7 Cutting and Shaping:

Once the CPE sheet is completely solid, we can cut it and give it the shape we want for what we're making. The sheet is flexible so it's easy to work with and use in different energy storage tools.

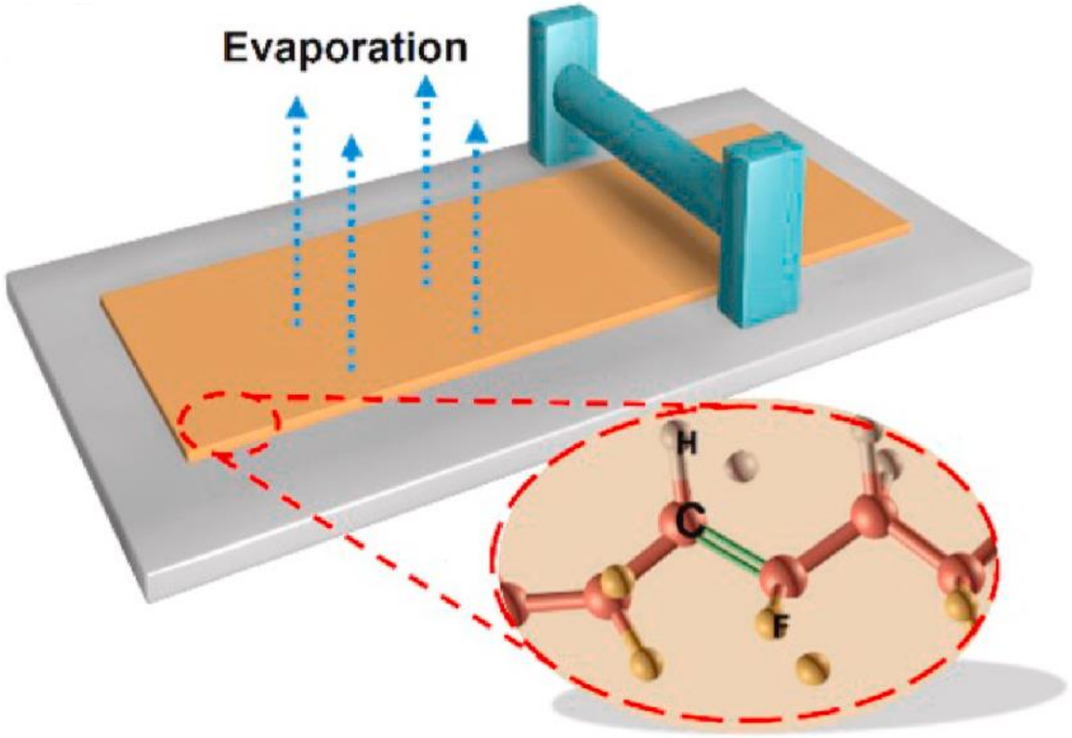

Figure 7 Schematic illustration for the preparation procedure of PVDF/LLTO-CPEs membrane [42].

Tape casting is a versatile manufacturing technique for producing thin and flexible sheets or tapes of composite polymer electrolytes. It allows for the precise control of material composition thickness and uniformity making it well-suited for applications in advanced energy storage devices.

Table 1 Composite polymer electrolytes synthesis using dopants nanofillers

Polymer	Dopant	Nanofiller	Nanofiller Particle sizes	Methods for CPE Preparation	Ref
Methyl Cellulose	$Mg(CH_3COO)_2 \cdot 4H_2O$	Co_3O_4	<50nm	Solution Casting	[43]
TPU/PEO	$LiClO_4$	HIPS	-	Melt Blend	[38]
PEO/PEGDMA /PEGMA	$LiBF_4$	SiO_2	11nm	In-Situ Polymerization	[44]
PEO	LiTFSI	SiO_2	-	Solvent-Free Mixing	[45]

PVDF-HFP	LiTFS	f-SiO_2 SiO_2 TiO_2	7nm 200nm 150nm	Electrospinning	[46]
PVDF-HFP	LiTFSI	Al_2O_3	30nm	Tape Casting	[47]

The choice of how to prepare the special material depends on a few things: the kind of tiny filler we want to use what we want the material to be like and how much it costs to make. One way to make this special material is by using something called solution casting. This is where we mix the material we want with a liquid and let it become solid.

1.19 Solution Casting Technique

1.19.1 Solution Casting

Solution casting is a really important and common way of making thin sheets special coverings and coatings in the world of materials science and engineering. It's a crucial part of creating special materials with specific properties for different uses. The process starts with making a solid material from a mix of the material we want and a liquid like a special type of paint. This method is really good when we need to be very precise with how thick and even the material is.

First, we mix the material we want with a liquid that can dissolve it or hold it well. The liquid we pick is really important because it affects how well the material mixes and how good the final material will be. Scientists are careful in picking the right liquid to make the material just right.

What's great about solution casting is that it works for lots of different materials like plastics ceramics metals and mixes of these. This means we can make films and coatings with different abilities like being clear conducting electricity or keeping things sealed. It's super useful in areas like electronics optics and plastics.

In many cases it's really important to have the material be just the right thickness and really even. Solution casting is awesome for this because we can make layers that are really thin or a bit thicker depending on what we need. This is super useful for making lots of things.

We use this method to make important stuff! In electronics it helps create thin layers on computer chips and coatings that let light pass through without bouncing back. In plastics it's used to make special batteries fuel cells and materials for filters. We can also use this to cover different things like glass metal and flexible materials making them better for use in lots of different devices and machines.

To sum it up solution casting is a super flexible and important way of making materials in the world of materials science and engineering. It lets us make thin sheets and coverings that are just the right thickness and evenness which is super important in industries where we need special thin layers coverings and coatings for lots of different uses. This method helps us make technology better in many different fields.

1.19.1.1 Dissolution

Dissolving things is a very important part of making thin sheets special covers and coatings. This is where we put a chosen material like a special kind of plastic a tiny computer chip piece or a type of metal salt into a special liquid that can dissolve it really well. We have to be very careful about picking the right liquid because it needs to dissolve the material nicely and then evaporate easily to leave the material behind. When this happens the material changes from a solid into a mix that's all the same and we can then spread it evenly on a surface. How fast and how much the material dissolves affect the final sheet's thickness evenness and what it can do. This is a super important part of using solution casting in making special things with materials.

1.19.1.2 Solution Preparation

When a material dissolves in a liquid during preparation it creates a mix called a solution or mix. We can change how much of the material goes into the mix by adding more or less of it. This helps us control how thick the final sheet or coating will be and what properties it will have. By adjusting the amount of the material scientists can make the sheet just the right thickness and make it do things like let light through conduct electricity or be strong. This is important in making materials that work in different fields like materials science electronics and coatings.

1.19.1.3 Casting

Once we've prepared the mix the next step in solution casting is putting it on a surface or something else. There are different ways to do this like putting the surface in the mix spraying the mix on or spinning it around. The way we do it depends on what we're making.

- Dip Coating: We put the surface in the mix so that the material sticks to it. This is good when we want the coating to be even on things with different shapes or when we want a thin sheet to have a certain thickness.
- Spray Coating: We break the mix into tiny drops and spray them on the surface. This is useful when we need a covering to be even and just right on a big area or things that aren't flat.
- Spin Coating: We drop the mix on the surface and spin it around really fast. This makes the mix spread out and form a thin sheet with just the right thickness. It's great for making thin sheets for small electronics and things that need to be clear.

The way we put the mix on the surface depends on what the surface looks like how thick we want the final sheet and what we want it to do. Each way has its own good points and helps us make different things in the right way. This is why solution casting is so flexible and helpful in creating just the right thin sheets coverings and membranes in materials science and engineering.

1.19.1.4 Solvent Evaporation

After spreading the mix on a surface, the next very important step in solution casting is getting rid of the liquid part which is called the solvent. This happens by letting the liquid evaporate or turn into vapor. There are a few different ways to make this happen and it depends on how quickly the liquid can turn into vapor and how we want it to happen.

Solvent evaporation can happen in different ways:

- Normal Air Conditions: We can just leave the surface with the mix in the open air and the liquid will naturally turn into vapor and go away. This works well for mixes with liquids that evaporate easily.
- Controlled Conditions: If we want to be more careful, we can put the surface in a controlled space like a special box or a glovebox where we can control the humidity (how damp the air is) and the temperature. This helps make sure the liquid goes away in a controlled and even way.
- Gentle Heating: If the liquid doesn't evaporate quickly on its own, we can gently warm it up to help it turn into vapor faster. This can be done using ovens hotplates or special lamps depending on what we need.

How we make the liquid turn into vapor depends on what the liquid is like how thick we want the final sheet or coating and what we want it to do. Being careful about how the liquid turns into vapor is really important to get the sheet or coating to be just the right thickness evenness and quality.

1.19.1.5 Solidification

When the liquid turns into vapor and goes away the material that was dissolved in it starts to become solid again. This is like when water turns into ice. As the material becomes solid its tiny parts start arranging themselves in a closely packed way on the surface where we put the mix. The properties of the sheet or coating like how thick it is how even it is and what it looks like are affected by things like how much material was in the mix how we spread the mix and how fast the liquid turned into vapor.

This change from a liquid mix to a solid sheet is a really important part of solution casting. It's during this change that the sheet gets the properties we want like being able to let electricity through having a certain look or being strong. Being able to change these properties makes solution casting a really useful and flexible technique in different fields like materials science and engineering.

1.19.1.6 Post-Treatment

After the sheet has become solid, we can often change its properties a bit more to make it better for what we want to use it for. This might mean doing more things to it based on how we want to use it and what it's made of. These extra things we do can include:

- Making it Stronger with Heat: We can heat the solid sheet in a controlled way to make it stronger and more organized. This is often done for certain plastics and thin materials used in electronics.
- Making it Tougher with Chemicals: We can use special chemicals to create stronger connections between the material's tiny parts. This makes the material stronger and able to resist things like heat and chemicals. This is often done for plastic films.
- Changing its Surface: We can use different methods to change how the surface of the sheet behaves like how sticky it is or how it looks. This helps the sheet do what we want it to do when we use it.
- Adding Special Elements: If the sheet is used in things like tiny computers, we can add special elements or compounds to make it better at letting electricity move through it.

Choosing what extra things to do to the sheet depends on what it's made of what we want it to do and how we want to use it. Doing these extra steps helps us make the sheet just right for how we want to use it whether it's in electronics optics or coatings.

1.20 Research Gap

Composite polymer electrolytes (CPEs) are promising materials for a variety of applications including lithium-ion batteries solid-state batteries and fuel cells. CPEs are made up of a polymer matrix and inorganic fillers which can improve the ionic conductivity mechanical strength and thermal stability of the electrolyte.

Despite the significant progress that has been made in the development of CPEs there are still a number of research gaps that need to be addressed. Some of the key research gaps include:

- Improving ionic conductivity at low temperatures: CPEs typically have lower ionic conductivity at low temperatures than liquid electrolytes. This limits their performance in applications such as electric vehicles which operate in a wide range of temperatures.
- Developing new polymer matrices with high compatibility with inorganic fillers: The compatibility between the polymer matrix and the inorganic fillers is important for achieving high ionic conductivity and mechanical strength in CPEs. However, there are still a limited number of polymer matrices that are highly compatible with inorganic fillers.
- Understanding the fundamental mechanisms of ion transport in CPEs: A better understanding of the fundamental mechanisms of ion transport in CPEs is needed to develop more effective strategies for improving ionic conductivity.
- Developing scalable and cost-effective fabrication methods for CPEs: The current methods for fabricating CPEs are often complex and expensive. This limits their commercialization potential.

In addition to these general research gaps there are also a number of specific research challenges that need to be addressed for different applications of CPEs. For example, in the case of lithium-ion batteries there is a need to develop CPEs that are compatible with lithium metal anodes and that have a wide electrochemical stability window.

There is a significant amount of research that still needs to be done on CPEs before they can be widely commercialized. However, the potential benefits of CPEs are enormous and there is a growing interest in this area of research.

1.21 Problem Statement and Hypothesis

1.21.1 Problem Statement

Current energy storage devices based solid electrolyte hinder their ability to efficiently store and release energy at scale. To overcome the problem related to solid electrolyte there is challenge to explore potential solutions, and propose novel strategies for enhancing energy storage efficiency and capacity.

1.21.2 Hypothesis

To reduce this limitation, using the solution casting technique to incorporate nanofillers into a polymer electrolyte will lead to improve ionic conductivity. The resulting composite polymer electrolyte is expected to exhibit superior performance and can be a promising solution for advanced energy storage devices, such as solid-state batteries.

1.22 Research Objectives

To overcome the existing challenges in energy storage devices following objectives were identified.

- The objective is to examine the ionic conductivity within a solid electrolyte made of high molecular weight.
- Study and analyze how the inclusion of an inorganic filler affects the ionic conductivity in a composite polymer electrolyte made of PEO.

1.23 Scope of Study

The following scope was established to ensure that the research would be carried out in the time available:

- Electrochemical Impedance Spectroscopy of composite polymer electrolyte represents one of the significant proceeding to explore the research focused area.
- This work has provided a comprehensive solution for interpreting a detailed description of sample preparation and characterizations (FTIR SEM and XRD).

1.24 Chapter Summary

This thesis comprises five chapters with each chapter's content detailed in the following sections:

- **Chapter 1** delivers vision of the subject background and contemporary problems related to the work. It also clarifies the problem statement scope of planned study and the research objectives.
- **Chapter 2** will sketch the literature review achieved to describe the previous work done on the composite polymer electrolyte. It also includes review based on solid electrolyte by introducing different kind of fillers used to enhance its properties.
- **Chapter 3** covers the methodology related to the sample preparation and characterization. Electrochemical Impedance Spectroscopy study for ionic conductivity of the prepared CPEs.
- **Chapter 4** delivers results and discussions. The material characterization experimental ionic conductivity to compare the experimental and the predicted values and its consequences are existed and explained based on various point of view.
- **Chapter 5** reviews all the findings and conclusions in the current study and provides the future recommendation for the related work.

Chapter 2

Literature Review

2.1 Literature Review

In a past study researchers explored how adding tiny particles of Al2O3 a Nano material affects the (PEO) LiTFSI solid electrolyte's thermal properties transport capabilities and dielectric properties. The study showed that when these particles have specific groups they significantly improve the electrolyte's ability to conduct electricity. The conductivity was most improved when the particles had acidic groups. In the prepared samples the measured ionic conductivity of the electrolyte was 2.2 x 10-4 S/cm at room temperature. These findings suggest that the increased conductivity is due to the creation of additional sites and better paths for ions to move facilitated by a chemical connection between the filler groups and ionic components. Importantly the primary movement of ions which is crucial for conductivity was not majorly affected by the presence of these particles [48].

To make a composite polymer electrolyte SiO2 Nano material are made within a PEO matrix. The authors propose a method that uses the non-hydrolytic sol-gel process to create strong chemical links among SiO2 Nano materials lithium salt and PEO polymer chains. The resulting composite polymer electrolyte shows significantly improved ability to conduct ions and remains stable electrochemically especially when compared to composite polymer electrolytes made in a different way. This nanocomposite demonstrated a conductivity of 1.10 × 10-1 mS cm-1 at normal temperature. The study also provides a detailed description of the electrolyte membrane and illustrates its use in a solid-state lithium battery. In testing it showed promising performance in terms of maintaining capacity and stability during multiple charge and discharge cycles [49].

A new type of safe and flexible solid electrolyte has been developed for lithium batteries that perform really well. This thin sheet is made of polypropylene oxide (PPO) and ZrO2 particles. It also contains a substance that makes it flexible and a framework made of cellulose. By adding lithium bis(oxalate)borate a reaction happens in the PPO making it good at conducting ions. At a temperature of 30 degrees, it can conduct ions very well about 9.62 × 10-1 mS/cm. The sheet is also very strong and can handle high temperatures making sure the lithium in the battery doesn't grow in a harmful way. Batteries made using this sheet can work well even if they're used a lot. The researchers believe this new safe sheet is a great choice for high-performance lithium batteries [50].

Table 2 TiO_2 nanofiller with different polymer and polymer blend ionic conductivity

Filler	Polymer/Polymer Blend	Ionic Conductivity S/cm	Ref
TiO_2	PEO	1.35×10^{-4}	[51]
TiO_2	PVC/PEMA	0.51×10^{-2}	[52]
TiO_2	PVA/CMC/PVP	2.88×10^{-11}	[53]
TiO_2	PVA	1.00×10^{-4}	[54]

R. H. Y. Subban and A. K. Arof [55] explored making special films using a mixture of PVC LiCF3SO3 and SiO2. These films are used in lithium batteries. They made these films using a method called "solution casting." They checked how well these films could conduct electricity at different temperatures. They also tested how the batteries behaved when charged and discharged at room temperature to see if these films are good for lithium batteries.

B.K. Choi K.H. Shine and Y.W. Kim [56] explored films made of a mix of materials like poly(ethylene oxide) (PEO) LiClO4 a mix of ethylene carbonate (EC) and butyrlactone (BL) and poly(acrylonitrile) (PAN). They were trying to find the best mix that would give good conductivity stability and consistency. They measured how well electricity could flow and looked at how the materials behaved when heated or cooled. They discovered that changing the mix affected how the film looked under X-ray and whether it turned into a kind of gel.

S. Selvasekarapandian and their team [57] made solid polymer electrolytes using a mix of PVAc and LiClO4. They made different versions of these by mixing the materials in different ways. Then they studied the structure surface and thermal behavior of these mixes. They used special tools like X-ray diffraction (XRD) scanning electron microscopy (SEM) differential scanning calorimetry (DSC) and ac impedance measurements to learn more about them. They found that these mixtures could conduct electricity and that their properties changed depending on how much LiClO4 was in them.

E. Zygadlo-Monikowska and colleagues [58] studied how to make a special kind of material called a solid polymer electrolyte. They used things like poly(ethylene oxide) (PEO) LiCF3SO3 and aluminum carboxylate to create it. They wanted to understand how this material carries ions (like Li ions) around. They found that one type of ion called triflate salt ions doesn't move much likely because of how the aluminum carboxylate and lithium salt combine.

W. Krawiec E. P. Gianneis and others [59] looked at a mixture made of polyethylene oxide (PEO) Al2O3 (a type of material) and LiBF4 (a kind of salt). They wanted to see how well it can conduct electricity and how stable it is when used in batteries. They found that adding Al2O3 makes it conduct electricity better and improves its stability.

N. Ogata S. Yamada and others [60] worked on creating a special type of material for batteries. They mixed different types of salts with other substances to make it. This new material could carry ions (like Li ions) much better than a common material called polyethylene oxide (PEO).

F. Alloin D. Benrabah and J. Y. Sanchez [61] compared different types of lithium salts mixed with a special network of materials. They were interested in seeing how well these mixtures could conduct electricity. They found that one type of mixture was very good at conducting electricity.

S. Rajendran and T. Uma [62] worked on creating another type of material for batteries. They mixed things like poly(vinyl chloride) LiBF4 and ZrO2. They wanted to see how well this new material could conduct electricity and how it behaves. They found that the more ZrO2 they added the better it conducted electricity.

A. A. Mohamad A. K. Arof and others [63] were interested in improving the properties of a material used in batteries. They added something called propylene carbonate (PC) to this material. They found that this addition improved how well it could conduct electricity and changed how it behaves when heated..

C. C. Tambelli J. P. Donoso and colleagues [64] looked into how adding Al2O3 (a type of material) affects a special kind of material called PEO-LiClO4. They found that although the temperature at which the material changes its structure (glass transition temperature) stays the same the amount of a specific structure in the material (crystalline phase) changes when the filler is added.

P. P. Chu and S. S. Sekhon [65] examined how adding a substance called dimethylacetamide (DMA) and oxalic acid influences a type of material made of polyvinyledenefluoride-hexafluoro propylene (PVdF-HFP). By adding a small amount of DMA they found that the material can conduct electricity better. This improvement was because of how the different parts of the material interacted as confirmed by special tests (FTIR studies).

A. Andrieu C. Fringant and T. Icedo [66] checked how using a specific type of substance called low molecular weight poly(ethylene oxide) as a plasticizer affects a material made of poly(ethylene oxide)/poly(propylene oxide). Adding the plasticizer improved how well the material could conduct ions (like Li ions).

S. A. Agnihorty and V. D. Gupta [67] studied how different substances and lithium salts affect a type of material made of poly(vinyl butyral). They found that the ability of this material to conduct ions changes depending on the substances used. A substance called n-butyl alcohol made the material conduct ions the best.

Qi Wang Jun Gao and Yaqin Qian [68] focused on how different factors like temperature and substances called plasticizers affect the ability of a special kind of material to conduct ions. They found that by changing the molecular weight or adding more plasticizer the material could conduct ions better.

Z. Florianczyk K. Such and others [69] explored how adding various lithium salts affects a certain kind of material made by heating methyl methacrylate with poly(ethylene oxide). They found that these materials have a certain part that isn't structured (amorphous phase) and can conduct ions well. This happens especially when adding a substance to make the material more flexible (plasticizer).

H. Bischoff R Sandner and their team [70] delved into improving how well a special kind of material can conduct ions. This material is made by mixing LiCF3SO3 with another material made by combining triethylene glycol dimethacrylate (TRGDMA) and acrylonitride (AN) at different ratios along with a substance to make it more flexible (plasticizer). They found that the ability of the material to conduct ions gets better as the ratio of AN to TRGDMA increases. Surprisingly the amount of AN doesn't affect this improvement.

Y. W. Chen -yang T. L. Chen and others [71] looked into how adding a substance called Al2O3 affects a material made of poly-(methoxyethoxyethoxy) phosphazene (MEEP) with lithium perchlorate salt. They found that adding Al2O3 makes the material conduct ions better.

D. Y. Zhou Y. H. Liao and their team [14] created a special kind of material by mixing acrylonitrile (AN) and methyl methacrylate (MMA). They characterized this material and found that it remains stable up to a high temperature of 300°C.

P. Santhosh T. Vasudevan and A. Gopalan [72] worked on a mix of materials comprising polyurethane (PU) and polyvinyledene fluoride) (PVdF). They checked the heat-related properties and how well this material can conduct ions. They also explored how the amount of PVdF affects its ability to conduct ions. They looked at how the molecules interact in this mix using special tests (FTIR studies).

A. Bac W Wieczorek and their team [73] investigated how adding certain types of material changes how well another material can conduct ions. They found that both the amount of LiClO4 salt and the type of additional material affect how a layer forms at the interface between the special material and the lithium electrode.

R. Baskaran T. Hattori and their team [57] studied a blend of two materials poly(vinyl acetate) (PVAc) and poly(methyl methacrylate) (PMMA) with LiClO4 as salt. They found that increasing the amount of salt in this blend makes the material conduct ions better. They also studied how this material behaves with temperature and found that it follows a particular pattern.

J. F. Le Nest M. Armand and their team [74] explored how to improve how a particular material can conduct ions. They used a special type of polymer made from polyethylene oxide triols and polyethylene oxide di-isocyanates. They tested how well this polymer could conduct ions how strong it was and at what temperature it changes. They did these tests both with and without adding certain salts and a substance to make the material more flexible (plasticizer). They found that adding salts and plasticizer made the material conduct ions better.

C. S. Harris and T. G. Rukavina [75] worked on making materials that can conduct lithium ions and protons (tiny particles). They wanted these materials to be stable at high temperatures and in electrical processes. They found that adding a substance called propylene carbonate to the mix made the material conduct ions better. Importantly they noticed that adding propylene carbonate did not harm the physical properties of the material.

Z. Yue I. J. McEwen and J. M. G. Cowie [76] looked into creating a special kind of material called a gel polymer electrolyte. They made this using a type of plastic LiCF3SO3 and another substance called propylene carbonate. They found that this material could conduct ions well and had good strength and the more propylene carbonate they added the better it conducted ions.

S. R. Majid and A. K. Arof [77] worked on creating thin films of a special kind of material that can conduct protons. They made this material using chitosan acetate and ammonium nitrate. Using special tests, they found that these substances formed a complex in the material. They found that the material conducted ions best when it had 45% ammonium nitrate at room temperature.

J. Travas -Sejdic P. Pickering and their team[78] explored a gel system made of a certain type of plastic mixed with lithium ions. They made this by creating a network of molecules in a mixture of special liquids. They studied how the mix's composition concentration and temperature affected how well it could conduct ions.

F. Croce L Settimi and B. Scrosati [79] showed how adding a superacid called ZrO2 affects how a certain kind of material can conduct ions. This material is a mix of poly(ethylene oxide) and lithium tetrafluoroborate. Adding ZrO2 makes this mix conduct ions even better.

S. Rajendran and T. Uma [11] talked about how changing the amount of salt and the temperature affects how well a certain kind of material can conduct ions. This material is a mix of poly(vinyl chloride) poly(methyl methacrylate) LiBF4 and dibutyl phthalate. They tested this mix at different temperatures and with different amounts of salt.

G. C. Li Y. P. Wu and others[39] worked on a special kind of material made of a specific plastic. They made this plastic in a way that left tiny holes in it. This material can conduct ions really well and could be used in batteries.

P. K. Singh and S. Chandra [80] looked into a special kind of material that can conduct ions. They made this material from a mix of poly(ethylene oxide) ammonium iodide and tiny particles of PbS and CdS. They found that they could make this material conduct ions better by making it in a certain way.

W. Chen Q Xu and R. Z. Yuan [81] talked about how changing a specific kind of plastic and the temperature affects how well a certain kind of material can conduct ions. This material is a mix of poly(ethylene oxide) and layered silicate. Changing the plastic makes the material conduct ions better especially at higher temperatures.

M. M. Doeff L. C. De Jonghe and their team [82] explored how the concentration of salt affects the ability of certain polymer electrolytes to conduct ions. They compared how well various combinations of salt and polymer conducted ions and found some that could be very useful in rechargeable lithium batteries.

D. R. MacFurlane M. Forsythand their colleagues [83] looked into how adding different plasticizers affects the ability of a certain kind of material to conduct ions and its thermal properties. They found that adding certain plasticizers increased the ionic conductivity of polymer electrolytes. This happens because the plasticizer makes the material's structure more flexible and helps the ions move more easily.

V. Aravindan P. Vickraman and T. Prem Kumar [84] studied the impact of adding a tiny particle called ZrO2 to a mix of specific plastics on the ionic conductivity. This material could be used in batteries. Adding ZrO2 up to a certain amount improved the ionic conductivity but beyond that it started to increase the material's crystallinity which wasn't as beneficial.

T. Steekanth U. V. Subba Rao and others [85] looked at a material made of poly(ethylene oxide) (PEO) with potassium bromate as the salt. They used techniques like differential scanning calorimetry (DSC) and dc conductivity to understand how ions move in this material.

V. Arivandan P. Vickraman and T. Prem Kumar [22] explored how adding Al2O3 to a specific mix of plastics and lithium salt affects the ionic conductivity. They found that adding up to a certain amount of Al2O3 improved the ionic conductivity but beyond that it started to decrease the conductivity.

F. Forsyth A. J. Hill and their colleagues [86] studied how adding TiO2 a specific kind of particle changes a polymer electrolyte's structure and ability to conduct ions. They found that adding TiO2 changed the environment around lithium ions increasing the available space for ions to move.

V. Gentili B. Scrosati and others [87] investigated the effect of adding certain ceramic particles to a specific mix involving lithium salts. These particles didn't dramatically affect the material's properties but they stabilized the interface with lithium and improved its mechanical properties.

G. B. Appetecchi B. Scrosati and their team [88] explored how adding ceramic powders affects the stability and ionic conductivity of a certain kind of polymer electrolyte. Adding these powders improved the stability at the interface and ionic conductivity.

M. Rikukawa and K. Sanui [89] delved into the properties of a special kind of polymer electrolyte that conducts protons. They found that these polymers made from hydrocarbons could be promising for making new high-performance proton-conducting polymer electrolytes.

E. M. Shembel D. Meshri and their team [90] explored how well certain materials made from poly(vinyl chloride) (PVC) and its modified form conducted ions. They checked the ionic conductivity using a method called impedance spectroscopy.

M. Walkowiak M. Osinka and their [91] colleagues worked on making a new kind of material that conducts lithium ions. They used a type of material called polysiloxane and added a special kind of compound called Si-tripodand centers. The resulting material conducted ions very well at regular room temperatures. They found that adding a substance called LiPF6 made this material conduct ions even better.

L. Reibel H. Majastre and others [92] studied how a material made from a particular type of plastic behaves when it comes to heat and conducting ions. At lower temperatures (below 50°C) the material acted like something that's partly crystalline. But as they increased the temperature above 50°C the material changed and became more amorphous like a solid without a specific structure.

C. Liebenow [93] looked into how the temperature and the mixture of ingredients affect a special type of material that can conduct magnesium ions. They used a substance called ethyl magnesium bromide dissolved in another material called poly(ethylene oxide). They found that by changing the amount of a specific ingredient they could make this material conduct ions better. The best conductivity was achieved with about 5-6% of magnesium content.

P. Ferloni A. Buttafava and others [94] looked into how exposing a material to a specific kind of radiation (gamma radiation) affects how it behaves in terms of heat and conducting ions. They used a material made of PEO containing LiClO4 as salt. When they exposed this material to gamma radiation it showed better mechanical properties and conducted ions more effectively compared to the same material that wasn't exposed to radiation.

M. A. K. L. Dissanyake I. Albinsson and other researchers [95] studied how adding a particular substance alumina filler affects the ability of a material to conduct ions. They used a type of material made from PEO LiCF3SO3 and alumina. They found that adding alumina filler increased the material's ability to conduct ions. This enhancement was because the ions interacted with specific parts on the surface of the filler. They observed two points where the conductivity improved the most and they explained this based on how the ions interacted with the surface.

M. M. E. Jacob S. R. S. Prabaharan and S. Radhakrishna [96] investigated what happens when they added a substance called PEO to a material made of PVdF and LiClO4. They wanted to see if this addition improved how the material conducts ions and how it handles heat. They used tools like XRD and DTA to see how well PEO and PVdF worked together. They also checked the structure of the material using a technique called XRD. By doing these studies they found that adding PEO made the material conduct ions better and become more stable when exposed to heat.

A. Subramania N. T. Kalyana Sundaram and N. Sukumar [97] studied a type of material made by blending two plastics PVA and PVC and looked at how the concentration of lithium salt affected its ability to conduct ions. They found that removing PVC from the blend made the material conduct ions better. They also looked at the structure and surface of the material using techniques like X-ray diffraction and SEM. These studies showed that the resulting material was stable at high temperatures.

A. M. Stephan N. Muniyandi and their fellow researchers [98] explored a mix of two plastics PVC and PMMA to see how it conducted ions under different conditions. They were especially interested in how much of a substance called a plasticizer should be added to make the material work best. By using a technique called AC Impedance spectroscopy they found that a mix with 70% plasticizer had good ionic and mechanical properties.

P. Lobitz and H. Fullbier [99] examined a material made from a mix of polyethylene oxide and lithium iodide salt to understand how it conducts ions. They also wanted to see how the composition and temperature affected this conductivity. They used a method called impedance to measure how well ions moved in the material. They observed that the movement of ions varied based on the concentration of the components and the temperature.

S. Ramesh and M. F. Chai [100] looked at how temperature affects the conductivity of a polymer electrolyte made from a high molecular weight poly(vinyl chloride) (PVC) mixed with lithium triflate (LiCF3SO3) salt. They measured the conductivity at different temperatures and explained the results using an Arrhenius relationship.

G P. Pandey S. A. Hashmi and R. C. Agrawal [101] explored how adding different amounts of SiO2 affects how well a polymer electrolyte based on poly(ethylene oxide) (PEO) with NH4HSO4 salt conducts ions. They used various tests like measuring electrical conductivity X-ray diffraction analysis Scanning electron microscopy and Fourier transform infra-red spectroscopy to understand the material better. They found that a complex polymer electrolyte system with 5 wt% of silica showed 2.5x10-4 S/cm ionic conductivity at room temperature.

S Pantaloni M. Andrei and their team [102] investigated the conductivity lithium ion transport numbers and electrochemical properties of polymer electrolytes made of ethoxy-ethoxy-ethoxy-vinyl ether with different lithium salts like LiClO4 and LiBF4. They discovered that the resulting system conducted ions three orders of magnitude better compared to polyethylene oxide-based polymers.

E Morales and J. L. Acosta [103] investigated the effect of different lithium salts like lithium perchlorate (LiClO4) lithium triflouromethanesulfonate (LiCF3SO3) lithium hexafluorophosphate (LiPF6) on the ionic conductivity and thermal behavior of solid polymer electrolytes made from poly(methylalkoxysiloxane). They found that the behavior of the prepared polymer electrolytes was influenced by the specific lithium salt used. They also confirmed the presence of amorphous regions in their samples.

E. M. Woo S. C. Lee and their [104] team conducted a study to understand how well poly(ethylene oxide) and poly(phenyl methacrylate) mix together. They used different methods like differential scanning calorimetry scanning electron microscopy and infrared spectroscopy to analyze and show how well these two substances mix. By looking at how the glass transition temperature behaves they concluded that there are weak interactions between them. This was further confirmed using Fourier transform infrared spectroscopy.

Chapter 3

Materials and Method

3.1 Raw Material

The TiO_2 used in this study was prepared previously reported method [105]. This TiO_2 served as the inorganic filler in the fabrication of the Composite Polymer Electrolyte (CPE). The PEO utilized in the experiment had a molecular weight of 1,000,000 g/mol^{-1}, and the Lithium Triflate salt was sourced from Shanghai Macklin Co. as well. Distilled water (DI water) was employed as the solvent in the experimental process.

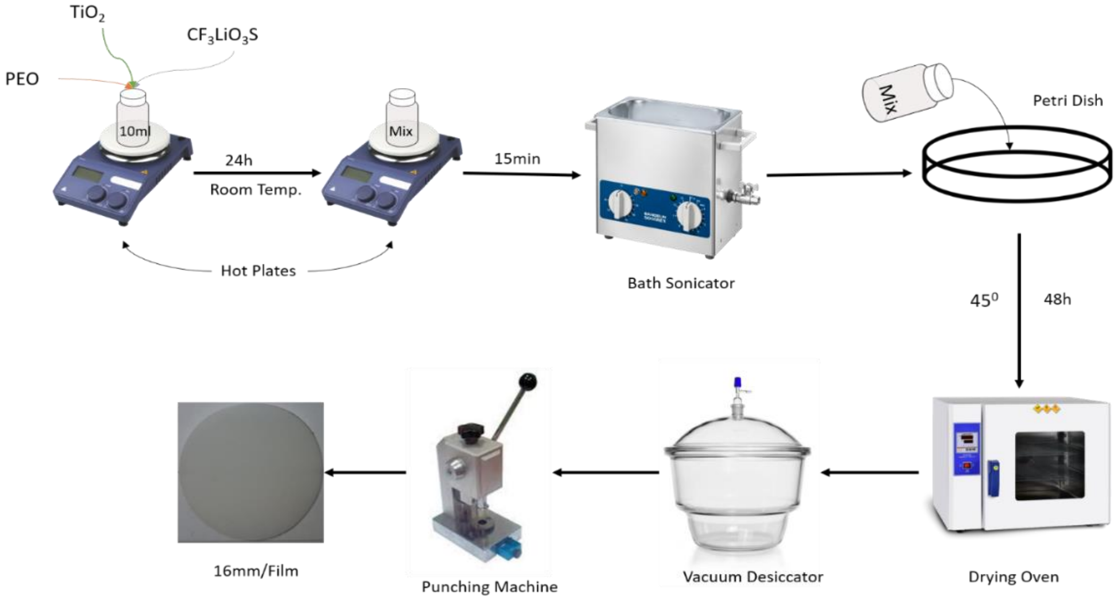

Figure 8 Schematic of sample preparation of composite polymer electrolyte

3.2 Synthesis of Composite Polymer Electrolyte

In the synthesis process, lithium triflate and prepared TiO_2 were use after undergoing vacuum drying at 90°C, while polyethylene oxide (PEO) was utilized as purchased. The Composite Polymer Electrolyte (CPE) films, denoted as PEO-Lithium Triflate-TiO_2, were fabricated through a solution casting technique. Distilled water was employed as the solvent for CPE preparation. Maintaining a fixed weight ratio of PEO to lithium salt at 10:1, the composition of the CPE films was varied by altering the amount of TiO_2 incorporated. The process involved dissolving PEO in 7ml of solvent at 60°C for 2 hours and separately mixing a predetermined quantity of lithium salt in 3ml of solvent at room temperature, both within separate containers while employing magnetic stirring. The lithium salt solution was introduced into the PEO solution dropwise, and TiO_2 was added to the same container. The mixture was kept at room temperature for the subsequent 24 hours with continuous magnetic stirring, and ultrasonication was employed to ensure the complete dispersion of TiO_2 in the solution. Once a homogeneous mixture was achieved, it was cast into petri dishes and subsequently dried in an oven for 48 hours at 45°C. Following this, the CPE samples underwent further drying under vacuum conditions at 40°C for 48 hours and were stored within a vacuum desiccator before undergoing subsequent testing procedures.

Table 3 List of samples investigated in this work

Sample	**Composition**		
	PEO (g)	**CF_3LiO_3S (g)**	**TiO_2 (g)**
PE-01	1.2	-	-
PE-02	1.2	0.12	-
PE-03	1.2	0.12	2.25
PE-04	1.2	0.12	2.25x5

3.3 Characterization

3.3.1 Scanning Electron Microscope

The morphological and dimensional analysis of composite polymer electrolytes (CPEs) containing different amounts of TiO_2 filler. The analysis was conducted using a scanning electron microscope (SEM). To prepare the samples for SEM analysis, a thin layer of gold was sputtered onto the surface of the samples to make them conductive.

The SEM is a powerful tool for imaging the surface morphology of materials. It uses a focused beam of electrons to scan the surface of a sample and create an image. The SEM can be used to image a wide range of materials, including polymers, ceramics, and metals.

Sputtering is a technique used to deposit a thin film of material onto the surface of a substrate. In this case, gold was sputtered onto the surface of the CPE samples to make them conductive for SEM analysis. Sputtering is a physical vapor deposition (PVD) technique, which means that it involves the physical removal of material from a source and its deposition onto a substrate.

The morphological and dimensional analysis of the CPE samples can provide information about the size, shape, and distribution of the TiO_2 filler particles in the polymer matrix. This information can be used to understand how the TiO_2 filler affects the properties of the CPE, such as its ionic conductivity and mechanical strength.

Prepared samples also CPEs which include TiO_2 with different wt% like 2.25%, and 2.25x5%, were subjected to morphological and dimensional analysis. This analysis was conducted using the JEOL JSM-6490LA analytical low vacuum scanning electron microscope. To render the surface conductive, a layer of gold was applied to the samples through sputtering of gold. Sputtering was conducted using the Ion Sputtering Machine JFC-1500, manufactured by JEOL Ltd, Japan, with an accelerating voltage of up to 20 kV.

3.3.3 X-Ray Diffraction

X-ray diffraction (XRD) is a non-destructive analytical technique that can be used to determine the crystal structure of materials. It works by directing a beam of X-rays at a sample and measuring the intensity and angle of the diffracted X-rays. The diffraction pattern can be used to identify the crystal structure of the material and to determine the size and orientation of the crystals.

The crystallinity of a sample is a measure of the amount of crystalline material in the sample. Crystalline materials have a well-defined crystal structure, while amorphous materials do not. The crystallinity of a sample can affect its properties, such as its strength, hardness, and electrical conductivity.

The patterns of Pure PEO, PEO-Lithium Triflate, and the composite polymer electrolytes were obtained using a Bruker D-2 Phaser instrument. This instrument features a copper sample holder and utilizes Cu-Kα radiation with a wavelength of 1.5406 Å. The apparatus functions with an applied voltage of 30 kV and a current of 10 mA. The samples subjected to XRD analysis were the same as those used for SEM analysis. From XRD analysis, we measured the percentage of crystallinity (Xc) using equation (i) [106]

$$\mathrm{Xc} = \frac{Ic}{Ic + Ia}\mathrm{x}100 \qquad \text{(i)}$$

Here, Ic denotes the integrated intensity associated with the crystalline phase, whereas Ia signifies the integrated intensity linked to the amorphous phase.

3.3.4 Fourier Transform Infrared Radiation

Fourier-transform infrared (FTIR) spectroscopy is a technique used to identify organic and inorganic materials by analyzing their infrared absorption spectrum. It works by passing infrared radiation through a sample and measuring the amount of radiation that is absorbed at different wavelengths. The infrared absorption spectrum of a material is unique to that material, so it can be used to identify unknown materials.

FT-IR analysis was carried out utilizing the PerkinElmer Spectrum 100 FT-IR Spectrometer, supplied by Waltham, MA, USA. This analysis carried on the pure PEO, PEO/salt and the composite polymer electrolytes with TiO_2 at 2.25% and 2.25 x 5% ratios. Infra-red (IR) radiation ranging from 4000 cm^{-1} to 400 cm^{-1} wave number was employed during the analysis.

3.3.5 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is a technique used to study the electrical properties of materials and systems. It works by applying a small, sinusoidal voltage to a sample and measuring the resulting current. The impedance of the sample is the ratio of the voltage to the current, and it can be used to characterize a variety of properties, including, conductivity, resistance, capacitance, Inductance.

EIS measurements were conducted using the Gamry Interface 1010E instrument. Films with a diameter of 16mm were prepared using a disc punching machine. These films were positioned between two stainless steel electrodes with the insertion of a spacer, and they were assembled in CR 2032 casings using a hydraulic press machine. The measurements were performed across frequency range from 1MHz to 0.1Hz. Following that, the ionic conductivity of each individual sample was calculated from bulk resistance obtained from Nyquist impedance plots, utilizing a 10mV amplitude and a 0.3 DC, using the equation (ii) [107]

$$\sigma = \frac{\mathrm{l}}{\pi r^2 \mathrm{Rb}} \qquad \text{(ii)}$$

Where, "l" denotes the thickness of the sample measured in centimeters, while "r" symbolizes the radius of the effective contact area between the sample and the electrodes, also expressed in centimeters. "R_b" represents the bulk resistance of the polymer electrolyte disc positioned between the electrodes. These electrodes serve as barriers that restrict the movement of lithium ions. The plots illustrate two discernible and well-defined domains: a semicircular region and a linear region. The semicircular region, which originates at higher frequencies from the bulk of the electrolytes present in the bulk. Conversely, the linear segment observed in the low-frequency range is a result of the impact exerted by the blocking electrodes [108]. In an ideal scenario, the impedance plot within the low-frequency region should ideally can be a straight line which would be parallel to imaginary axis. Existence of a high-frequency semicircle signifies that specific characteristic of the electrolyte, such as bulk resistance (Rb) and bulk capacitance (Cb), originate from the migration of lithium ions and the polarization of the polymer electrolyte, respectively. The spike observed in the low-frequency region is a result of additional contributions from capacitance and resistance, originates from phenomena such as dielectric relaxation and ion trapping [109]. The point at which the semicircle intersects with the low-frequency region denotes the bulk resistance of the materials. Notably, bulk resistance exhibits a decrease as the temperature of the sample rises [110].

Chapter 4

Results and Discussion

4.1 Results and Discussion

The surface properties and crystalline structure of a solid electrolyte are pivotal factors influencing its electrical conductivity. In particular, when examining polymer electrolytes, those with smoother surface characteristics often exhibit significantly improved ionic conductivity. This phenomenon can be attributed to the reduced hindrance or obstruction of ionic transport caused by surface irregularities or imperfections. Hence, a smoother surface not only minimizes the resistance to ion movement but also facilitates more efficient charge transfer within the material, making it a desirable trait for solid electrolytes in various electrochemical applications [111]. The SEM image of the solid polymer electrolyte depicts a surface with a textured topography, consisting of numerous crystalline domains. The presence of a smooth surface is closely associated with reduced PEO crystallinity, primarily attributable to interactions occurring between PEO segments and lithium ions [112]. After introducing Li salt, a significant enhancement in surface smoothness is observed, transforming the surface from rough to smooth Figure 9a. The figure clearly illustrates that the inclusion of TiO_2 filler brings about a notable change in the surface structure of the solid electrolyte Figure 9b, changing from rough to smooth surface. This change indicates the consistent dispersion of the filler within the polymer-salt matrix. The composite polymer electrolyte's smooth surface is linked to the decreased crystalline nature of the PEO component [113]. This smooth surface facilitates the transportation of ions within the polymer electrolyte, thereby increasing its conductivity [114]. It is observed from Figure 9b and Figure 9c that there is significant change in film morphology upon the addition of TiO_2 at 2.25% and 2.25 x 5% respectively. From Figure 9b evenly distribution of nano particles observed. Figure 9d is the magnified image of Figure 9c, which is made of high wt% of TiO_2 content in PEO, reveals the presence of aggregated particles resulting from the tendency of small particles to form larger aggregates. Consequently, the CPE films that exhibit heterogeneous film morphologies due to the aggregation of filler particles create a hindrance in charge carrier transport. This hindrance cause decrease in conductivity [56].

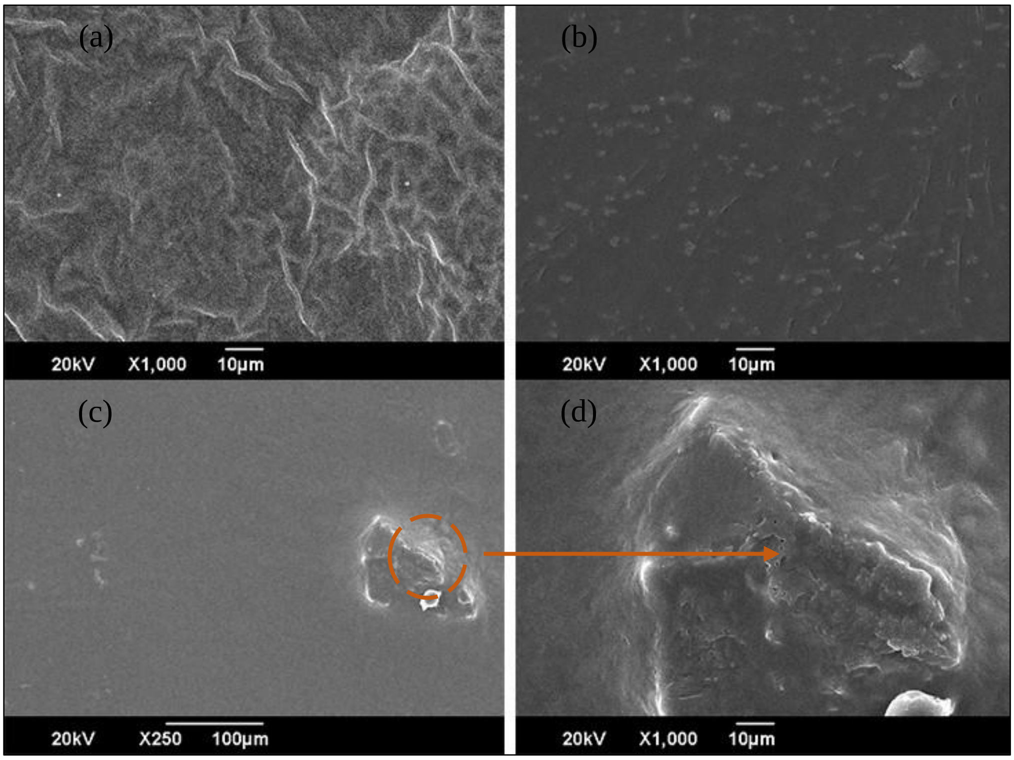

Figure 9 SEM images of (a) $PEO_{10}(CF_3LiO_3S)$ (b) $PEO_{10}(CF_3LiO_3S)$2.25% TiO_2 (c) $PEO_{10}(CF_3LiO_3S)$2.25 x 5% TiO_2 (d) Magnified image c

The impact of incorporating salt and TiO_2 into PEO becomes evident when examining the X-ray diffraction patterns as illustrated in Figure 10. The XRD pattern of the pure PEO exhibits noticeable diffraction peaks positioned at $2\theta = 19.19°$, signifying the existence of the crystalline region within PEO polymer matrix, and at 23.32°, indicating the presence of both the (0 3 2) and (1 1 2) crystallographic planes [115]. The inclusion of $LiCF_3SO_3$ salt led to a reduction in the crystalline structure of the PEO, as it is observed the decrease in the intensity of the prominent peaks located at 19.06° and 23.32°. Decrease in the crystalline region of the PEO material can be attributed to the complex interaction between PEO and lithium ions, which effectively hinders the crystallization process of PEO [116]. Furthermore, it was noted that the intensity of the peaks in PEO polymer diminished with incorporation of TiO_2 at different weight percentages. The reason behind this decline in crystallinity may be due to the ability of TiO_2 to create hindrance in chain's diffusion towards the crystal growth front of the polymer [117]. Ultrasonication can be applied to the composite solutions to ensure the complete dispersion of the fillers peak broadening of the composites in figure 10 observed the main peak that is located at 19.19^0 indicating the displacement to a lower angle resulting an increase of d-spacing [118].

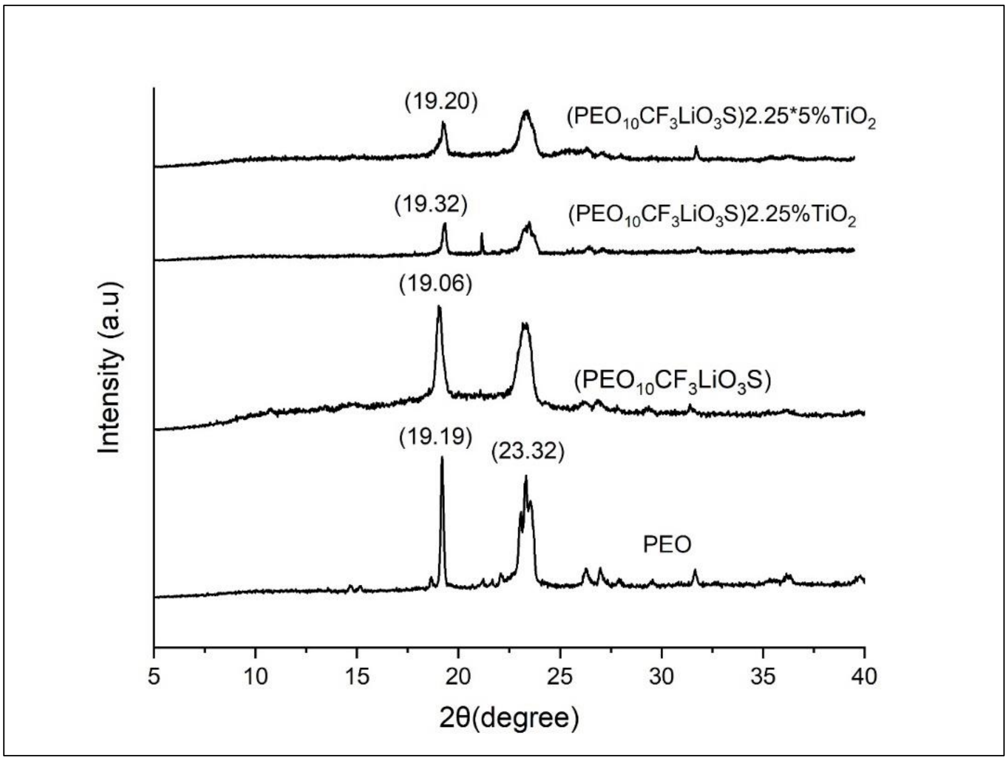

Figure 10 Xray diffraction patterns of (a) Pure PEO (b) PEO$_{10}$(CF$_3$LiO$_3$S) (c) PEO$_{10}$(CF$_3$LiO$_3$S)2.25% TiO$_2$ (d) PEO$_{10}$(CF$_3$LiO$_3$S)2.25x5% TiO$_2$

The confirmation of complexation involving CF$_3$LiO$_3$S salt and TiO$_2$ filler in combination with the PEO polymer is additionally validated through the analysis of FTIR spectra. The FTIR spectra of (a) Pure PEO (b) PEO$_{10}$(CF$_3$LiO$_3$S) (c) PEO$_{10}$(CF$_3$LiO$_3$S)2.25% TiO$_2$ (d) PEO$_{10}$(CF$_3$LiO$_3$S)2.25x5% TiO$_2$ are shown in Figure 11. The FT-IR technique can be employed to explore the complex bonding between Li+ ions and polymer matrices [102]. However, the FT-IR spectra of the fabricated samples, observed in Figure 11, which demonstrates that the peak around 3500 cm^{-1} correspond to the distinctive band of –OH groups within PEO. Meanwhile, the weak band at approximately 1642 cm^{-1} could be linked to C=O peak. For TiO$_2$, the bands situated at approximately 640 cm^{-1} are indicative of Ti–O bond [101]. Additionally, the band around 1112 cm^{-1} corresponding to the distinctive peak of PEO [119]. However, the peak at approximately 2970 cm^{-1} can be attributed to the existence of C–H bonds within the polymer's helix [120]. Upon introducing TiO$_2$ filler into the PEO-salt complex some peaks ranging from 400–700 cm^{-1} characteristic of pure PEO disappeared. This observation suggests the integration of the filler into the PEO-salt matrix, indicating complexation [121].

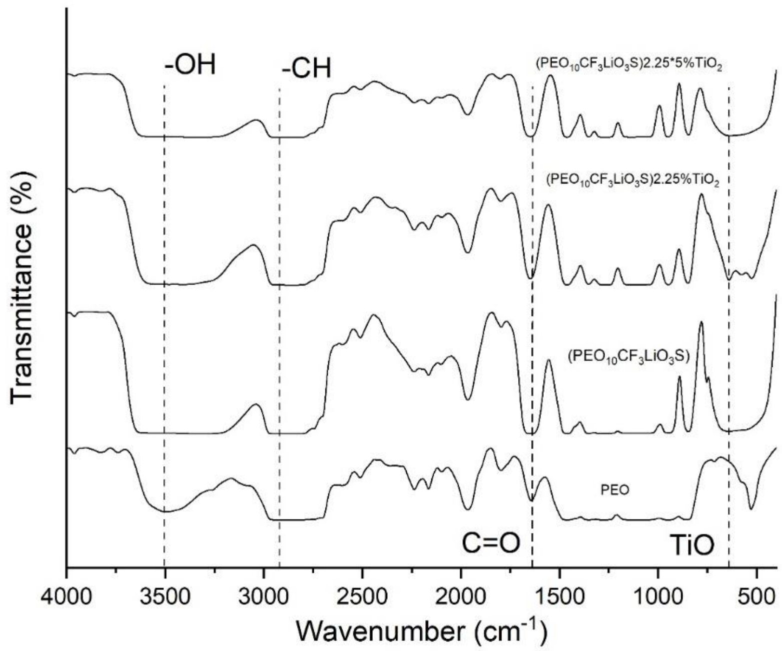

Figure 11 FTIR patterns of (a) Pure PEO (b) $PEO_{10}(CF_3LiO_3S)$ (c) $PEO_{10}(CF_3LiO_3S)2.25\%$ TiO_2 (d) $PEO_{10}(CF_3LiO_3S)2.25x5\%$ TiO_2

4.2 Ionic Conductivity

Different electrolytes have different ionic conductivities aqueous electrolytes tend to have lower resistance than non-aqueous electrolytes. Hence, the ionic conductivity of the electrolyte is an important parameter that affects the performance and efficiency of lithium metal batteries. Balancing high ionic conductivity with other desirable properties, such as stability and compatibility, is crucial for the practical application of electrolytes in lithium metal batteries [122]. On the other hand more concentrated electrolytes have greater ionic conductivity, and therefore lower resistance [123]. While temperature exerts a vital influence on the conductivity of electrolytes, as high temperature leads to an increment in conductivity, consequently reducing their resistance [57]. Another factor which affects ionic conductivity of the solid electrolyte is the presence of impurities which can increase resistance and hence reduced ionic conductivity [124].

4.2.1 Nyquist Plots

The ionic conductivity of pure PEO is low because the PEO chains are tightly packed together in the crystalline state. This prevents the ions from moving freely. PEO is a semi-crystalline polymer, which means that it has both crystalline and amorphous regions. The crystalline regions are ordered and have a high density, while the amorphous regions are disordered and have a lower density. Ions can only move freely in the amorphous regions of PEO. The crystalline regions of PEO block the movement of ions, which reduces the overall ionic conductivity of the material.

The PEO chains are long and flexible. This allows them to entangle with each other, which further reduces the ionic conductivity of the material. To increase the ionic conductivity of PEO, it is necessary to disrupt the crystalline structure and reduce the entanglement of the PEO chains.

Sharanappa Chapi obtained ionic conductivity of pure poly(ethylene oxide) (PEO) at room temperature, around $8.6x10^{-8}$ S cm-1 [125]. Wright and Armand reported the findings of their research on the ionic conductivity of PEO, which measured approximately 10^{-7}S cm^{-1} at room temperature [126]. Hawzhin and Omed found that the ionic conductivity of pure PEO methylcellulose blend film for weight ratio 60:40 was calculated $6.55x10^{-9}$ S cm^{-1} at ambient temperature [127]. Hashim and Subban found the ionic conductivity of pure PEO film at ambient temperature was $1.43x10^{-8}$ S cm^{-1} [128].

From figure 12, the bulk resistance was calculated through the intersection of the high frequency semicircle at real impedance axis which was $1.67x10^{-6}$ ohms. By converting we get ionic conductivity of pure PEO $6.20x10^{-6}$ mS/cm at normal temperature.

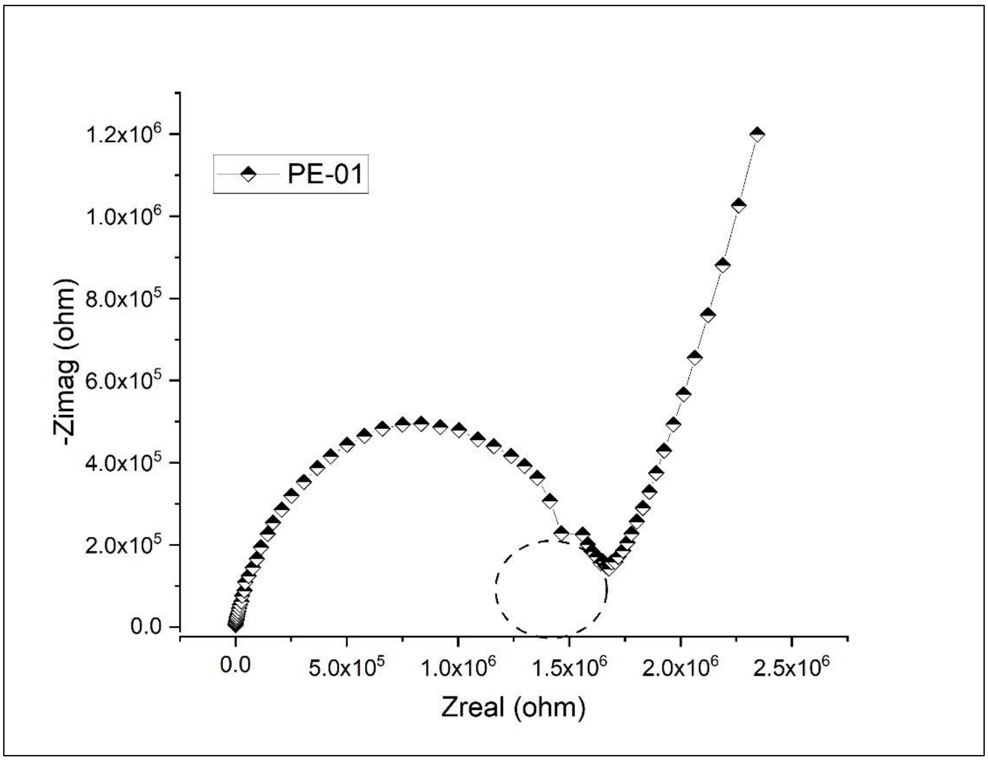

Figure 12 Nyquist Plot of Pure PEO

The ionic conductivity of solid polymer electrolytes (SPEs) based on PEO is affected by the type of lithium salt used. Different lithium salts have different dissociation constants, which affects the number of free ions available for transport. Additionally, the size and shape of the lithium salt anion can also affect the ionic conductivity.

Mong and Kim found a high Li-ion conductivity of 0.712 mS cm^{-1} from the synthesized self-assemblable PSEs [129]. Yifei and Lina obtained High room-temperature ionic conductivity of 1.4×10^{-5} from solvent-free solid electrolyte [130]. Qingya and et al calculated the ionic conductivity of solid electrolyte film which was 1.05×10−4 S cm^{-1} at 30°C [131].

From figure 13 it can be seen that the resistance of the solid electrolyte is approx. 75 ohms which is suitable for energy storage devices in batteries may also be in supercapacitors. On conversion we obtained ionic conductivity of $2.08x10^{-1}$ mS/cm.

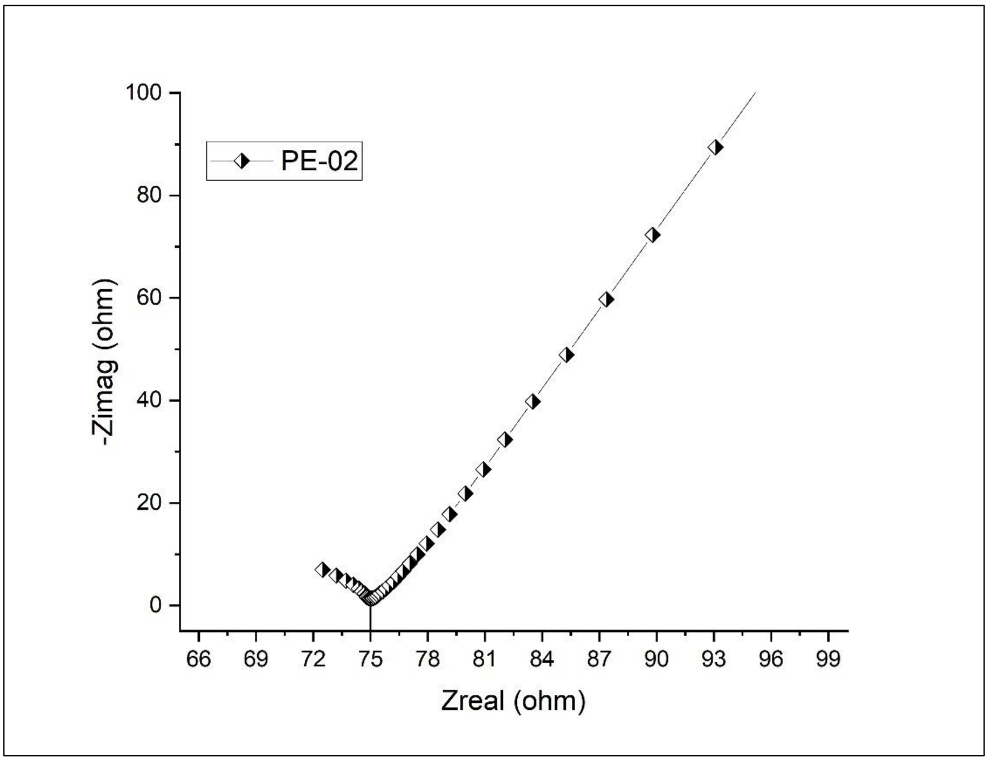

Figure 13 Nyquist Plot of $PEO_{10}(CF_3LiO_3S)$

Elham and Mehdi calculated the highest ionic conductivity of composite polymer electrolyte for lithium-ion batteries $1.35x10^{-3}$ S/cm [132]. Emad and et al. found the high ionic conductivity $1.08 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$ at room temperature [133]. Nikita and Alexander calculated the ionic conductivity 3.8mS/cm at 25^0C [134]. Omed and Bakhan found a maximum conductivity of 5.52×10^{-3} S cm^{-1} at 303 K has been achieved for the NCPE containing 8 wt.% of TiO_2 NPs [135].

Figure 14 and Figure 15 showing two different Nyquist Plots of composite polymer electrolytes with improved ionic conductivity than Pure PEO which has lowest ionic conductivity at room temperature. By comparing both graphs it can be seen that composite with higher TiO_2 wt% has high conductivity than composite containing 2.25 wt% of TiO_2. Through SEM results it can be seen that higher TiO_2 containing agglomerates of TiO_2 with smooth surface but in less amount of TiO_2 has evenly dispersion of nano filler which could lead to rough surface may has less ionic conductivity.

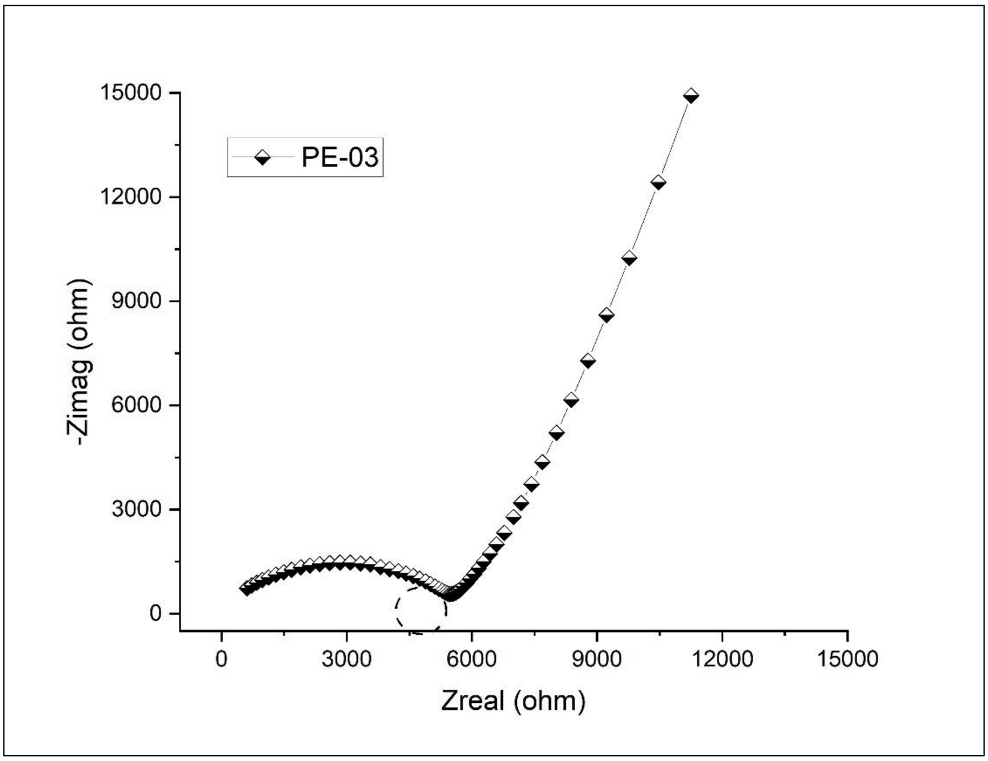

Figure 14 Nyquist Plot of $PEO_{10}(CF_3LiO_3S)$2.25% TiO_2

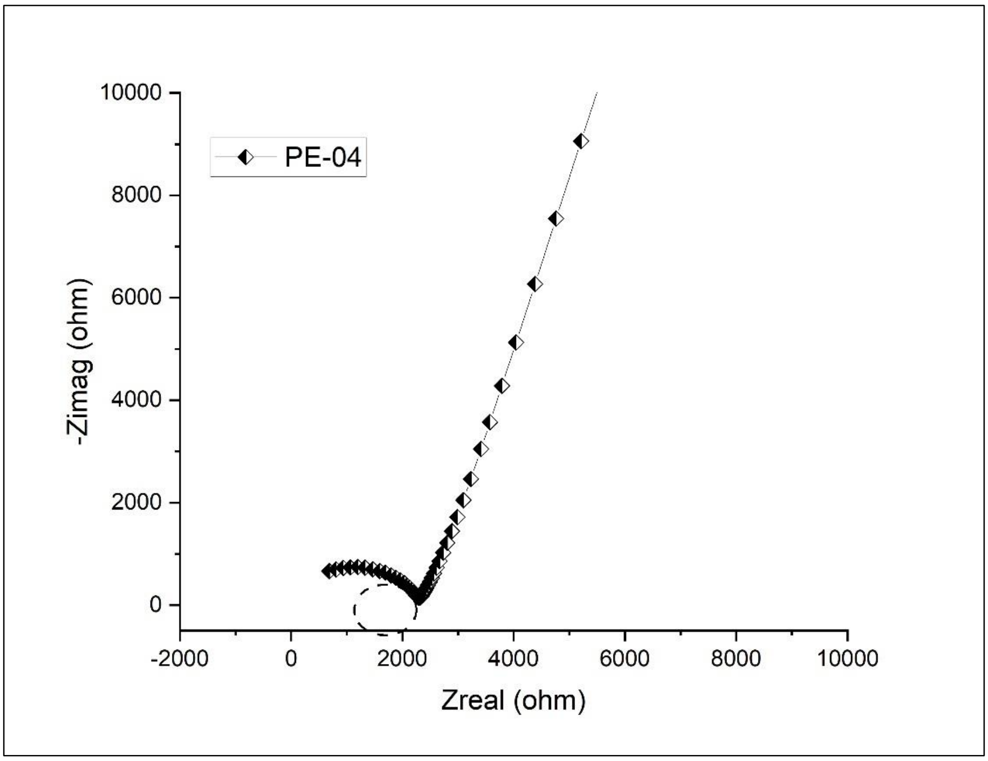

Figure 15 Nyquist Plot of $PEO_{10}(CF_3LiO_3S)$2.25x5% TiO_2

From all these Nyquist Plots of solid electrolytes, it is not possible to say definitively which factor is responsible for the observed variation in resistance without further information. It is desirable to have a low-resistance electrolyte. Here are some specific examples of how the factors mentioned above can affect the resistance of a solid electrolyte. The concentration of the electrolyte can also affect its resistance. For example, a more concentrated electrolyte will have lower resistance. This is because there are more ions per unit volume in a more saturated electrolyte, which increasing the conductivity [60]. Additionally, the temperature of the electrolyte plays a role in determining its resistance. As the temperature rises, the conductivity of electrolytes increases, resulting in a decrease in their resistance. This happens because at higher temperatures, the vibrational energy of a molecular segment becomes enough to overcome the hydrostatic pressure imposed by neighboring atoms. This permits the segment to generate a small void around its own spatial domain, enabling vibrational motion to occur more freely, which in turn enhances ionic conductivity and reduces resistance [136].

Table 4 Ionic Conductivity of the samples

Sample	**Avg FT (μm)**	**Bulk Resistance (Ω)**	**σ (mS/cm)**	**Xc (%)**
PE-01	197	-	$6.20 \mathrm{x} 10^{-6}$	60.40
PE-02	301	75.00	$2.08 \mathrm{x} 10^{-1}$	30.00
PE-03	136	5515.85	$1.28 \mathrm{x} 10^{-2}$	50.70
PE-04	140	2297.84	$3.16 \mathrm{x} 10^{-2}$	38.00

The results depicted in Table 4 and Figure 16 demonstrate a trend where the resistance of the solid electrolyte composites decreases as the TiO_2 content increases, while the ionic conductivity increases. In pure PEO, crystallinity is around 60–80% depending on molecular weight and processing conditions [137]. This finding aligns with prior research, which has indicated that TiO_2 nanoparticles can increase the conductivity of ion in solid polymer electrolytes by reducing crystalline structure of the polymer matrix. This reduction in crystallinity makes it more accessible for ions to move, creating additional pathways for ion conduction. Additionally, TiO_2 nanoparticles can interact with the polymer to form stable complexes, further improving ion mobility [138]. Highest conductivity, measured at 3.16×10^{-2} mS cm^{-1}, was achieved in the solid polymer electrolyte (SPE) composite containing 2.25% TiO_2. This conductivity level is notably higher compared to the pure PEO with a conductivity of 6.2×10^{-6}

mS/cm. The substantial improvement in ionic conductivity observed in the SPE composites including TiO_2 nanoparticles positions them as promising candidates for applications in electrochemical devices, particularly in lithium-ion batteries [139]. The observed decrease in resistance and increase in conductivity of ions with increasing TiO_2 content is due to the addition of TiO_2 nanoparticles to the PEO matrix reduces its crystallinity. This is because the TiO_2 nanoparticles disrupt the packing of the polymer chains, making it easier for ions to move [140]. Additionally, the TiO_2 nanoparticles provide additional pathways for ion conduction. This is because the TiO_2 nanoparticles have a high surface area, and ions can be transported through the pores and channels in the TiO_2 nanoparticles [141]. The combined effect of these factors is to reduce the resistance and increase the conductivity of ions in the SPE composites with increasing TiO_2 content. The conductivity might be going up because of added filler that helps ions move more easily and also helps the polymer parts move around better [121].

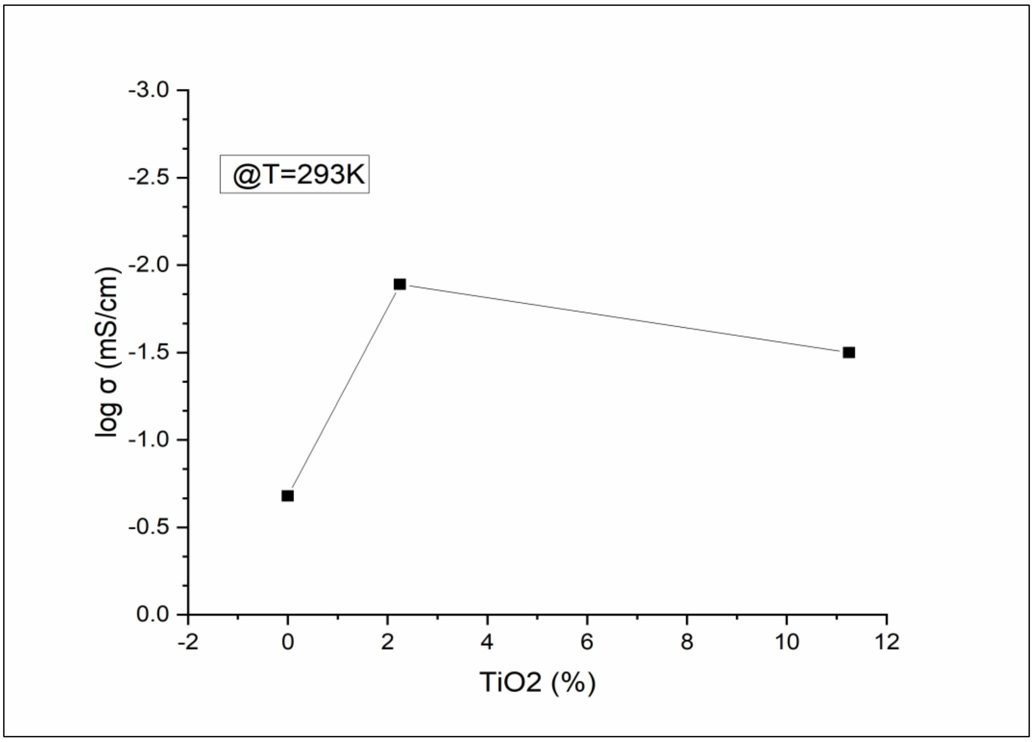

Figure 16 Variation in ionic onductivity which is a function of wt% of TiO_2 of solid polymer electrolyte

Table 5 Comparison of ionic conductivity with previous work

CPE	**σ (mS/cm)**	**Ref**
$PEO_{12}(LiTDI)8wt\% TiO_2$	$2.11x10^{-2}$	[104]
$PEO(CF_3SO_3Li)3\%$ chem-SiO_2	$1.73x10^{-2}$	[142]
PVDF-HFP doped with TiO_2–PMMA	$2.77x10^{0}$	[143]
$PEO_{10}(LiClO_4)$	$4.47x10^{-2}$	[73]
$PEO_{10}(CF_3LiO_3S)$	$2.08x10^{-1}$	our work
$PEO_{10}(CF_3LiO_3S)2.25x5\% TiO_2$	$3.16x10^{-3}$	our work

Table 5, represents the comparison of ionic conductivity with previous reported data, with different weight percentages TiO_2 in PEO complex with salts. Showing that the conductivity of solid electrolyte is higher than that of the PEO/salt/TiO_2 composites. This suggests that the TiO_2 nanoparticles are disrupting the connection between the lithium ions and the PEO helix, which can be reducing the ionic conductivity. However, it is important to note that the ionic conductivity of the PEO/salt/TiO_2 composites is still significantly higher than that of pure PEO. This is because the TiO_2 nanoparticles are still providing additional pathways for ion conduction and reducing the crystallinity of the polymer matrix. Overall, the results in Table 5 suggest that TiO_2 nanoparticles can be used to boost the conductivity of ions in PEO electrolytes, but they should be used in moderation to avoid disrupting the interaction between the Li+ ions and the PEO chains. Here is a possible explanation for the observed decrease in ionic conductivity with increasing TiO_2 content in the PEO/salt/TiO_2 composites. Addition of TiO_2 nanoparticles to the PEO/salt complex disrupts the interaction between the lithium ions and the PEO chains. This is because the TiO_2 nanoparticles compete with the lithium ions for binding sites on the PEO chains. As a result, fewer lithium ions are able to bind to the PEO chains, which reduces the ionic conductivity. Additionally, the TiO_2 nanoparticles can aggregate and form clusters, which can block the pathways for ion conduction. This can also contribute to the decrease in ionic conductivity with increasing TiO_2 content. Despite these drawbacks, the TiO_2 nanoparticles still provide some benefits to the PEO/salt electrolyte. For example, the TiO_2 nanoparticles can be reducing the crystallinity of the polymer material and provide additional pathways for ion conduction. Resulting, the conductivity of ions in

PEO/salt/TiO_2 composites is still significantly higher than that of pure PEO. The optimal amount of TiO_2 nanoparticles to add to the PEO/salt electrolyte will depend on the specific application. If high ionic conductivity is the primary concern, then it is best to use a low concentration of TiO_2 nanoparticles. However, if other factors such as mechanical strength or thermal stability are also important, then it may be necessary to use a higher concentration of TiO_2 nanoparticles [144].

Conclusion

Composite polymer membranes containing PEO, CF_3LiO_3S, and TiO_2 nanoparticles through the solution casting technique were made. In addition, ultrasonication was employed to achieve a homogenous dispersion of TiO_2 within the solution. The resulting composite polymer electrolyte membranes were designed for application in lithium-ion batteries, aiming to enhance their performance and safety. The investigation revealed that the implementation of ultrasonication effectively facilitated the uniform dispersion of TiO_2 nanoparticles within the sample PE-03 but in sample PE-04 forms aggregates due to higher concentration of TiO_2. Decrease in the crystalline nature of the pure PEO component observed. The introduction of TiO_2 filler into the electrolytes brought changes in their structural morphology, which created more conducive environment for ionic conduction. The SEM image indicates that the composite polymer electrolytes (CPEs) have become more amorphous comparing pure PEO, which results in better movement of ions. This leads to improved ion transportation properties in the synthesized polymer electrolytes. Incorporating salt into the polymer matrix increase the conductivity of ions by approximately five times of magnitude. The CF_3LiO_3S salt plays a vital role in enabling the transportation of positively charged lithium ions. An increase in TiO_2 in $PEO-10\%CF_3LiO_3S-TiO_2$ system provided with high ionic conductivity than pure PEO. Observed ionic conductivity of the pure PEO and PEO with fixed amount of salt, $6.20x10^{-6}$ mS/cm and $2.08x10^{-1}$ mS/cm respectively. Hence there is significant increase in conductivity by introduction of salt in host polymer PEO. Also observed amorphous region of the polymer is responsible for the transportation of ions within matrix.

Future Recommendations

- To obtain a deep understanding of lithium-ion mobility, the transference number can be computed using the Evans–Vincent–Bruce equation. This calculation involves applying an impedance technique both before and after potentiostatic polarization.
- To assess the mechanical characteristics of composite polymer electrolytes and enhance the durability and safety the lithium solid-state batteries, Ultimate Tensile Strength (UTS) testing can be conducted.
- To assess the electrochemical stability of Composite Polymer Electrolytes (CPEs) for the purpose of creating longer-lasting and more dependable solid-state lithium-ion batteries, Linear Sweep Voltammetry (LSV) experiments can be carried out. For these experiments configuring a half-cell with a lithium metal electrode would be more suitable to facilitate lithium-ion conduction.

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