Investigation of ion transport and electrochemical performance of fluorinated and lithiated gel polymer electrolytes for lithium ion batteries

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FLUORINATED AND LITHIATED GEL
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**SCHOOL OF MATERIALS SCIENCE AND
ENGINEERING**

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Summary

One of the main challenges that restrict the large scale application of lithium ion batteries for high energy and high power density applications is the electrolyte. An electrolyte that has high ionic conductivity, high lithium ion transference number, and good mechanical and thermal stability is the need of the day. Polymer based electrolytes offer several advantages such as easy processibility, good mechanical properties and reasonable ionic conductivity. Amongst the polymer electrolytes, gel polymer electrolytes (GPEs) are most promising, because they offer comparable performance to the currently used commercial liquid electrolytes, while offering the added advantage of shape flexibility. However, there are still several issues that need to be tackled before the GPEs can be put to large scale commercial use.

This thesis focusses on the study of GPEs for application in lithium based batteries. High ionic conductivity poly (vinylidene fluoride-co-hexafluoropropylene) (P(VdF-*co*-HFP)) based GPEs and high lithium transference number poly (4-lithium styrene sulfonic acid) (PSSLi) based gels were explored as alternate electrolytes. The main problem associated with P(VdF-*co*-HFP) based GPEs is the mutual exclusivity of ionic conductivity and mechanical properties. The main problem with the PSSLi based gels is lower ionic conductivity, due to the reduced number of mobile charge carriers. This thesis mainly focusses on addressing the two most common issues affecting gel polymer electrolytes-improving the electrochemical properties while maintaining

the mechanical integrity and improving the lithium ion transference number without affecting the ionic conductivity.

The effect of adding fillers and a second polymer to improve the ionic conductivity while maintaining the mechanical properties was explored. The ionic conductivity of gel polymer electrolytes is affected by several factors. The various factors which affect ionic conductivity were compared and the factors that have the most pronounced effect were identified.

The effect of reduced ionic coupling, increased lithium ion dissociation and increased chain segmental motion on the ion transporting abilities of the P(VdF-*co*-HFP) GPE and PSSLi gel was systematically studied. It was seen that increased lithium dissociation was the best approach to obtain liquid like conductivity. The ionic conductivity at 30 °C of the P(VdF-*co*-HFP) GPEs increased from 2.9 mS/cm to 9.6 mS/cm, while for the PSSLi system the conductivity improved from 1.4 mS/cm to 2.5 mS/cm. The transference number of the P(VdF-*co*-HFP) GPEs improved from 0.42 to 0.68 leading to increased lithium transport.

Based on the results, it was seen that the mechanism of ion transport in the two systems was very different. The P(VdF-*co*-HFP) GPEs resembled the commercially used liquid electrolytes. Ionic conductivity in these systems was mainly dependent on increasing the lithium ion concentration in the system. However, in the PSSLi gel, it was seen that beyond an optimum concentration of lithium, the ionic conductivity begins to drop. To account for this behaviour,

fundamental studies on the ion transport mechanism of PSSLi based gels was undertaken using NMR and AC impedance. The mechanism by which the fillers and blends affect the ion transport in PSSLi gels was also elucidated. The effect of using high transference number PSSLi on the high rate performance of the lithium ion battery was also examined.

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$$D^{\sigma} = \frac{\sigma_{dc} kT}{Nq^2}, \quad (1)$$

$$2d \sin \theta = n\lambda \quad (2)$$

$$X_c (\%) = \frac{\Delta H_m^{Sample}}{\Delta H_m^*} \times 100 \quad (3)$$

$$\text{Tensile strength} = \frac{\text{Load at break point}}{\text{Original width} \times \text{original thickness}} \quad (4)$$

$$\text{Percentage elongation} = \frac{\text{elongation at break point}}{\text{Initial gauge length}} \times 100 \quad (5)$$

$$\text{Young's modulus} = \frac{\text{Stress}}{\text{Strain}} \quad (6)$$

$$P (\%) = \frac{M_{\text{BuOH}} / \rho_{\text{BuOH}}}{M_{\text{BuOH}} / \rho_{\text{BuOH}} + M_m / \rho_p} \times 100 \quad (7)$$

$$\delta (\%) = \frac{M - M_0}{M_0} \times 100 \quad (8)$$

$$R = \frac{M_{\text{PE}}}{M_{\text{PE, saturated}}} \quad (9)$$

$$\sigma = t / R_b A \quad (10)$$

$$X = G.K \quad (11)$$

$$T^+ = \frac{I_{ss}(\Delta V - I_0 R_0)}{I_0(\Delta V - I_{ss} R_{ss})} \quad (12)$$

$$\sigma = \sum N_i R_i \dot{E}_i \quad (13)$$

List of abbreviations

T _g	Glass transition temperature
TGA	Thermogravimetric analysis
DSC	Differential Scanning Calorimetry
FE-SEM	Field Emission Scanning Electron Microscopy
LSV	Linear Sweep Voltammetry
SIC	Single ion conductor
LiBETI	Lithium bis(perfluoroethanesulfonyl)imide)
LiBOB	Lithium bis(oxalato)borate
PMMA	Poly(methyl methacrylate)
PAA	Poly(acrylic acid)
DBP	Dibutyl phthalate
PP-13-TFSI	<i>N</i> -Methyl- <i>N</i> -propylpiperidinium bis(trifluoromethanesulfonyl)imide
PEGMA	Poly(ethylene glycol) methyl ether methacrylate
PVAc	Poly vinyl acetate
EIS	Electrochemical impedance spectroscopy
DMAc	Di methyl acetamide
LTO	Lithium titanium oxide
SS	Stainless steel
GBL	Gamma-Butyrolactone

1 Chapter 1 Introduction

1.1 Background

In view of the ever increasing demand for energy and the growing concern over global warming, renewable sources of energy and efficient energy storage systems are at the forefront of research [1–5]. Renewable sources of energy such as solar, wind, thermal and geothermal are the need of the day. Along with alternate sources of energy, improved energy storage devices are also critical. The major player in the automobile market is lead acid battery, while nickel cadmium and nickel hydride battery are popular for aerospace applications [6]. Currently lithium ion batteries are used for portable applications like cameras, mobiles and computers. As seen in Fig.1.1, rechargeable lithium ion batteries are lighter, smaller and provide higher energy density when compared to the traditional energy storage systems and therefore offer more potential.

Fig.1.1 Ragone plot of batteries [7]

1.2 Motivation

Lithium ion batteries (LIBs) have been steadily acquiring a large market share of the energy storage needs of the consumer electronics industry. Since the first commercial LIB was introduced by Sony corporation in 1991 [8], there has been a leap in the production of LIBs for powering cell phones, laptops etc. From Fig.1.2, it is seen that hardly any progress has been made in battery sales for hybrid electric vehicles (HEVs). The main reason attributed to this is that the current state of the art cathodes, anodes and electrolytes are not capable of meeting the requirements of HEVs. The estimated market of HEVs is expected to rise steadily every year (Fig.1.3) and hence the market demand for sufficiently high energy/ power density LIBs is also expected to go up. Significant advancements in terms of both energy density, power density, safety, thermal and mechanical stability, life cycle (>5000 cycles), lifetime (about 5 years) and a reasonable cost are necessary to meet the requirements [9].

Fig.1.2 Evolution of LIB sales in consumer and HEV Markets [4]

Fig.1.3 Evolution of HEV Market [4]

There are two major material challenges that limit the application of LIBs for HEV applications. One is the development of high energy and high power density electrodes with fast discharge kinetics and stability [10]. The second challenge is the development of improved electrolytes with high ionic conductivity, transference number, flexibility and good mechanical properties. Conventional liquid electrolytes used in LIBs are a mixture of a lithium salt in a high dielectric carbonate based solvent system, most commonly LiPF_6 in EC:DEC (1:1 w/w) [11].

Though the current liquid electrolytes provide sufficiently high ionic conductivity and relatively stable performance, the lack of shape flexibility is a limiting factor [12]. This prevents batteries from being used for printable and wearable applications. Also as we move towards high power batteries, the containment of large amounts of liquid electrolyte might lead to very large and

heavy batteries and loss of flexibility of design [10]. In order to find large scale application in the future, higher energy density and power density batteries which are flexible and shape effective are needed for meeting the demands caused by miniaturization of electronics [13].

For achieving high energy and high power density, apart from flexibility, the electrolyte must have sufficiently high ionic conductivity (1 mS/cm). The maximum power attainable from a battery is directly linked to the conductivity of the electrolyte system. High ionic conductivity will translate to better ion mobility between the electrodes, improved solid electrolyte interface (SEI) layer formation and improved performance. Also, to improve the power density, battery packs in series or parallel need to be assembled. For efficient packaging of batteries, multiple stacks have to be assembled within one cell to maintain the flexibility and the handleability of the cell. Currently prismatic cells with liquid electrolytes are used for most applications, but liquid electrolytes cannot be used for multiple cell configurations because of their lack of flexibility, mechanical strength and handleability [13]. Therefore, there is a need for developing flexible, high ionic conductivity, thermally and mechanically stable and reliable electrolytes [10].

Another important electrolyte parameter for achieving high energy and power density batteries is the transference number, which determines the fraction of current being carried by the cations and anions [10]. The transference number of the conventional liquid electrolytes is less than 0.4 [11,14], which implies that bulk of the current is still being carried by the anion. At low charge-discharge rates, the low transference number does not significantly affect performance. But

at high current densities, a non-unity transference number leads to severe concentration polarization in the cell [14]. This leads to lack of full utilization of the active materials and severely reduces the battery performance [14]. The maximum current which can be extracted from a cell is dependent on the transference number and therefore for maximum utilization of active materials and working of cell at high current rate, a high transference number is essential [15]. Therefore an electrolyte which has ionic conductivity, high lithium ion transference number, thermal and mechanical stability, flexibility and easy handleability is of prime importance [15].

Compared to liquid and ceramic electrolytes, polymer electrolytes offer several advantages. They are flexible, easy to process, have moderate ionic conductivity and fair mechanical properties. Gel polymer electrolytes (GPEs) are more similar to liquid electrolytes when compared with solid polymer electrolytes (SPEs). They have similar ionic conductivity with the added advantages of improved flexibility and mechanical stability. Ceramic electrolytes are safe and have good mechanical properties, but owing to their lack of flexibility and low ionic conductivity they are not desirable for large scale room temperature applications.

With the emergence of lithium based systems such as lithium air and lithium sulfur batteries, the development of alternate polymer electrolytes with high ionic conductivity, high lithium ion transference number, good flexibility, handleability, mechanical and thermal stability is critical. Hence this thesis focuses on the key challenges highlighted above: (1) development of electrolytes

with high ionic conductivity, high lithium ion transference number and easy handleability for lithium ion batteries; and (2) understanding the mechanism of ion transport in these electrolytes.

1.3 Research objectives and scope

The objectives of this thesis are

- (1) Investigate the effect of polymer composition and morphology on the electrochemical properties of gel polymer electrolytes

Several polymers have been studied as host matrices for preparing gel polymer electrolytes (GPEs). The two main classifications of host polymers are lithiated polymers and non-lithiated polymers. Amongst the non-lithiated polymers, polyvinylidene fluoride (PVdF) and its co-polymer poly (vinylidene fluoride-co-hexafluoropropylene) (P(VdF-co-HFP)) offer several advantages when compared to the other matrices. PVdF has high dielectric constant ($\epsilon \approx 8.4$), which leads to higher dissociation of lithium salts leading to higher conductivity [15–17]. It has good anodic stability due to the presence of strong electron withdrawing fluorine group [15–17]. P(VdF-co-HFP) differs from PVdF owing to the presence of amorphous HFP which will help entrap large amounts of liquid electrolyte, leading to higher ionic conductivity [16,17].

Among the lithiated polymers, poly (4-lithium styrene sulfonic acid) has low glass transition temperature (T_g) and high thermal stability when compared to the commonly reported poly (2-acrylamido-2-methylpropane sulfonic acid) P(AMPS). The lower T_g leads to increased flexibility and the presence of lithium attached to the backbone increases the lithium transference number. The presence

of lithium on the backbone eliminates the need for an external additional source of lithium. The effect of polymer structure and composition on the electrochemical performance was studied using AC impedance spectroscopy and charge discharge property evaluation.

Apart from polymer composition, the performance of the gel polymer electrolyte is strongly dependent on the morphology of the host polymer membrane. The effect of membrane morphology was studied by comparing phase inversion membranes with electrospun membranes. The impact of the different morphologies was studied using various characterizations such as field emission scanning electron microscopy (FE-SEM), thermal evaluation and mechanical property evaluation. The electrochemical properties were characterized using electrochemical impedance spectroscopy (EIS), interface property evaluation, linear sweep voltammetry and galvanostatic charge discharge analysis.

(2) Investigate the effect of fillers and polymer blends on the ionic conductivity and electrochemical performance of gel polymer electrolytes

As previously mentioned, gel polymer electrolytes based on PVdF, P(VdF-co-HFP) and PSSLi offer several promising attributes for lithium ion battery application. The main problem associated with porous gel polymer electrolytes is the loss of mechanical strength after the addition of plasticizer during processing. The ionic conductivity and mechanical strength of GPEs are mutually exclusive. In order to overcome the aforementioned issue, composites/blend GPEs were

prepared using fillers and a polymer blend. Composite formation/blending helps to improve both ion transport properties and mechanical strength of the GPEs.

To study the effect of fillers on the electrochemical and mechanical properties, electrospun gel polymer electrolytes based on P(VdF-*co*-HFP) were prepared using clay, butanedinitrile (BDN), lithium aluminum germanium phosphate (LAGP) as fillers and poly ethylene oxide (PEO) to form a polymer blend. In order to overcome the problem of lowered charge carriers in the PSSLi system, composite/ blend PSSLi gels were prepared using silicon dioxide (SiO₂), butanedinitrile (BDN) as fillers and PEO as the second polymer to improve both electrochemical and mechanical properties. An optimization of the lithium ion concentration to achieve best electrochemical properties was carried out. Several factors such as ion association-dissociation, ionic coupling, polymer chain segmental motion, charge carrier diffusion etc. affect ionic conductivity. The effect of using fillers/ polymer blends to improve the above mentioned factors was investigated by studying their ion transport properties. The factor which has the most pronounced effect on ionic conductivity was determined.

A thorough study of morphology (FE-SEM), thermal properties (TGA and DSC), and mechanical properties was undertaken. The electrochemical properties were studied using EIS, interface property evaluation and electrochemical stability window study (LSV), to understand the mechanism by which the fillers and polymer blends improve the electrochemical properties and mechanical properties of the GPEs.

(3) Fundamental studies on the ion transport mechanism in gel polymer electrolytes

Mechanism of ion transport in polymer electrolytes is complex and less understood. In the lithiated polymers, the mechanism of ion motion is lithium ion hopping between fixed anionic sites. In non-lithiated polymers, the mechanism is similar to liquid electrolytes. The ion motion is predominantly by diffusion, but this diffusion is controlled by several factors as mentioned previously. Hence to design alternate polymer electrolytes which are flexible, good ionic conductors, sufficiently strong and easily processable, a thorough understanding of the extent to which these factors affect the ion transport mechanism is required. The identification of the most critical factors is also necessary.

The focus in this work was towards understanding ion transport mechanism in composite and blend gel polymer electrolytes. Systematic studies were done by comparison of EIS and NMR data. The diffusion coefficient was calculated from ionic conductivity using Nernst-Einstein equation and the diffusion coefficient of the cations and anions were measured using NMR. The diffusion coefficients were compared to study the extent of association or dissociation in the system to understand the effect of filler addition and blending on lithium ion diffusion. In addition the transference number was measured using the DC polarization method and pfg-NMR, and compared to understand the mechanism of improved transference number by composite formation. With these objectives in mind, it is hoped that a clearer understanding of the factors which affect ion mobility in gel

polymer electrolytes can be achieved. This will help in designing of improved gel polymer electrolytes for future applications.

1.4 Thesis organization

This thesis is organized as follows. Chapter 2 briefly introduces the mechanism of lithium ion batteries, followed by a review of solid polymer electrolytes and gel polymer electrolytes, including a review of PVdF, P(VdF-*co*-HFP), PSSLi systems and fundamental studies that have been conducted. Chapter 3 describes the various techniques employed in this thesis including synthesis, characterization and electrochemical studies. Chapter 4 deals with the experimental results for the various systems studied, followed by a cross examination and comparison of the various systems and a detailed discussion in Chapter 5. Chapter 6 presents the conclusions and Chapter 7 provides recommendations for future work.

2 Chapter 2 Literature survey

2.1 Basic Principle of LIBs

The first ever lithium ion primary battery was commercialized in the 1970s [18]. The first commercial secondary rechargeable lithium ion battery was introduced in 1991 [18]. Fig.2.1 shows the schematic representation of a typical LIB. It is a rechargeable electrochemical cell in which the conversion from chemical to electrical energy is reversible. A LIB is composed of three main components; cathode, anode and electrolyte i.e. (i) Li metal oxide (LiCoO_2) cathode, (ii) carbonaceous anode (graphite) and ; (iii) ionically conductive, carbonate based organic electrolyte with Li containing salt such as LiPF_6 .

Fig.2.1 Schematic of a typical lithium ion battery [1]

The two electrodes of the LIB have different chemical potentials, as determined by the chemistry that occurs at each end. When the LIB is charged, lithium ions are driven by external voltage, extracted from the cathode, diffuse through the electrolyte and inserted into the anode (intercalation/lithiation). On discharging, the lithium ions are released (deintercalation/delithiation) by the

anode and follow the reverse route back to the cathode. During this process, electrons flow in the outer circuit giving rise to electrical current.

Goodenough *et al.* [19] pioneered the research on layered metal oxide cathodes while Yazami *et al.* [20] contributed significantly towards introducing graphite as the anode in commercial LIBs. The commercially used cathode materials are 4 V cathode materials and hence electrolytes need to be stable upto 4.5 V vs Li for successful working of the battery. Tarascon *et al.* [21], worked on several combinations of lithium salts in various organic solutions to find the best suited electrolyte. This led to heightened interest in finding suitable organic electrolytes for both LIBs as well as lithium metal batteries [21].

The electrolyte plays a very important part in the functioning of the LIB. It is responsible for ions moving from the cathode to the anode while also preventing electrical shorting. The slightest oxidation of the electrolyte in the electrochemical window of the battery is extremely detrimental to battery performance [21]. The oxidation of the electrolyte leads to unwanted side reactions, which increases the irreversible capacity. This leads to larger volume of electrolyte being needed for construction of the cell, meaning less active material, leading to reduced initial capacity [21]. Although the commercially used liquid electrolyte has high ionic conductivity, good rate capability and stable cycle performance, it has several disadvantages. Firstly the containment of large amount of liquid electrolyte is a problem, because it leads to batteries being very bulky and lacking flexibility. Also as we move towards high energy, high power density and larger batteries, the volume occupied by the electrolyte reduces the specific

energy that can be obtained [15]. Therefore we need bigger batteries to perform the same functions [15]. The usage of liquid electrolyte also restricts the geometry of the fabricated LIBs, because sealing of liquid electrolyte is difficult [15].

Hence it is clear that for future applications in traction, plug in hybrid electric vehicles and electric vehicles, we need to find alternate electrolytes which have a wide electrochemical stability, high transference number, high ionic conductivity, low chemical reactivity, flexibility and printability [15].

2.2 Electrolytes for lithium ion batteries

The basic requirements of an electrolyte for LIBs are; (1) high electrochemical stability window (2) high ionic conductivity and transference number (3) high chemical, thermal and mechanical stability and (4) environmental friendliness [11]. Electrolytes are divided into three categories based on the composition and physical state: Liquid electrolytes, ceramic/inorganic electrolytes and polymer electrolytes. Polymer electrolytes offer several advantages over both liquid and ceramic electrolytes [10]. They are advantageous in terms of low cost, ease of processing, flexibility, high dimensional stability and prevention of dendrite formation [10].

2.3 Polymer electrolytes

A polymer electrolyte must have the following properties to realize practical application [22,23]:

- 1) Adequate ionic conductivity, together with high electronic resistivity

The liquid electrolytes commonly used in LIBs have ionic conductivities in the range of 10 to 1 mS/cm and hence to match the performance of liquid electrolytes, polymer electrolytes need to have conductivities approaching 1 mS/cm at room temperature [23].

2) High cation transference number (cation transference number approaching 1)

Most of the existing systems, whether polymeric, ceramic or liquid, have transference numbers lesser than 0.5, which implies that not more than half the ionic charge is transferred by lithium ions. This implies that ion pairs and anions play a significant role in charge transport. Increase in transference number can reduce the concentration gradient during cycling leading to higher power density [23].

3) Good mechanical properties

Polymer electrolytes should be able to relax elastically when under stress for improved shape versatility [22].

4) Chemical and thermal stability

The polymer electrolyte electrically separates the cathode and the anode and therefore no undesired chemical reactions should happen between the polymer electrolyte and either/both of the electrodes [23].

5) Large electrochemical stability window

The electrochemical stability window of the polymer electrolyte must be such that it does not limit the choice of electrode materials. Ideally the polymer electrolytes should have an electrochemical stability window >5 V.

6) Ease of processing, better shape flexibility and cost effectiveness

The need for lighter and smaller batteries that can be used for high energy density applications necessitates the use of rectangular construction over the cylindrical one [23]. Thin film polymer electrolytes which are cost effective and easy to process on a large scale would be an ideal choice.

There are several classifications of polymer based electrolytes, though broadly all of them are referred to as polymer electrolytes. One of the ways polymer electrolytes can be classified is based on the mechanism for ion mobility in them, as suggested by Wright [24];

- 1) Solvent free salt polymer system or solid polymer electrolytes (SPEs)
- 2) Gel polymer electrolytes (GPE)
- 3) Lithiated single ion systems (SICs)
- 4) SPEs where the ion motion is not coupled to the polymeric chain motion.

The SICs are lithiated polymers, where the anion of the lithium salt is attached to the polymeric backbone. SICs can be SPEs or GPEs based on whether they are plasticized or not.

2.3.1 Solid polymer electrolytes for lithium ion batteries

As the name suggests, these are completely liquid free systems, where ion motion is coupled to the micro-brownian motion of the polymer chain segments above its glass transition temperature (T_g) [24]. Although several matrices have been reported for the preparation of SPEs, PEO remains the most popular choice because of the presence of the oxygen bond which helps the ion motion above the glass transition temperature [25]. In SPEs, both the anions and cations are mobile and coupled to the segmental motion of the polymer [24]. The lithium ion transference numbers of the SPEs are usually very low, in the range of 0.2-0.3 [25]. The absence of liquid provides several advantages like improved safety, convenience of fabrication, flexibility in design, leak proof construction etc. The main disadvantage is that the ionic conductivity of these electrolytes reaches practically required values ($\sim 1\text{mS/cm}$) only above 60°C which represents the melting temperature of PEO. The increased amorphous content at temperatures above the crystalline melting temperature of PEO is responsible for the increased ionic conductivity.

Several research efforts were taken to improve the ambient temperature ionic conductivity of these SPEs. Since the ion mobility in SPEs is by polymer segmental motion, ion transport and conductivity is limited to the amorphous phase of the polymer [15]. Thus low crystallinity structures at room temperature were studied. Graft polymers, block co-polymers and cross linked polymers, where PEO is the main polymer on which structural modifications are made have been studied [15]. Apart from PEO based systems, comb polymers and flexible

polymers like polysiloxanes have also been studied [10,15,24]. Table.2.1. shows the highest reported ionic conductivity of SPEs. The ionic conductivity of the SPEs can be increased by adding more lithium salt, but this leads to the reduction of mechanical strength and transference number due to ion pair formation [25].

A popular approach to improve the ionic conductivity of SPEs is the preparation of polymer composites. Weston and Steele [26] first demonstrated that incorporation of electrochemically inert particulates into the polymer matrix increases both the electrochemical properties and the mechanical properties of the polymer electrolyte [10,26].

Some of the commonly studied fillers are ceramic particles like ZrO_2 , Al_2O_3 , TiO_2 , CuO , MgO , and SiO_2 which have been shown to be effective in improving the ionic conductivity of SPEs [15,17,24,27,28]. Another approach to improve ionic conductivity is the addition of ionic liquids, which helps to weaken the interaction between the polymer chain and lithium ions [10,29]. Block copolymerization, random co-polymerization and blending have also been used to improve the ionic conductivity and transference number, by lowering the transport of the corresponding anion [10,30,31]. Incorporation of plasticizers like ethylene carbonate (EC), propylene carbonate (PC), diethylene carbonate (DEC), succinonitrile (SCN), citric acid etc have been reported to improve the performance of SPEs [10,15,32,33]. Although these studies have shown improvement in ionic conductivity of solid polymer composite electrolytes, the conductivity values still remains too low for practical application at ambient temperatures [10].

Table.2.1.Ionic conductivity of SPEs at ambient conditions

Polymer matrix	Lithium salt/additive/Blend	Ionic conductivity at 30 °C (mS/cm)	References
PEO	LiBETi [O/Li=16]	0.2	[34]
PEO	LiTFSI [O/Li=10]	0.063	[35]
PEO	LiClO ₄ [O/Li=8]	0.0032	[31]
PEO	LiBOB [O/Li=20]	0.0063	[36]
PEO	PMMA/ LiBOB [O/Li=3]	0.012	[30]
PEO	PAA/PMMA/LiOH (0.3)/LiClO ₄	0.984	[31]
PEO	SCN	0.2511	[34]
PEO	CuO (5%)/DBP (10%)/LiCF ₃ SO ₃	0.264	[27]
PEO	LiTFSi [O/Li=9]/15% Al ₂ O ₃ /50% (7.5EC:2.5PC)	0.012	[28]
PEO	[LiCF ₃ SO ₃ /PEO/Epoxidized natural rubber 7:3)][O/Li=3]	0.014	[37]
PEO	LiTFSI/PP-13TFSI	0.00893	[29]
(PS-block- PPEGMA ₂)	LiBETi [O/Li=0.03]	0.0025	[38]

2.3.2 Gel polymer electrolytes for lithium ion batteries

In gel polymer electrolytes, large amounts of plasticizers are incorporated into a polymer matrix to form a stable gel [23,39]. The conduction mechanism in GPEs is very similar to conventional liquid electrolytes, but they have improved safety

and shape flexibility over the liquid electrolytes [10]. Gels possess both cohesive properties of solids and diffusive property of liquids [16]. The addition of plasticizers to the polymer to form the GPE serves two purposes; it helps in softening the polymer to improve the segmental motion of the polymeric chain and it also serves as a solvation medium for the lithium salt, to ensure higher diffusion of lithium ions through the electrolyte. Though the first report on gel polymer electrolytes was in 1975 by Feuillade *et al.* [40], it took about 20 years for intensive research to begin on GPEs [24].

The first commercial battery that used a gel electrolyte was introduced in 1991 by Sony and it had a reported ionic conductivity of ~ 3 mS/cm at room temperature [24]. Since then several polymeric hosts have been studied for preparing GPEs. Some of the commonly studied polymers are Poly(acrylonitrile) (PAN) [41], Poly (methylmethacrylate) (PMMA) [42], Poly(ethylene oxide) (PEO) [43], Poly(vinylidene fluoride) (PVdF) [44] and its co-polymer P(VdF-*co*-HFP) [45]. Each of these hosts has its own advantages and disadvantages.

The GPEs have an ionic conductivity in the range of 0.1 to 1 mS/cm at room temperature, which is almost as much as the conventionally used liquid electrolytes. This makes them closer to practical application. The mechanism of ion conduction in GPEs is through the gel phase, thus higher the content of gel phase, the faster is the ion mobility. One of the pre-requisites for high ionic conductivity in GPEs is that the polymeric membrane should be highly porous, so that the uptake of the plasticizer and subsequent gelling is higher, thus increasing the fraction of gel phase [24].

Amongst the various polymers that have been investigated as host matrices for GPEs, PVdF and its co-polymer P(VdF-*co*-HFP) have generated great interest due to their appealing properties [10,15–17,23]. PVdF has high dielectric constant ($\epsilon \approx 8.4$), which leads to higher dissociation of lithium salts leading to higher conductivity [15–17]. It is also anodically stable because of the presence of the strong electron withdrawing group [15–17]. P(VdF-*co*-HFP) scores over PVdF because of the presence of the amorphous HFP part which will help entrap large amounts of liquid electrolyte, leading to higher ionic conductivity [16,17].

2.3.2.1 PAN based GPEs

PAN based GPEs offer several advantages. The $\text{--C}\equiv\text{N}$ groups in PAN interact with --C=O groups of the organic solvents used to gel them and with lithium ions leading to better compatibility [46,47]. PAN is also reported to decrease dendrite growth [48]. It was assumed that PAN is inert and only provides mechanical stability [46,47]. Watanabe *et al.* [49] first reported GPEs based on PAN. They reported an ionic conductivity of 0.00758 mS/cm at room temperature with 40% EC [49,50]. Abraham *et al.* [51] reported a conductivity of 1 mS/cm at room temperature. But this increase in conductivity was accompanied by loss of mechanical strength [51]. PAN based GPEs have transference number between 0.3-0.5 [51].

Croce *et al.* [52] studied the performance of PAN based GPEs with varying lithium salts. It was seen that although high ionic conductivity and high transference number were achieved, passivation of lithium electrode takes place making it unsafe for use in lithium metal batteries [52]. To further improve the

ionic conductivity of PAN based GPEs, Slane *et al.* [53] studied the effect of zeolite addition of the properties of PAN. It was seen that the addition of zeolite prevented the crystallization of the PAN matrix and ionic conductivities greater than 1 mS/cm were achieved [53].

Table.2.2.Ionic conductivity of PAN based GPEs at ambient conditions

Polymer	Lithium salt/ Plasticizer	Ionic conductivity at 30 ° C (mS/cm)	References
PAN	LiClO ₄ /EC (12.7/36.6)	0.0214	[49,50]
PAN	LiClO ₄ /EC/PC (8/38/33)	1	[51]
PAN	LiAsF ₆ /EC/PC/MEOX (33.8/27.7/11.5/6)	2.98	[41]
PAN	LiClO ₄ /SCN (92.5% 1M)	5-6	[56]
PAN	LiTFSI (92.5% 1M)	7	[56]
PAN	EC/PC/LiCF ₃ So ₃ (42/32/7)	1	[57]
PAN	EC/PC/LiClO ₄ (40/40/8)	2	[58]

Another approach to improve the ionic conductivity of PAN based GPEs was studied by Peramunage *et al.* [41], by the addition of ternary solvents butylene carbonate (BC) or 3-methyl-2-oxazolidinone (MeoX) to the mixture of EC and PC [41]. Lithium NMR studies on PAN based GPEs, showed that the initial assumption that PAN was inactive was not valid and that PAN impeded ionic motion [54]. Despite all the advantages of PAN, it has a poor interface with lithium metal which severely restricts its application. PAN is also reported to experience liquid extraction from the gel during storage which severely affects its

dimensional and mechanical stability [55]. The ionic conductivities of reported GPEs based on PAN are tabulated in Table.2.2

2.3.2.2 PMMA based GPEs

PMMA was first studied as a host for preparing plasticized GPEs in 1985 by Ijima *et al.* [59]. It was seen that high conductivity was obtained for lower percentages of PMMA [59]. PMMA is a high molecular weight polymer which acts as a stiffener, increasing the viscosity of the gel, thereby maintaining almost liquid like conductivity [60]. But increasing the polymer concentration to about 30-35 wt.% resulted in conductivity reducing by two orders of magnitude [60]. This reduction was attributed to interactions between the polymer and the solvents at higher polymer concentration. The transference number of PMMA based electrolytes were found to be lower than those based on PAN [16,60]. Appetechi *et al.* [61] compared the performance of PAN and PMMA based GPEs and found that although their conductivity was similar, PMMA has better stability towards lithium [61]. However it was seen that some lithium is consistently lost during cycling, which shows that PMMA based electrolytes are not suitable for lithium metal batteries [61]. Similar to other GPEs, composite and blend GPEs based on PMMA have been studied [62–66]. The highest reported ionic conductivities of PMMA based GPEs are tabulated in Table.2.3.

Table.2.3.Ionic conductivities of PMMA based GPEs at ambient conditions

Polymer	Lithium salt/plasticizer/blend	Ionic conductivity at 30 °C (mS/cm)	References
MG30(natural rubber grafted with 30% MMA)	LiTFSi/PC(15/76)	4	[62]
PMMA	PVAc/LiClO ₄ /PC(6.5/8/67)	0.0415	[63]
PMMA	PVAc/LiClO ₄ (25/10)	0.00167	[64]
PMMA	P(VdF- <i>co</i> -HFP)(1:2)/1M LiPF ₆ in EC:DMC	2	[65]
PMMA-b-PEO	PVdF(0.5)/1MLiClO ₄ in EC:PC	2.79	[66]

2.3.2.3 PVdF and P(VdF-*co*-HFP) based GPEs

PVdF is a semi crystalline polymer with crystallinity between 40-60%. It exhibits 4 polymorphs with different properties [67,68]. Amongst the polymorphs, the β form is polar and thus the most interesting [67,68]. PVdF has several advantages which makes it a promising material as a host polymer for the preparation of GPEs. The presence of electron withdrawing functional group ($-C-F$) is expected to make the material very stable towards lithium [23,39,69]. Also PVdF has a high dielectric constant ($\epsilon = 8.4$) which helps in improving the ion dissociation in the GPE [16]. Blending of PVdF with HFP to form the co-polymer effectively reduces the crystallinity due to the presence of the amorphous HFP [70].

The first study of PVdF was undertaken by Watanabe *et al.* [71] in 1981. It was seen that PVdF can form homogenous stable films when activated with a mixture of lithium salt and plasticizers in proper proportions [71]. A significant breakthrough that made it possible for GPEs to become commercial was made by Gozdz *et al.* [72] and Tarascon *et al.* [73]. Before this, GPEs were made by dissolving a polymer matrix into a mixture of low boiling solvent and a Li salt and casting this mixture [23]. This usually resulted in mechanically unstable, but high ionic conductivity GPE [16,23]. The low mechanical strength of these GPEs required either physical or chemical hardening treatment before use. Also this process of preparing GPEs needed a completely moisture free environment because of the presence of the hygroscopic lithium salt [16,23,73].

To overcome these shortcomings, Gozdz *et al.* [73] chose P(VdF-co-HFP) because of the presence of amorphous HFP which is capable of retaining large amounts of liquid electrolyte. The presence of crystalline PVdF in the co-polymer provides sufficient mechanical stability, thus eliminating the need of a crosslinking step [73]. To overcome the problem of processing the GPE in moisture free environment, they used a lithium free plasticizer initially and substituted it with liquid electrolyte containing lithium in the last stage of assembly [16,23,73]. The ionic conductivity of such GPEs is thus mainly dependent on the extent of electrolyte uptake, which in turn is highly dependent on the porosity of the GPE. Thus preparing highly porous polymeric membranes became the focus of research in GPEs [10,16,23,39,74]. Bellcore's (Now,

Telcordia) process otherwise called phase inversion method is one of the established methods to make porous polymeric membranes [73].

PVdF and P(VdF-*co*-HFP) membranes prepared by phase inversion method have been reported [44,45,66,75–79]. The ionic conductivities of these GPEs exceed the conductivities of the membranes prepared by traditional solution casting method. These GPEs had conductivities approaching of 1 mS/cm at ambient temperature [44,45,66,75–77]. However, with increasing porosity, mechanical strength of the GPE tends to deteriorate. To improve the mechanical strength and integrity of these GPEs, the addition of fillers to prepare polymer composites was explored [79–82]. The addition of these fillers led to improvement of both ionic conductivity and mechanical strength [16,17]. The ionic conductivity of these composite GPEs were in the range of 1.5 mS/cm [79–82].

Another method to improve the porosity of GPEs is to use electrospun membranes as the host matrix for making GPEs. Electrospinning is a method used to achieve highly porous membranes. GPEs based on electrospun PVdF and P(VdF-*co*-HFP) have been reported for LIB application [55,74,83–87]. However, similar to membranes prepared by phase inversion, electrospun membranes also suffer from poor mechanical strength. Preparation of electrospun composite GPEs is an approach to improve the mechanical stability and electrochemical properties of the GPE. The addition of fillers into the electrospun membranes helps improve the ionic conductivity and interfacial stability of the GPE [87–90].

Although PVdF and P(VdF-*co*-HFP) possess many advantages, there are a few reports reporting that they have poor interfacial properties because of the presence of strong electron withdrawing groups [10,15–17,23]. Blending of PVdF and P(VdF-*co*-HFP) with other polymers is an approach to circumvent this issue [55,75,78,91]. The ionic conductivity of such GPEs activated with LiPF₆ in EC:DEC, based on electrospun membranes are in the range of 1-3 mS/cm [10,15–17].

2.3.2.3.1 Current status and issues in P(VdF-*co*-HFP) based systems

The ionic conductivity of GPEs is influenced by the amount of gel phase, therefore increasing the amount of gel phase was the primary concern of researchers working on GPEs [55,74,83–87]. The increasing gel phase which leads to increased ionic conductivity results in reduction of mechanical stability because of lowered crystallinity. Although the use of fillers has been able to improve the mechanical properties, there is no clear understanding of the rationale behind the selection of appropriate fillers. Also the role of fillers on the transference number has not been studied. The key challenges that need to be resolved in the P(VdF-*co*-HFP) based GPEs systems are (1) designing a selection criteria for the fillers and blends by a clearer understanding of the mechanisms involved, (2) obtaining information about the effect of such modifications on the transference number and (3) balancing the ionic conductivity with the mechanical stability. Some of the highest reported values of GPEs based on PVdF co-polymer are tabulated in Table.2.4.

Table.2.4.Ionic conductivities of PVdF and P(VdF-*co*-HFP) based GPEs at ambient conditions

Polymer	Lithium salt/plasticizer/blend	Method	Ionic conductivity at 30 ° C (mS/cm)	Reference
P(VdF- <i>co</i> -HFP)	1M LiPF ₆ in EC:DEC(1:1 w:w)	Solution casting	1	[92]
P(VdF- <i>co</i> -HFP)	1 M LiCO ₄ in EC:PC(1:1)	Phase inversion	1.5	[93]
P(VdF- <i>co</i> -HFP)	1M LiBF ₄ in EC:GBL (1:3 w/w)	Phase inversion	3.5	[94]
P(VdF- <i>co</i> -HFP)	1M LiPF ₆ in EC:DEC(1:1)	Phase inversion	1.2	[95]
P(VdF- <i>co</i> -HFP)	0.5M LITFSI in BMITFSI	Electrospinning	2.3	[96]
P(VdF- <i>co</i> -HFP)	1M LiPF ₆ in EC:DMC (1:1)	Electrospinning	5	[85]
P(VdF- <i>co</i> -HFP)	1M LiPF ₆ in EC:DMC (1:1)/SiO ₂	Phase inversion	3.1	[45]
P(VdF- <i>co</i> -HFP)	1 M LiClO ₄ in EC:DEC(1:1)/LiAlO ₂ /PVA	Phase inversion	8.1	[97]
P(VdF- <i>co</i> -HFP)	1 M LiClO ₄ in EC:DEC(1:1)/ZrO ₂ /PVA	Phase inversion	11	[98]
P(VdF- <i>co</i> -HFP)	1M LiPF ₆ in EC:EMC(1:3)/PAN	Electrospinning	6.7	[99]

Similar to efforts on other host polymers, polymeric blends and composites GPEs have been studied for P(VdF-*co*-HFP) [55,67,75,78–82,91]. Although higher ionic conductivity was achieved for these composites, there is still scope for improvement. The highest reported conductivity is 2.8 mS/cm, while the ionic conductivity of liquid electrolyte is 7 mS/cm. The highest reported transference number of these systems is 0.42. Also as mentioned previously, mechanical properties and electrochemical properties are mutually exclusive and therefore a balance between the two opposing factors needs to be identified.

2.4 Lithiated polymers

Although almost liquid like conductivity has been obtained for GPEs based on PVdF and P(VdF-*co*-HFP) [55,67,75,78–82,91], the lithium ion transference number still ranges between 0.4 to 0.6 [55,67,75,78–82,91]. This implies that a large amount of the current is still being carried by the anions. Although this does not significantly affect the battery performance, it was seen through simulation, that for electrolytes with non-unity transference number, large concentration gradients are established in the cell [14]. Because of this concentration gradient, very little lithium is able to reach the back of the porous electrode [14]. After initial insertion, no more electrolyte is able to diffuse into the electrode [14]. This leads to lack of full utilization of the active material at high discharge rates [14].

To achieve a polymer electrolyte with unity transference number, the anion of the lithium salt has to be immobilized by attaching it to the backbone of the polymer [14,100]. By doing this, it is clearly understood that ionic conductivity will be significantly reduced, because of the number of mobile ions

is now reduced by more than 50% [14,100]. The mechanism of ion motion in such systems resembles that of SPEs and hence the ionic conductivities also resemble SPEs rather than GPEs. Similar to SPEs, plasticizing the lithiated SIC to improve its conductivity has been explored [101–105]. Upon plasticizing, lithiated GPEs are obtained. The ionic conductivity of these plasticized lithiated SICs are generally lower than non-lithiated GPEs, however they offer several advantages [24].

In lithiated SICs, the spatial anion distribution is uniform, which prevents concentration gradients which gives rise to polarization in the cell [24]. Other advantages are lower joule heating per unit of current, steadier control over cell temperature and reduced possibility of thermal runaway [24]. Based on simulation it is seen that a cell with unity transference number shows a high current density without capacity loss at high discharge rates [14]. However, it is necessary that these systems have ionic conductivity at least 80% of that of the previously mentioned systems to be practically feasible and therefore improvement in ion transport properties is necessary [14,100]. The highest reported value for the lithiated GPE is in the order of 0.1 mS/cm at 30 °C.

2.4.1 Current status and issues in lithiated gel polymer electrolytes

The lithiated SICs have been studied for application in LIBs from the early 90s, but owing to their lower ionic conductivity, not been successful. Lithiated SICs based on Poly(2-acrylamido-2-methyl-propane-1-sulphonic acid), PAMPS has been studied extensively [103,104,106,107]. It was seen that by adding high dielectric constant plasticizers, the ionic conductivity can be improved by

improving the dissociation of lithium ions [106]. Watanabe *et al.* [102,108]; studied the effect of using bulky anions which have electron withdrawing groups attached to the point of contact of the anionic moiety with the polymeric chain [102,108]. It was seen that by plasticizing these systems, an ionic conductivity of 0.1 mS/cm can be achieved at room temperature [102,108].

Another approach that was studied to improve the ionic conductivity of these lithiated SICs was copolymerizing the lithiated SIC with another block, which acts a spacer separating the lithium ions from each other [103,104,109–111]. Another approach that was studied, was the use of ceramic particles to form composites to improve the ionic conductivity of PAMPS based SICs [104,111]. These lithiated SICs showed ionic conductivities in the range of 0.001-0.01 mS/cm at ambient condition, ruling out their practical application. The addition of ceramic fillers to these lithiated SICs improved the conductivity to 0.05 mS/cm at ambient conditions [103,104,111]. It was also seen that increasing the concentration of the polymer in the gel leads to a decrease in ionic conductivity, due to repulsion between the lithium ions [103,104,111]. Thus achieving a balance between the number of charge carriers and the mechanical stability of the gel is of importance.

Recently, Cai *et al.* [112] and Maier *et al.* [113] have successfully demonstrated the preparation of SIC gels based on ion exchange membranes, having ambient temperature conductivity in the range of 0.1mS/cm. But their mechanical strength needs further improvement. Electrospinning of PAMPS and plasticizing it similar to GPEs was also explored [114]. Crosslinking or structural

modification by means of grafting the lithiated SIC to a stronger polymer matrix can be explored to improve the performance. Attaching the mobile cation to a bulkier fixed anionic site is another approach to improve the ionic conductivity, as this might result in faster diffusion of Li-ions [101].

The glass transition temperature of PAMPS is 190 °C. PSSLi offers several advantages over PAMPS. PSSLi has a glass transition temperature of 80 °C, and the presence of the electron withdrawing benzene ring can help faster lithium ion dissociation. The higher chain flexibility of PSSLi will also improve the lithium ion diffusion rate. Till now, there has been only few reports on PSSLi and it is seen that PSSLi is a good candidate for lithium battery application [101,115]. However, an improvement in ionic conductivity is necessary for practical application. Further work is required to synthesize and characterize SIC gels with good mechanical stability and high ionic conductivity and apply them as polymer electrolytes in LIB.

2.5 Polymer membranes for battery application

The performance of polymer electrolytes in lithium ion batteries is significantly dependent on the porosity and the pore size [24]. Membranes prepared by solution casting [71], phase inversion [44,45,66,75–79], plasticizer extraction [116] and electrospinning, [85,99,117,118] have been used as host matrices to prepare GPEs. The membranes prepared by electrospinning serve as good host matrices for preparing GPEs, because the interlaying of fibers results in high porosity (> 80%), with pores of micron-submicron diameter. A highly porous structure leads to high surface area, which leads to high electrolyte uptake, easier transportation

of ions and high ionic conductivity. There are several reports on the use of electrospinning to prepare various polymer membranes for application as polymer electrolytes [83,85–87,96,118–143].

2.6 Electrospinning

The first patent on electrospinning was filed in 1934 by Forhmals [144]. Since the 1980s, interest in electrospinning has grown because of its ability to produce large scale nanofibers [145]. Electrospinning is a simple and efficient method to prepare polymer membranes with fully interconnected pore structure [86,87]. A typical laboratory setup of electrospinning is shown in Fig.2.2. It consists of a nozzle, a high voltage power supply, a holder for the polymer solution, and a target for collecting the fibers. A polymer solution is first prepared by choosing appropriate solvents. The polymer solution is then fed into the holder and one end of the high voltage source is connected to the nozzle through which the polymer solution flows out. The other end of the high voltage source is connected to the collector, therefore an electric field is applied between the polymer solution and the grounded collector.

The application of the electric field induces charge on the polymeric jet [130,144,145]. There are now two forces which act on the polymer surface: surface tension of the polymeric droplet and the applied electric field [130,145]. As the intensity of the field increases, the polymer solution begins to stretch to form the Taylor cone [130,145]. With further increase in applied electric field, the electric force overpowers the surface tension and the polymer solution begins to flow [130,145]. The jet undergoes elongation and a bending instability due to the

interaction between the polymeric jet and the external electric field, which leads to thinning of the jet [137]. During this course, the solvent slowly evaporates leading to a dry polymeric film, depositing on the collector [130,137,145].

The parameters affecting electrospinning of polymer solutions are classified into three categories: system and solution, process and ambient [130,137,145]. System and solution parameters are the molecular weight and molecular weight distribution of the polymer, solution concentration, viscosity, electrical and thermal conductivity. Process parameters are the applied voltage, flow rate, gap between the needle and target, type of collector, and its speed. Ambient parameters include temperature, humidity and air velocity [130,137,145].

Amongst the various parameters that affect electrospinning, solution parameters have the most significant influence on the electrospinning process and electrospun fiber morphology [130,137]. It was seen that the solution concentration and viscosity plays an important role in the fiber diameter of the electrospun membrane [130,137,145]. The solution concentration is largely dependent on the molecular weight of the polymer. It was seen that with increasing solution concentration, fibers with larger diameter are formed [130,145–147]. It was also seen that with increasing solution concentration, uniform bead free morphology was obtained [148].

Another factor which contributes to fibers with larger diameter is the applied voltage. The higher the applied voltage, the more is the polymeric

solution at the tip and therefore the larger the fiber diameter [149]. The solvent also plays an important role on the fiber diameter. It was seen that with increasing dielectric constant of the solvent, larger fibers are formed [150]. It is generally known, that the higher the flow rate, the larger is the fiber diameter, but using a very high flow rate results in severe beading because the fibers dry before reaching the collector [151,152].

Fig.2.2 Schematic of typical laboratory type electrospinning setup

The distance between needle tip to collector is also important in determining whether the fibers have beads or not. There is an ideal distance for every system, which is based on all the above said parameters, any distance shorter or longer than the ideal distance leads to beading [153]. Collectors with various geometries have been studied: parallel plates, rotating drums, flat plate,

frame collectors etc [130,137,145]. The selection of the collector is based on the intended application of the final electrospun fiber.

The ambient parameters have also been studied. It was generally seen that with increasing temperature, there is a decrease in viscosity and this leads to fibers with smaller diameter [154]. It was seen that several parameters affect electrospinning and thus a careful control over the parameters is essential to achieve the final desired morphology, fiber diameter and size. Selection of the correct solvent system, operating parameters and monitoring the environmental conditions is very critical to achieve the desired properties in the final membrane intended for application as GPE in lithium ion batteries.

2.7 Fundamental studies on ion transport mechanism

The high sensitivity of lithium metal to the atmosphere demands that the lithium battery be sealed for all charge/ discharge processes. This makes it difficult to study the actual processes taking place in a working battery. Also for polymer electrolytes interactions exist not only between the ions but also between the cation and the polymer and the anion and the polymer. These interactions are fundamentally very different from each other [155]. Also in gel polymer electrolytes, the mechanism of ion motion not only depends on the diffusion of lithium salts; complexation of anions and cations with the polymer lead to relaxation of the polymeric chain also being involved.

Ionic conductivity is the most common parameter that is studied to judge the performance of an electrolyte, but conductivity provides only a limited insight

into the transport mechanism [155,156]. Ionic conductivity measures the movement of just the free ions, but ion pairs are also mobile in polymer electrolytes [155–157]. Also in highly viscous media such as gels, even without the presence of ion pairs, the anions have significant effect on the motion of the cations [156]. Several techniques like pulsed field gradient NMR (pfg-NMR) [158–161], dielectric measurements [43,162], concentration and temperature dependent conductivity [54,105,163,164], DC polarization [88,155,156,165–167], EIS for electrode-electrolyte interface study [155,156] have been used to study the ion transport mechanism of ion motion in polymer electrolytes.

Evans and Vincent [168] suggested the DC polarization technique for the measurement of transference number. But it was found that this measurement is valid only for ideal solid electrolytes or very dilute solutions. Another method to study the transference number was introduced by Ma *et al.* [169]. However owing to gel polymer electrolytes following the VTF fitting rather than the linear Arrhenius fit for ideal binary solutions, a more appropriate measurement of the transference number can be given by pulsed field gradient NMR [88,155,156,165–167] and also stimulated echo and spin echo sequence [170,171].

Saito *et al.* [159,160,171–173] used the pulsed field gradient NMR technique to understand the extent of ion dissociation and its effect on ion transport. It is seen that neither conductivity nor NMR can provide complete information about the mechanism and hence both the techniques are important and a comparison is essential to fully elucidate the mechanism.

Haijin *et al.* [157] used the Nernst-Einstein equation to extract the diffusion coefficient of the diffusive species from the measured ionic conductivity.

According to the Nernst-Einstein equation,

$$D^{\sigma} = \frac{\sigma_{dc} k T}{N q^2}, \quad (1)$$

where $k = 1.3806505 \times 10^{-23}$ [J K⁻¹] is the Boltzmann constant, T [K] is the absolute temperature. N is the particle density of the charge carriers and q [C] is the charge of the ions [157]. A comparison of the diffusion coefficients from the measured conductivity and NMR would give a clearer picture about the ion association especially for the lithiated systems. In lithiated systems, since the ion conduction mechanism is hopping solely by the cations, the degree of dissociation is very critical.

The effect of addition of fillers and preparation of composites was studied by Saikia *et al.* [174]. It was seen that the effect of the filler on impeding the anionic motion is different for different fillers and the diffusivity measured by ⁷Li NMR is affected by the nature of the polymer, lithium salt, plasticizer and the added fillers.

2.8 Challenges, Gap Analysis and Motivation

Although numerous studies have been dedicated to understanding polymer electrolytes, they still remain a huge limiting factor in the performance and large scale high power application of lithium ion battery. The number of parameters

involved in developing and understanding a polymer electrolyte are many and thus it makes it very difficult to fine tune the performance. It is seen that the nature of the polymer matrix, the preparation method, the type and concentration of lithium salt, the dielectric properties of the solvent, the composition and the nature of the additives significantly affect the properties of the final polymer electrolyte.

Firstly, it is important to achieve a high conductivity, mechanically stable electrolyte using proper fillers (clay, LAGP) which not only decrease the crystallinity of the system, but also improve the mechanical stability, form stable SEI layer, increase the lithium ion concentration and reduce ionic coupling whilst improving the lithium ion transference number. This will ensure a low resistivity, high conducting, mechanically and thermally stable polymer electrolyte that will improve the capacity and performance of the battery.

Also materials with intrinsic high lithium ion transference number like (PSSLi) can ensure better performance at high current densities with no concentration polarization. However, the ionic conductivities of such systems have to be significantly improved by understanding their ion transport mechanism. A careful tuning of parameters to achieve the best performing polymer electrolyte is needed for the development of safer lithium ion batteries with long cycle life, high energy density and good stability.

Thus to summarize, the effect of polymer composition and morphology will be studied to identify the most promising polymer matrices for further

evaluation. The effect of adding fillers and other polymers to prepare composite and blend GPEs will be studied. The mechanism by which the fillers affect ion transport and mechanical properties will be examined. A thorough understanding of the various aspects that have an effect on the electrochemical properties will be obtained. The ionic conductivity of unity lithium transference number systems based on PSSLi will be improved by using the same approaches as the GPEs. A fundamental understanding of the parameters that affect lithium diffusion and transference will be obtained by using electrochemical and spectroscopic techniques.

3 Chapter 3 Materials and methods

3.1 Materials

The various materials used in the experiments for this thesis work are as follows. P(VdF-*co*-HFP), Kynar Flex 2801 ($M_w = 4.77 \times 10^5$, VdF/HFP ratio: 88/12, Elf Atochem), PVdF (M_w : 53,4000, Sigma Aldrich), PEO (M_v : 100,000 Sigma Aldrich), Acetone (HPLC grade, Aldrich), *N,N*-dimethyl acetamide (DMAc) (HPLC grade, Aldrich), Poly (4-styrene sulfonic acid) (M_w 75,000, Sigma Aldrich), Lithium hydroxide monohydrate ($\text{LiOH} \cdot \text{H}_2\text{O}$, Sigma Aldrich), Tetrahydrofuran (anhydrous, $\geq 99.9\%$, Aldrich), DMSO (anhydrous, $\geq 99.9\%$, Aldrich), Nanomer 1.28 E natural Wyoming montmorillonite/smectite clay (Hydrated sodium calcium aluminum magnesium silicate hydroxide) (Nanocor, Aldrich), BDN (99% purity, Aldrich, $M_w = 80.09$), $\text{CH}_3\text{CO}_2\text{Li} \cdot 2\text{H}_2\text{O}$ (99 %, Alfa Aesar), $\text{AlN}_3\text{O}_9 \cdot 9\text{H}_2\text{O}$ (98 %, GCE Chemicals), P_2O_5 (95%, Fisher Scientific), $\text{C}_2\text{H}_4\text{O}_2$ (99.5 %, Fisher Scientific), $\text{Ge}(\text{CH}_3\text{O})_4$ (95%, Sigma Aldrich), $\text{C}_6\text{H}_8\text{O}_7$ (99.5 %, GCE Chemicals), Li_2CO_3 (Alfa Aesar), Al_2O_3 (Aldrich, particle size $< 10\mu$), GeO_2 (Alfa Aesar), $\text{NH}_4\text{H}_2\text{PO}_4$ (Acros organics), $\text{C}_2\text{H}_6\text{O}_2$ (99.5 %, Merck), Tetraethyl orthosilicate (reagent grade, 98%, Sigma-Aldrich), Potassium peroxodisulfate (puriss. p.a., ACS reagent, $\geq 99.0\%$, Sigma Aldrich) and SiO_2 ($< 9\mu$ microns, Aldrich).

3.2 Synthesis

In this section, synthesis methods of various materials studied in this thesis are discussed in detail.

3.2.1 Preparation of membranes by phase inversion

Phase inversion is one of the commonly reported methods to prepare porous membranes [44,45,66,75–79]. The method used here was similar to that reported in literature [45,66,75–79]. A uniform solution of polymer in Acetone/DMAc (7:3, w/w) was prepared by magnetic stirring for 24 h at room temperature. The polymer/solvent (w/w) ratios for all the final solutions were 16 wt.% solid content. The solution was degassed to remove air bubbles before casting into the glass mould. Porous membranes were prepared by two step wet non-solvent phase inversion process.

The casting procedure was an improvised doctor blade technique in which a clean glass rod was used to spread the solution to form a uniform film. Sufficient amount of the free flowing polymer solution was poured onto the glass mould and the glass rod was run over it at a uniform speed. The cast film was kept at room temperature for 2 min for controlled solvent pre-evaporation. Then it was immersed in a coagulation bath filled with deionized water, for 2 h for phase inversion to generate pores. The resultant free standing membrane was vacuum dried at 60 °C for 12 h to remove the traces of solvent. The dried membranes were then transferred to a dry box at 30 °C (H₂O level <20 ppm).

3.2.2 Preparation of membranes by electrospinning

A uniform solution of the polymers in a mixed solvent of Acetone/DMAc (7:3, w/w) was prepared by magnetic stirring for 24 h at room temperature. Polymer/solvent (w/w) ratios for all the final solutions were kept at 16 wt.% solid content. The resulting solution was degassed for 15 min to get bubble free clear

solution. The solution was fed to the steel needle using a syringe infusion/withdrawal pump (KD Scientific, Model-210). The tip of the needle was connected with high voltage source and the solution was electrospun. The essential electrospinning parameters were as follows: applied voltage 16-20 kV (depends on the viscosity), working distance from collector to tip of the spinneret ~20 cm, bore size of the needle 0.6 mm, solution feed rate 0.2 ml min^{-1} and collector drum rotation speed 150 rpm.

The as-spun fibers in the form of free standing non-woven membranes of average thickness ~150 μm with sufficient mechanical strength were collected on a grounded, aluminum drum wrapped with a thin aluminum foil, rotating at specified speed. Further, the membranes were dried at room temperature on the drum for 6 h to prevent the shrinking of fibers and then removed from the collection drum. Final drying of the membranes was carried out in a vacuum oven at 60°C for 12 h to remove any traces of solvent. The dried membranes were transferred to a dry box at 25°C (H_2O level $< 20 \text{ ppm}$).

3.2.3 Preparation of P(VdF-co-HFP)-clay composite membranes by electrospinning

For the preparation of the composite, Di-tallow dimethylamine (quaternary amine) treated Nanomer 1.28 E natural Wyoming montmorillonite/smectite (Hydrated Sodium Calcium Aluminium Magnesium Silicate Hydroxide) (Nanocor) clay was selected, because it is relatively inexpensive, easily available and has good intercalation capacity. The clay is hydrophilic and inorganic in nature, while the polymer is hydrophobic and organic. Therefore before clay is

dispersed in the polymer, a surface modification of clay is necessary to make it organophilic. This conversion requires ion exchange of hydrated inorganic gallery cations on the surface of clay with cationic organic surfactants such as alkyl amines. The clay studied here has been treated with quaternary amines.

For the preparation of exfoliated clay composite, first clay was dispersed uniformly in DMAc (10wt.%). Clay dispersion was taken in an air tight glass container and subjected to ultra-sonication for 48 h at room temperature. This resulted in the clay particles breaking into very fine size, and forming a uniform dispersion in DMAc.

For preparing the P(VdF-*co*-HFP)-clay homogeneous composite solution, required amount of clay dispersion was added to the P(VdF-*co*-HFP) solution to achieve the desired weight ratio of P(VdF-*co*-HFP) to clay (0-2 wt.%) and mechanically stirred for 24 h in a round bottom flask fitted with double jacketed spiral condenser. All clay percentages were normalized with respect to the weight of P(VdF-*co*-HFP). The resulting composite solution was degassed for 15 min to get bubble free clear solution before electrospinning.

3.2.4 Preparation of P(VdF-*co*-HFP)-BDN composite membranes by electrospinning

A uniform solution of 16 wt.% P(VdF-*co*-HFP) in a mixed solvent of acetone/DMAc (7:3, w/w) was prepared by magnetic stirring for 24 h at room temperature. Varying content of BDN was added to the solution and stirred for another 6 h to get a uniform solution. The BDN content was varied from 3-9% by weight of P(VdF-*co*-HFP). The resulting P(VdF-*co*-HFP)-BDN solution was kept

undisturbed for 15 min to get a bubble free clear solution. The solution was electrospun using the same conditions as mentioned above.

3.2.5 Melting quenching synthesis of Lithium Aluminium Germanium Phosphate (LAGP)

Li_2CO_3 , Al_2O_3 , GeO_2 and $\text{NH}_4\text{H}_2\text{PO}_4$ were used as received. A 30 gram batch of composition $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ was prepared following the previously reported method [175]. The chemicals were weighed, mixed, and ground before it was ball milled overnight for further homogenization. The milled batch was placed in a platinum crucible and heated to 450°C at the rate of $0.5^\circ\text{C}/\text{min}$ and held at that temperature for 2 h. Then the temperature was increased to 1400°C at the rate of $1^\circ\text{C}/\text{min}$ and the glass was melted for 2 h. The clear, homogeneous, viscous melt was poured onto stainless steel substrate and pressed by another steel plate to obtain the transparent glass sheets. The glass sheet was annealed at 550°C for 2 h to release the thermal stresses and then allowed to cool to room temperature. These annealed specimens remained in the glassy state. The glass sample was then annealed at 850°C for 6 h. The glass transformed into glass–ceramic and the colour changed from colourless to bluish opaque. The glass–ceramic sheets were broken into chunks, crushed to powder, and screened to obtain a powder with a particle size range of 1–38 μm .

3.2.6 Sol gel synthesis of LAGP

$\text{CH}_3\text{CO}_2\text{Li}\cdot 2\text{H}_2\text{O}$, $\text{AlN}_3\text{O}_9\cdot 9\text{H}_2\text{O}$ and P_2O_5 were weighed in stoichiometric proportions and dissolved in ethylene glycol (0.001 mol of LAGP: 100 ml of ethylene glycol) and heated at 90°C with continuous stirring. After which, acetic

acid $\text{C}_2\text{H}_4\text{O}_2$ (0.001 mol of LAGP: 10 ml of acetic acid) was added into the mixture. The mixture was stirred until a clear solution was obtained. $\text{Ge}(\text{CH}_3\text{O})_4$ was added and the solution was stirred for 5 min. Following that, powder citric acid (CA) $\text{C}_6\text{H}_8\text{O}_7$; gelation agent (4 mol of CA: 1 mol of LAGP) was added and stirred continuously for 1 h obtaining a clear final solution. The final solution was placed in an oven at 100°C until gelation was complete. The gel was then placed in an alumina crucible and heated to 900°C at a ramping rate of $2^\circ\text{C}/\text{min}$ with a 10 h dwelling time in ambient conditions. After the process was completed, the powder was collected for further characterisation.

3.2.7 Preparation of P(VdF-*co*-HFP)-LAGP composite membranes by electrospinning

For preparation of the composite, required amount of LAGP was weighed and a uniform dispersion was made in DMAc using mortar and pestle. A uniform solution of 16 wt.% of P(VdF-*co*-HFP) with varying LAGP content in a mixed solvent of acetone/DMAc (7:3, w/w) was prepared by magnetic stirring for 24 h at room temperature. The required amount of LAGP slurry was added for making the solution. The LAGP content was varied from 3-15% by weight. The resulting P(VdF-*co*-HFP)-LAGP solution was degassed for 15 min to get bubble free solution. The solution was electrospun using the same conditions as mentioned above and dried under vacuum.

3.2.8 Preparation of P(VdF-*co*-HFP)-LAGP/PEO composite membranes by electrospinning

For preparation of the composite, right proportion of polymers and required amount of LAGP dispersion were added in a mixed solvent of acetone/DMAc (7:3, w/w) and stirred for 24 h at room temperature to get uniform composite solution. The solid content for the final solutions was carefully kept at 16 wt.% and are left in air tight container for 15 min to get bubble free clear solution. The LAGP content in the composite was kept constant at 6 wt.%. The PEO content was varied between 5-20 wt.%. The composite solution was electrospun at ambient atmosphere. For in-situ porosity generation, the electrospun membranes were immersed in a heated water bath (70 °C) for 48 h to leach out the PEO present in the electrospun membranes. PEO is water soluble, while P(VdF-*co*-HFP) is insoluble; therefore PEO was preferentially isolated and removed from the membranes. The membranes were then dried in an air oven at 60 °C followed by vacuum drying at 80 °C for 24 h. For comparison P(VdF-*co*-HFP)/PEO membranes were prepared without LAGP using electrospinning.

3.2.9 Preparation of gel polymer electrolytes

Gel polymer electrolytes were prepared by activation of the various membranes synthesized with liquid electrolyte. For this, the membranes were passed between stainless steel twin rollers and then punched into circular discs of diameter 18 cm (~ area 2 cm²). The membranes were then dried at 60 °C under vacuum overnight and then transferred into the glovebox. The membranes were then immersed into the liquid electrolyte and left inside for 12 h to ensure maximum saturation. After

gelation, the GPE was removed from the electrolyte and excess liquid electrolyte wiped off gently using weighing paper and used to assemble the GPE for various tests.

3.3 Synthesis of lithiated polymer

3.3.1 Synthesis of Poly (4-lithium styrene sulfonic acid)(PSSLi)

Poly (4-styrene sulfonic acid) and lithium hydroxide monohydrate were dissolved in DMSO in the ratio 1:10 in a glass reactor with a mechanical stirrer. The mixture was stirred at 90 °C for 12 h and the polymer was precipitated out using excess tetrahydrofuran. The polymer was isolated using filtration and washed several times with ethanol to remove any trace impurities. Poly (4-lithium styrene sulfonic acid) was precipitated as a yellowish powder, which was then dried under vacuum at 120 °C overnight before storing it in a dry box for further characterization and use.

3.3.2 Preparation of PSSLi composites and blends

For preparation of the composites, stoichiometric proportions of PSSLi and SiO₂ (<9microns, Aldrich)/BDN were dispersed in water and stirred continuously at 40 °C overnight. The uniform solution was then cast onto a Teflon petridish and dried under vacuum at 80 °C overnight before further use. Blends of PSSLi and PEO were also prepared using the same method as above.

3.3.3 Preparation of PSSLi gels

For measurement of electrochemical properties, gels were made using DMSO as solvent. Required amounts of PSSLi/composite/blend was weighed and dissolved

in DMSO at 80 °C overnight to obtain a clear transparent gel. The composition was varied between 5 wt.% PSSLi to 25 wt.% PSSLi.

3.3.4 Preparation of electrospun PSSLi

A 20 wt.% solution of PSSLi in a mixed solvent EtOH/H₂O (varying ratios) was prepared by magnetic stirring for 24 h at room temperature. The essential electrospinning parameters were as follows: applied voltage 20 KV, working distance from collector to tip of the spinneret ~17 cm, bore size of the needle 0.6 mm, solution feed rate 0.3 ml/h and collector drum rotation speed 50 rpm. The solution temperature was maintained at (20±5) °C and the chamber temperature was maintained at (25±2) °C. The humidity was maintained at (15±5%). The membranes were dried at 100 °C under vacuum for 48 h before further use.

3.4 Characterization studies

3.4.1 Morphological characterisation of the composite and blend polymeric membranes

The morphology of membranes was studied with high resolution field-emission scanning electron microscope (FE-SEM: JEOL JSM7600F) at an accelerating voltage of 15 kV and transmission electron microscope (TEM, JEOL 2100F) in high resolution mode operating at 200 kV. The samples were mounted on metal stubs using conductive double-sided carbon tape, and a thin layer of platinum was sputtered on the sample using JEOL JFC-1200 prior to scanning. Average fiber diameter (AFD) (~300 fibers) was estimated from the micrograph taken at high magnification. For cross-section analysis, the membranes were freeze-fractured in liquid nitrogen. Energy-dispersive X-ray (EDX) spectrum of the required samples

was recorded with computer interfaced INCA mapping software attached with FE-SEM.

3.4.2 Structural characterisation of LAGP and clay composites

X-ray diffraction (XRD) data for the powders prepared by solid state and sol gel methodologies were obtained using Bruker Advanced D8 XRD diffractometer operating at 40 kV, CuK α radiation over the angular range 10 to 80 ° 2 θ at 0.02 ° incremental step. The XRD data was characterized using crystallographic software, TOPAS 3, to determine the formation of LAGP and other phases.

The P(VdF-*co*-HFP)-clay samples were scanned with Bruker-D8 Advance Thin-film diffractometer operating at a voltage of 40 kV and a current 40 mA using CuK α radiation ($\lambda=0.15406\text{nm}$) with copper target and Ni filter at room temperature. The samples were scanned in the 2 θ range of 2 to 40 ° at a scan rate of 2.5 °/min [123]. The intercalation of the polymer chains usually increases the interlayer spacing of the clay platelets. The distance between the clay platelets, was estimated using Bragg's formula.

$$2d \sin\theta = n\lambda \quad (2)$$

where n is an integer ($n=1$), θ is the diffraction angle giving the primary diffraction peak, and λ is the X-ray wavelength.

3.4.3 Thermal and mechanical characterization

Thermal properties were studied using differential scanning calorimetry (DSC: Q 10, TA Instruments) at a heating rate of 10 °C/min from -90 °C to 350 °C and

thermo gravimetric analysis (TGA: Q500 TA Instruments) at a heating rate of 10 °C/ min from room temperature to 800 °C under N₂ atmosphere, respectively. From the DSC data, crystallinity of the samples was calculated according to the following formula.

$$X_c (\%) = \frac{\Delta H_m^{Sample}}{\Delta H_m^*} \times 100 \quad (3)$$

where X_c is crystallinity, ΔH_m^{Sample} is the apparent enthalpy of fusion per gram of polymer sample, which was obtained from the integral area of the base line and each melting curve in DSC, ΔH_m^* is the apparent enthalpy of fusion per gram of totally crystalline polymer. For PVdF, $\Delta H_m^* = 104.7$ J/g [86].

Mechanical properties of the membranes were measured by universal testing machines (UTM, Instron 5567 Instruments) using a 10 N load cell. Tensile strength, Young's modulus and percentage elongation were evaluated using die punched dumbbell shaped samples as per ASTM D 638 using type V die. The extension rate was kept at 5 mm/min and the load was applied till the sample breaks. The dimensions of the sample used were 15 cm × 2 cm × 50 μm. Five samples were studied for each membrane. Bluehill software was used for the calculations.

The tensile strength was calculated using the formula

$$\text{Tensile strength} = \frac{\text{Load at break point}}{\text{Original width} \times \text{original thickness}} \quad (4)$$

The percentage elongation (strain) was calculated using the equation

$$\text{Percentage elongation} = \frac{\text{elongation at break point}}{\text{Initial gauge length}} \times 100 \quad (5)$$

Young's modulus was calculated from the initial linear portion of the load (stress) versus extension (strain) curve, by choosing two points to calculate the change in stress and strain using the equation

$$\text{Young's modulus} = \frac{\text{Stress}}{\text{Strain}} \quad (6)$$

3.4.4 Porosity, electrolyte uptake and electrolyte retention

Porosity (P) was determined by immersing the dry membrane in n -butanol for 1 h.

The following relation was used to calculate P :

$$P (\%) = \frac{M_{\text{BuOH}} / \rho_{\text{BuOH}}}{M_{\text{BuOH}} / \rho_{\text{BuOH}} + M_{\text{m}} / \rho_{\text{P}}} \times 100 \quad (7)$$

where M_{m} is the mass of the dry membrane, M_{BuOH} is the mass of n -butanol absorbed, ρ_{BuOH} and ρ_{P} are the densities of n -butanol and polymer, respectively [86]. The capacity of the membrane to absorb liquid electrolyte, i.e. electrolyte uptake (δ) was calculated using the relation:

$$\delta (\%) = \frac{M - M_0}{M_0} \times 100 \quad (8)$$

where M_0 is the mass of the dry membrane and M is the mass of the membrane after soaking in the electrolyte. The weight of the wet membrane was

determined at different soaking intervals, after removing excess electrolyte on the surface by wiping softly with a tissue paper.

The capacity of the GPE to retain entrapped liquid was measured by its relative absorption ratio. The membranes were immersed in the electrolyte solution for 4 h until they reached a state of equilibrium. The excess liquid electrolyte was removed from the surface of the membranes and it was placed between two filter papers and squeezed using a pressure 10 Pa. The weight changes were measured. The results were presented as a relative absorption ratio following the formula below.

$$R = \frac{M_{PE}}{M_{PE, \text{ saturated}}} \quad (9)$$

where R is the relative absorption ratio of the liquid electrolyte, $M_{PE, \text{ saturated}}$ is the mass of the polymer electrolyte when the membrane is fully saturated with the liquid electrolyte and M_{PE} is the mass of the polymer electrolyte after a time interval when the saturated polymer electrolyte is squeezed by pressing it between two filter papers [86,137].

3.4.5 Fourier transform infrared spectroscopy (FTIR)

FTIR was recorded on pellets of materials mixed with KBr using a Perkin Elmer Spectrum GX FTIR, in the range of 4000-400/cm (step size 2/cm). When required thin film samples were prepared and the spectrum recorded using the same conditions as above.

3.4.6 Nuclear magnetic resonance studies

^7Li and ^1H pfg-NMR diffusion measurements were performed on a Bruker Avance III 300 wide bore spectrometer equipped with a 5 mm diff 50 pulse-field gradient probe using the stimulated spin-echo (STE) pulse sequence. The sample temperatures for the variable temperature (VT) experiments were calibrated by using the relative chemical shift separation between the OH resonance and CH_3 resonance in dry methanol [176]. The samples were packed to a height of 50 mm in a 5 mm Schott E NMR tube in a nitrogen-filled glove box and sealed with Teflon tape and a cap. The pulsed-field gradient stimulated echo (PFG-STE) pulse sequence was used to obtain the diffusion coefficients of different species [177].

3.5 Electrochemical characterisation

3.5.1 Ionic conductivity of gel polymer electrolytes

Ionic conductivity (σ) was calculated using the formula

$$\sigma = t/R_b A \quad (10)$$

where t and A denote the thickness and area respectively of the polymer electrolytes and R_b denotes the bulk resistance of the electrolyte obtained as the x-axis intercept of the complex AC impedance response with frequency [178]. Ionic conductivity of the GPEs was measured between -20 to 70°C by sandwiching the GPE between two stainless steel (SS) blocking electrode using Swagelok[®] cells. The assembled cells were placed in a temperature controlled environmental chamber and kept at each measuring temperature for a minimum of 30 min to ensure thermal equilibration before measurement. The measurements were carried out on a computer interfaced AC impedance frequency analyzer using Solartron

1470E and SI 1255B Impedance/gain-phase analyzer coupled with a potentiostat over the frequency range 10 mHz to 1 MHz at an AC amplitude of 20 mV. The results were presented in a $\log \sigma$ versus $1000/T$ plot with T measured in Kelvin.

3.5.2 Ionic conductivity of PSSLi gels

For measuring the ionic conductivity, a custom made conductivity probe with platinum electrodes was used. The conductivity cell was first standardized using 0.01 M KCl solution to obtain the cell constant. The measurements were carried out on a computer interfaced AC impedance frequency analyzer using Solartron 1470E and SI 1255B Impedance/gain-phase analyzer coupled with a potentiostat over the frequency range 1 mHz to 1 MHz at an AC amplitude of 10 mV.

The ionic conductivity is calculated using the equation

$$X = G \cdot K \quad (11)$$

where G is the conductance and K is the cell constant.

3.5.3 Interfacial resistance, linear sweep voltammetry and transference number measurement

Time dependent interfacial resistance (R_f) between lithium electrode and GPE was evaluated by monitoring the complex impedance response on Li/GPE/Li cells over a period of 12 days at room temperature using the same conditions of the ionic conductivity measurement. The electrochemical stability was determined by linear sweep voltammetry (LSV) of Li/GPE/SS cell at a scan rate of 1 mV/s over the range of 2-5.5V at 25 °C and a cyclic voltammetry (CV) of Li/GPE/SS cell at

a scan rate of 1 mV/s over the range of -0.3-0.3V using the CHI electrochemical workstation [85].

The transference number was measured using the method reported by Bruce and Vincent [168]. For this method, a combination of AC and DC pulses were used. The initial impedance of the cell was measured and then a small DC bias of 10mV was applied to the cell and the response of the current was monitored till a steady state current was reached. The cell was then left at open circuit voltage for 24 h to remove all concentration gradients and then the steady state impedance was measured. The transference number is calculated using the equation

$$T^+ = \frac{I_{ss}(\Delta V - I_0 R_0)}{I_0(\Delta V - I_{ss} R_{ss})} \quad (12)$$

where I_0 is the initial current, I_{ss} is the steady-state current, ΔV the applied potential, and R_0 and R_{ss} the electrode resistances before and after polarization respectively [168]. The transference number was also measured by NMR by measuring the diffusion coefficients of ^7Li and ^{19}F .

3.5.4 Cell fabrication and electrochemical studies

Two-electrode lithium coin cells were assembled by sandwiching the GPEs between lithium metal anode (~300 μm thick) and lithium iron phosphate (LiFePO_4) composite cathode. The composite cathode was prepared by mixing active material (LiFePO_4), conducting additive (Super P Li carbon) and PVdF binder (Kynar 2801) (75:15:10), using *N*-methyl pyrrolidinone (NMP) as solvent.

The resulting slurry was coated on to Al foil (20 μm in thickness) using doctor blade technique and subsequently dried in the oven at 70 $^{\circ}\text{C}$. The composite anode was prepared by mixing active material (LTO), conducting additive (Super P Li carbon) and PVdF binder (Kynar 2801) (80:10:10) using *N*-methyl pyrrolidinone (NMP) as solvent. The resulting slurry was coated onto copper foil and dried in the oven at 70 $^{\circ}\text{C}$. The coated foils were pressed between stainless steel twin rollers to ensure good adhesion and punched in to circular discs of 16 mm dia. Counter electrode lithium foil (~ 0.59 mm thick, Hohsen Corporation, Japan) of the same diameter was used for cell fabrication.

The test cells were fabricated in CR2016 coin cell. For comparison, cells were constructed using Celgard 2400 separator. The electrochemical tests of the cells were conducted in an automatic galvanostatic charge-discharge unit, battery cycler (BTS XWJ, Neware Tech. Co.), between 2.5-4.0 V or 1-3V at room temperature at a current density of 0.1 C based on cell configuration. Rate capability of the cells was also studied between 0.1 C to 3C rate.

4 Chapter 4 Results and Discussions of the various studied systems

This chapter explains the results of the various experiments conducted for this thesis. Firstly, a justification was provided for choosing electrospinning as the method to prepare the fluorinated gel polymer electrolytes for lithium battery application. The effect of polymer composition and morphology was studied and electrospun P(VdF-*co*-HFP) and PSSLi gel were chosen as matrices. To understand the effect of fillers and polymer blends on the electrochemical properties of P(VdF-*co*-HFP) based GPEs, composite and blend GPEs were prepared. Each of these fillers target one or more of the factors affecting ionic conductivity. As mentioned previously, ionic conductivity is dependent on a number of factors. This study was done to identify the most critical factors affecting ionic conductivity. The following composites and blends were studied.

- 1) P(VdF-*co*-HFP)-clay composite-The effect of reduced ion coupling on the electrochemical properties of the resulting GPEs was examined (Section 4.3.1.1).
- 2) P(VdF-*co*-HFP)-BDN composite-The effect of increased ion dissociation on the electrochemical properties of the resulting GPEs was studied (Section 4.3.1.2).
- 3) P(VdF-*co*-HFP)-LAGP composite-The combined effect of reduced ion coupling and increased lithium ion content was compared with each individual factor (Section 4.3.1.3).

- 4) P(VdF-*co*-HFP)/PEO blend-The effect of increased polymeric segmental motion on the ion transport properties of the GPEs was studied (Section 4.3.1.4).
- 5) P(VdF-*co*-HFP)/PEO-LAGP composite-The effect of further increasing lithium ion concentration was studied and compared with reduced ion coupling (Section 4.3.1.5).

It was seen that reduced ion coupling and increased lithium ion concentration influenced the ion transport properties more than the increased chain segmental motion. To further test this hypothesis, and understand which factor is most critical, a novel in-situ porosity generation method was designed. P(VdF-*co*-HFP)/PEO-LAGP membranes were prepared and PEO was isolated and removed from the composite, to prepare a highly porous matrix. The highly porous matrix leads to absorption of larger quantity of liquid electrolyte and thereby higher lithium ion concentration. LAGP was used as a filler to reduce ion coupling and maintain the mechanical strength of the resulting porous structure. The LAGP content was kept constant. The effect of further increasing the lithium ion concentration on the ionic conductivity was studied and compared with the effect of reduced ion coupling. The most critical factor affecting ionic conductivity was identified by comparing all the systems.

Apart from improving the ionic conductivity of GPEs, the desire for high lithium ion transference number also led to exploration of single ion conductors based on PSSLi. A systematic study of the ion transport properties of PSSLi was conducted. The effect of morphology and processing method was investigated.

The lithium ion concentration, for achieving best ionic conductivity was optimized. Similar to the P(VdF-*co*-HFP) system, the effect of fillers and blends on the ion transport of PSSLi gels was studied. The following composites and blends were studied.

- 1) PSSLi/PEO blend-To study the effect of increased segmental motion (Section 4.3.2.1).
- 2) PSSLi-BDN composite-To study the effect of increased dissociation (Section 4.3.2.2).
- 3) PSSLi-SiO₂ composite-To study the effect of decreased ion coupling (Section 4.3.2.3).

The difference in mechanism of ion conduction between the P(VdF-*co*-HFP) based GPEs and the PSSLi gels was further elucidated. Transference number and lithium ion diffusion coefficient was studied using both electrochemical and NMR methods and compared. A correlation of the various factors which affect ion transport and diffusion in GPEs was studied using various materials and electrochemical characterization techniques.

4.1 Influence of morphology on the electrochemical properties of gel polymer electrolytes

This section discusses the effect of morphology on the properties of PVdF based GPEs. The physical and electrochemical properties of PVdF based GPEs prepared by phase inversion and electrospinning are studied and compared.

4.1.1 Phase inversion vs Electrospinning

The morphology of the PVdF membranes prepared by phase inversion method and electrospinning is shown in Fig.4.1. The electrospun membrane (Fig.4.1(a)) shows a uniform three dimensional multi-layered structure. Each layer consists of several ultra-thin micron sized fibers, leading to a loose packing of fibers. The interlaid fiber structure provides good mechanical stability to the fibers.

The phase inversion membranes shown in (Fig.4.1(b-d)) showed very different morphology when compared to the electrospun membranes. It was seen that phase inversion membrane showed two distinct morphologies at the top and bottom surface. A two phase solution was formed almost instantaneously when the membrane was soaked in the non-solvent coagulation bath. This was due to the penetration of excessive non-solvent. A polymer rich phase and a polymer lean phase were formed, with the polymer rich phase solidifying immediately after phase separation. The polymer lean phase resulted in the formation of the porous morphology by leaking out of the solvent during the de-mixing process.

When the film was first immersed in water bath, water (non-solvent), acetone (solvent) de-mixing and high mass transfer takes place at the top surface [123]. This leads to the formation of a large number of small pores and a very thin skin layer.

Fig.4.1 Surface morphology of (a) electrospun PVdF; phase inversion membranes (b) top surface, (c) bottom surface, (d) cross sectional view

As the process proceeds towards the bottom surface, the glass substrate acts as a barrier to the de-mixing process. This leads to rapid solidification of polymer rich phase, leading to the formation of dense skin layer with macro-pores [123]. From the cross sectional image it was seen that the membrane has a closed cellular, reticular fabric structure [123].

The porosity of PVdF membranes prepared by phase inversion was 75%, while the porosity of the electrospun PVdF was 80%. The higher porosity of the electrospun membrane is beneficial for achieving better ion transport. From the FE-SEM images, it was seen that the surface roughness of the electrospun membranes is higher than the membrane prepared by phase inversion. The

increased surface roughness is advantageous for improved adhesion of the GPE with lithium metal resulting in better electrochemical properties

The thermo gravimetric trace of the membranes is shown in Fig.4.2. The traces of both the membranes showed similar characteristics. The initial decomposition temperature for the membrane prepared by phase inversion was 432 °C and for electrospun PVdF it was 433 °C. The char yield at 700 °C for both the membranes was 20%. The thermal property of the membranes prepared by both the methods was not significantly different.

Fig.4.2 TGA of PVdF membranes prepared by phase inversion and electrospinning

The crystallinity of the membranes was examined using DSC. The DSC trace of the membranes is presented in Fig.4.3. The crystallinity was calculated by following the procedure mentioned above, using Equation (3) (Sec 3.4.3). The crystallinity of electrospun PVdF was calculated to be 48%. The crystallinity of the membrane prepared by phase inversion was calculated to be 42%. The higher crystallinity of the electrospun membrane was probably due to the fiber orientation when it was drawn out as fibers on the collection drum [87].

Fig.4.3 DSC of PVdF membranes prepared by phase inversion and electrospinning

The mechanical strength of the membranes was studied using the procedure mentioned in Chapter 3, section 3.4.3. The mechanical properties are tabulated in Table.4.1.

Table.4.1.Mechanical properties of PVdF membranes prepared by electrospinning and phase inversion

Methodology	Young's modulus(MPa)	Tensile strength(MPa)
Phase inversion	10 .1	6.1
Electrospinning	11.9	7

The higher mechanical stability of the electrospun membrane can be attributed to the fact that the fibers are randomly oriented, and thus have a better load bearing capacity. The higher crystallinity of the electrospun membrane also leads to better mechanical properties. The typical stress strain curves are shown in Fig.4.4.

Fig.4.4 Stress-strain curves of PVdF membranes prepared by phase inversion and electrospinning

The electrolyte uptake, which is one of the most important factors which affects ionic conductivity, was studied and the results are shown in Fig.4.5. The electrolyte uptake strongly depends on the porosity and pore size. The nature of the pores also affects the electrolyte uptake. Higher porosity leads to availability of more pores for the electrolyte to seep into, resulting in higher absorption of liquid electrolyte. As expected, the electrolyte uptake of the electrospun membrane was significantly higher than the membrane prepared by phase inversion. The membrane prepared by phase inversion had a 26% lower electrolyte uptake, because of the absence of interconnected pores. The higher electrolyte uptake of the electrospun membranes can be attributed to the higher porosity, interconnected pores and partial swelling of fibers upon activation.

Fig.4.5 Electrolyte uptake of PVdF membranes prepared by phase inversion and electrospinning

The stability of the gel polymer electrolyte prepared by activating the membranes with liquid electrolyte was studied by examining their retention characteristics. The electrolyte retention ratio of the membranes is shown in Fig.4.6. The partial swelling of fibers forms a stable gel phase in the electrospun matrix. The electrospun membrane showed a low leakage with a loss of 12% electrolyte after 2 h. The PVdF membrane prepared by phase inversion methodology showed lower electrolyte retention, with a leakage of 17% over 2 h. The higher retention of the electrospun membranes implies the formation of higher amount of gel phase with higher stability and lower leakage.

Fig.4.6 Electrolyte retention of PVdF membranes prepared by phase inversion and electrospinning

The ionic conductivity (σ) of the PVdF membranes was studied between - 20 and 70 °C. The $\log \sigma$ vs $1000/T$ curves are shown in Fig.4.7. The ionic conductivity is mainly influenced by the number of active charge carriers, which is controlled by the electrolyte uptake. Higher electrolyte uptake leads to higher ionic conductivity. The ionic conductivity at 30 °C for PVdF membranes prepared by electrospinning and phase inversion was 1.7 and 0.78 mS/cm respectively. The higher ionic conductivity of the electrospun membrane is due to the higher porosity and electrolyte uptake. An enhancement in conductivity with temperature was seen for both the GPEs (Fig.4.7). This can be attributed to the increase in concentration and mobility of charge carriers with increasing temperature [141]. Increasing temperature also leads to higher lithium salt dissociation and increase in mobility of Li^+ ions due to the high activation energy [141].

Fig.4.7 Temperature dependent ionic conductivity of GPEs prepared by phase inversion and electrospinning

The curvature seen in the $\log \sigma$ vs $1000/T$ curve (Fig.4.7) indicate that the mechanism can be explained by the VTF function [141]. This implies that ionic conductivity is influenced by both increased dissociation of lithium salt and increased chain segmental motion [141]. The ionic conductivity data was fitted using nonlinear least square fitting and the results are shown in Fig.4.7. The parameter values are tabulated in Table 4.2.

Table 4.2 VTF parameters of the phase inversion and electrospun GPEs

GPE	σ_0 (S/cm/K)	E_a (eV)	T_0 (°C)
Phase inversion	0.17	0.16	104
Electrospun	0.18	0.10	107

The interface between the GPEs and lithium metal was evaluated over a period of 7 days. The time dependent interfacial resistance is shown in Fig.4.8. The initial interfacial resistance of the GPEs prepared by phase inversion and

electrospinning were 116 and 475 Ω respectively. It was seen that the interface between the GPE prepared by electrospinning and lithium metal was more stable when compared to the GPE prepared by phase inversion. The higher interfacial resistance of the GPE prepared by phase inversion can be attributed to the lower ionic conductivity and smoother surface. Surface roughness is beneficial for good adhesion between the two surfaces leading to the formation of a stable SEI layer.

Fig.4.8 Time dependent interfacial resistance of GPEs prepared by phase inversion and electrospinning

The final interfacial resistance of the GPE prepared by phase inversion was 250% more than the GPE prepared by electrospinning. The interfacial resistance of both GPEs increased with time indicating the growth of the passivation layer. The growth of the passivation layer was faster for the electrospun GPE, where the interface properties stabilized within 4 day. For the GPE prepared by phase inversion, stabilization was not complete even after 7

days. The lower increase in interfacial resistance over time for the electrospun GPEs implies that there was no loss of electrolyte from the pores. Thus high ionic conductivity was maintained with storage.

The stability of the GPEs against lithium was also evaluated using linear sweep voltammetry (LSV). The LSV curves are shown in Fig.4.9. The electrochemical stability window of the electrolyte is an important parameter in determining the suitability of the practical application of the electrolyte in a battery. The voltage corresponding to the onset of a steady and continuous increase of current indicates the electrochemical stability limit of the electrolyte [179].

Fig.4.9 Electrochemical stability window of GPEs prepared by phase inversion and electrospinning

The GPE prepared by electrospinning showed a stability window of 4.6V, while the GPE prepared by phase inversion showed a lower stability of 4.2V.

Higher stability window implies that the stability of the electrospun GPE was higher than the GPE prepared by phase inversion. The increased electrochemical stability resulted from lower interfacial resistance, higher surface roughness and higher ionic conductivity. The higher anodic stability of the electrospun GPE can also be attributed to the better affinity of the fibers to the carbonate based liquid electrolyte solution.

The GPEs were also tested in Li/LiFePO₄ cells to study their cycling stability. The cycling characteristics of the cells at 0.1C rate over 50 cycles are shown in Fig.4.10.

Fig.4.10 Cycling properties of Li/LiFePO₄ cells with GPEs prepared by phase inversion and electrospinning

The initial discharge capacities of the cells with GPEs prepared by electrospinning and phase inversion were 142 and 139 mAh/g respectively. The

higher initial discharge capacity of the cell with electrospun GPE can be attributed to its higher ionic conductivity. Both the cells showed good capacity retention with a capacity loss of $< 12\%$ over 50 cycles. The cell with GPE prepared by electrospinning showed a higher capacity and more stable behaviour over continuous cycling. The advantageous characteristics of the electrospun membrane like higher porosity, electrolyte uptake, mechanical strength, higher ionic conductivity, better interfacial properties and improved cycling behaviour led to it being chosen for further study.

4.2 Influence of polymer composition on the electrochemical properties of gel polymer electrolytes

The first part of this section discusses and compares the physical and electrochemical properties of electrospun PVdF and P(VdF-*co*-HFP). The second part of this section discusses lithiated PSSLi. The effect of processing method of PSSLi on the electrochemical properties is compared by studying samples prepared by pelletizing, electrospinning and gel formation. The optimization of lithium ion concentration for achieving best electrochemical properties in the system is also discussed.

4.2.1 Comparison of electrospun PVdF and P(VdF-*co*-HFP)

The morphology of the electrospun PVdF and P(VdF-*co*-HFP) membranes was studied under FE-SEM and the images are shown in Fig.4.11. It was seen that both the membranes exhibit a three dimensional network structure. The membranes exhibit highly fibrous morphology with a large number of

interconnected pores. Random orientation of fibers and layered structure provides good mechanical handleability.

Fig.4.11 Surface morphology of electrospun (a) P(VdF-co-HFP) and (b) PVdF

The average fiber diameter (AFD) of PVdF was 1.8 μm while for P(VdF-co-HFP) it was 1.5 μm . It was seen that the fibers exhibit uniform fiber diameter with the P(VdF-co-HFP) membrane having a slightly lower average fiber diameter. The difference in AFD was due to the difference in viscosity of the spinning solution. The viscosity of PVdF solution is higher than that of P(VdF-co-HFP). Higher viscosity solution makes thicker jet leading to deposition of thicker and closely packed fibers resulting in decreased porosity.

Porosity of the prepared membranes was determined by n-butanol uptake method. The n-butanol penetrates the pores and occupies all the available pores and thus gives a measure of the total pore volume of the membrane [139]. The porosity of PVdF and P(VdF-co-HFP) membranes was measured to be 80 and 83 % respectively. As seen in the previous section, porosity is one of the key factors which determine the electrolyte uptake and ion transport properties. The

electrolyte uptake properties are directly proportional to porosity of the electrospun matrix.

The electrolyte uptake was studied over a period of 2 h and the results shown in Fig.4.12. It was seen that the electrolyte uptake of P(VdF-*co*-HFP) membranes was significantly higher than PVdF membrane. The steady state uptake of P(VdF-*co*-HFP) was 400% while for PVdF it was 262% ,which is 35% lower. The presence of amorphous HFP in the co-polymer leads to this difference in uptake. Although the porosity of electrospun P(VdF-*co*-HFP) was higher than PVdF, the difference is not significant to produce this difference in uptake. The lower crystallinity, increased amorphous content and the partial solubility of HFP in the organic solvents leads to the higher uptake and the formation of a more stable gel [84].

Fig.4.12 Electrolyte uptake of electrospun PVdF and P(VdF-*co*-HFP)

To test the stability of the gel phase, the electrolyte retention characteristics were studied and the results are shown in Fig.4.13. It was observed that leakage characteristics tend to reach an equilibrium state within 2 h. It was seen that both the gels are stable with a very low leakage after 2 h.

Fig.4.13 Electrolyte retention of electrospun PVdF and P(VdF-co-HFP)

The P(VdF-co-HFP) gel was more stable with a retention ratio of 0.90 after 120 min implying the formation of a low leak, stable gel. The retention ratio of PVdF was 0.88, which was lower than the co-polymer gel. This difference is due to the better affinity of the amorphous HFP to the organic solvents used to activate the electrospun membranes.

Thermal properties of the electrospun membranes were studied using TGA and DSC. Fig.4.14 shows the DSC plots of the electrospun membranes. The melting temperature of PVdF and P(VdF-co-HFP) was 157 and 147 °C respectively. The mass fraction degree of crystallinity for all the membranes was

calculated from the heat of fusion. The heat of fusion was obtained from the endotherm area bounded by the melting curve and base line. The crystallinity of PVdF and P(VdF-*co*-HFP) was found to be 48 and 43% respectively. The crystallinity of PVdF was higher than P(VdF-*co*-HFP) due to absence of amorphous HFP. The lower crystallinity of P(VdF-*co*-HFP) is beneficial for better ionic conductivity and electrochemical performance of the resulting gel.

Fig.4.14 DSC of electrospun PVdF and P(VdF-*co*-HFP)

The thermal stability of the electrospun membranes was studied with TGA. The TGA curves are shown in Fig.4.15. The onset decomposition temperature of PVdF and P(VdF-*co*-HFP) was 432 and 400°C respectively. The char yield at 700 °C for PVdF and P(VdF-*co*-HFP) was 26 and 21% respectively. The higher onset decomposition temperature and the higher char yield for PVdF was due to the higher crystallinity of PVdF when compared to its co-polymer. Higher degree of crystallinity leads to more rigidity in the matrix resulting in better thermal stability.

Fig.4.15 TGA of electrospun PVdF and P(VdF-co-HFP)

The ionic conductivity of the gel polymer electrolytes based on PVdF and P(VdF-co-HFP) was studied in the temperature range -20 to 70 °C and the results shown in Fig.4.16. It was seen that the ionic conductivity of P(VdF-co-HFP) was higher than PVdF. The higher ionic conductivity is attributed to the lower crystallinity and higher electrolyte uptake. Ionic conductivity is related to the number of active charge carriers by the equation

$$\sigma = \sum N_i R_i \dot{E}_i \quad (13)$$

where N_i , R_i and $\dot{E}_i$ are number of charge carriers, ionic charge and ionic mobility, respectively. Higher electrolyte uptake leads to a higher number of charge carries and therefore a higher ionic conductivity. The ionic conductivity of PVdF and P(VdF-co-HFP) GPE at 30 °C was 1.7 and 2.9 mS/cm, respectively. As seen in Fig.4.16, the $\log \sigma$ vs $1000/T$ curves for both the GPEs are slightly curved. Therefore, the activation energy for ionic conduction E_a can be obtained using the Vogel-Tamman-Fulcher (VTF) model $\{\sigma = \sigma_0 T^{-1/2} \exp [(-E_a/R(T-T_0))]\}$ instead of

the simple Arrhenius model ($\sigma = \sigma_0 \exp(-E_a/RT)$) used for the treatment of the linear Arrhenius plots.

The ionic conductivity was fitted using nonlinear least square fitting and the results shown in Fig.4.16. The VTF parameters are tabulated in Table 4.3. The slightly lower activation energy for P(VdF-co-HFP) GPE further supports the higher ionic conductivity. It was seen that a good fit was obtained between the observed and fitted values. An enhancement in conductivity with temperature was seen over the entire temperature range studied (Fig.4.16). The sharp decrease in conductivity below 0 °C can be attributed to the freezing property of carbonate solvents in the electrolyte solutions [84].

Fig.4.16 Temperature dependent ionic conductivity of PVdF and P(VdF-co-HFP) GPEs

Table 4.3 VTF parameters of PVdF and P(VdF-co-HFP) GPE

GPE	σ_0 (S/cm/K)	E_a (eV)	T_0 (°C)
P(VdF-co-HFP)	0.19	0.08	109
PVdF	0.18	0.10	107

The formation of stable Li^+ ion conducting interfaces between GPE and lithium metal is essential for achieving a good cycling performance for lithium ion batteries [141,178]. The compatibility of the GPEs with lithium metal was analyzed by evaluating the impedance variation of symmetrical Li/GPE/Li cells over storage up to 12 days. Fig.4.17 shows the initial interfacial resistance of the GPEs under open circuit voltage conditions, at ambient temperature.

Fig.4.17 Initial interfacial resistance of PVdF and P(VdF-co-HFP) GPEs

The impedance response evolved as a semi-circle containing the charge transfer process and the passivation layer formation. The frequency decreases from left to right in the graph. The real axis intercept at the high frequency end (left extreme) of the spectrum denotes the R_b of the polymer electrolyte and the real component of the impedance at the lowest frequency (right extreme) is representative of the Li/electrolyte interfacial resistance (R_f). The lower R_b value for the P(VdF-*co*-HFP) GPE supports the higher ionic conductivity discussed previously.

The time dependent interfacial resistance (R_f) was studied and the results shown in Fig.4.18. It was seen that the R_f of both the GPEs increased with storage time. The R_f value of P(VdF-*co*-HFP) GPE is lower than PVdF GPE throughout the studied time period.

Fig.4.18 Time dependent interfacial resistance of PVdF and P(VdF-*co*-HFP) GPEs

The electrochemical stability window of the GPEs was studied and shown in Fig.4.19. The voltage corresponding to the onset of a steady and continuous increase of current indicates the electrochemical stability limit of the electrolyte [179]. It was seen that both the GPEs show a high anodic stability $> 4.0\text{V}$. The P(VdF-*co*-HFP) GPE exhibits a slightly higher anodic stability when compared to PVdF based GPE. The difference is due to the better affinity of the P(VdF-*co*-HFP) membrane to the carbonate based liquid electrolyte solution. The high anodic stability of the GPEs makes it possible for them to be used with high voltage cathode materials

Fig.4.19 Electrochemical stability window of PVdF and P(VdF-*co*-HFP) GPEs

The GPEs were tested in Li/LiFePO₄ cells to test the practical applicability. The cycling stability at 0.1C rate over 50 cycles is shown in Fig.4.20. The cells with GPE based on PVdF and P(VdF-*co*-HFP) delivered initial discharge capacity of 142 and 149 mAh/g respectively. The higher initial discharge capacity of the GPE based on P(VdF-*co*-HFP) can be attributed to the

higher ionic conductivity, better interfacial properties and low leak nature. After 50 cycles, the capacity retention of the P(VdF-*co*-HFP) GPE was 4% higher than that of the PVdF GPE.

Fig.4.20 Cycling properties of Li/LiFePO₄ cells with PVdF and P(VdF-*co*-HFP) GPEs

The cycling stability of the GPEs at various current densities was studied and the results are shown in Fig.4.21. The cells were cycled between 0.2C rate and 3C rate for 10 cycles each and then cycled again at 0.2 C rate. The cells with both GPEs showed good discharge capacity and cycling performance even at higher C-rate. They retain similar capacity after the current density was changed back to 0.2C-rate after 40 cycles. This clearly demonstrated high capacity retention of the cells. The higher ionic conductivity, interfacial stability and cycling stability make P(VdF-*co*-HFP) a better matrix for preparing GPEs when compared to PVdF. Thus it was chosen for further study.

Fig.4.21 Rate capability of Li/LiFePO₄ cells with PVdF and P(VdF-co-HFP) GPEs

4.2.2 Poly(4-lithium styrene sulfonic acid)

To investigate the effect of unity transference number on the electrochemical performance, PSSLi based electrolytes was studied. The mechanism of ion motion in PSSLi is lithium ion hopping from one fixed anionic moiety to the next one, which implies the material exhibits unity lithium ion transference number. The reaction scheme for the synthesis of PSSLi is shown below in Fig.4.22. Polystyrene sulfonic acid was lithiated, to obtain the lithium ion conducting PSSLi.

Fig.4.22 Reaction scheme for the synthesis of PSSLi

Poly(4-sodium styrene sulfonic acid) (commercial Sigma Aldrich 99% purity) (PSSNa) was also lithiated using the same lithiation procedure to synthesize poly (4-lithium styrene sulfonic acid), as a comparison. The FTIR spectra of PSSLi and PSSNa are shown in Fig.4.23.

Fig.4.23 FTIR spectra of (a) PSSNa and (b) PSSLi

The FTIR spectrum obtained from the lithiation of PSSH and PSSNa yielded the same spectrum. The OH stretching vibration of H₂O in the region of 3000–3700/cm and H₂O scissor vibration in the region of 1570–1700/cm were

observed in the FTIR spectra of PSSNa and PSSLi [115]. The characteristic peaks of PSSLi were found at about 833, 1070, 1430 and 1500/cm [115]. The S-O antisymmetric vibration can be assigned to the peaks at 1430 and 1500/cm [115]. Peaks at 833 and 1070/cm can be assigned to the symmetric vibration of S-O [115]. This result indicated that PSSLi was successfully formed from both PSSH and PSSNa.

The TGA curve of PSSLi is shown in Fig.4.24. It was seen that the thermal decomposition happens in four steps. The first peak extended between 110 °C and 220 °C. The second decomposition peak was observed at 450 °C. The third decomposition peak was seen at 540 °C and the fourth peak at 590 °C.

Fig.4.24 TGA of PSSLi

The first peak corresponds to a weight loss of 10%. The second decomposition peak also contributes to 10% weight loss. The third short decomposition peak corresponds to a weight loss of 4% and the last

decomposition peak amounts to 5% weight loss. The char yield at 700 °C was 59%. The first peak corresponds to a cleavage of the C-S bond in PSSLi and the formation of styryl and SO₃Li radical [101]. This was followed by a reaction between the styryl radical and the hydrogen units of the polymeric chain. At the second decomposition peak, polystyrene degradation happens with the formation of benzene, styrene and methyl styrene [101]. The non-volatile residue was due to the presence of the lithium salt that is left behind.

The DSC curve of PSSLi is shown in Fig.4.25. It was seen that PSSLi exhibits a glass transition temperature of 80 °C. No crystallization or melting endotherm was observed up to 300 °C indicating that the polymer is amorphous. The glass transition temperature of polystyrene was 100 °C, therefore the decrease in glass transition temperature may indicate less structural rigidity of the lithiated sample.

Fig.4.25 DSC of PSSLi

To measure the ionic conductivity of PSSLi, it was dissolved in DMSO at 80 °C and stirred overnight and cast on a Teflon petridish under inert atmosphere. After several days of drying, a free standing membrane was not formed. The poor mechanical stability of PSSLi may be the reason for the poor stability of the film. The sample was then pelletized and the ionic conductivity was measured to be 0.0002 mS/cm at 90 °C. For testing PSSLi in a device, the ionic conductivity has to be of the order of at least 0.1 mS/cm.

To further enhance the ionic conductivity of PSSLi, a mixture of EC: DEC (1:1 w/w) was incorporated to reduce the crystallinity and glass transition temperature and improve the ion dissociation capability. For this, PSSLi was electrospun and then activated with organic solvent.

The morphologies of the electrospun PSSLi with various solvent ratios are shown in Fig.4.26. It was seen that the morphology of the fibers changed from flat fibers to circular fibers with decreasing EtOH content. When the EtOH content was higher, the outer surface of the polymeric jet dried faster than its core and, thus the flat fibers were obtained. When the EtOH content decreased, the difference in drying rate decreased, leading to a more rounded fiber structure [114]. All the membranes showed a three dimensional network of ultrathin fibers with high porosity. The porosity of all the membranes was in the close range of 85 ± 3 %. The network structure helps in the fast diffusion of lithium ions after activation with solvent. The very hygroscopic nature of PSSLi makes it very difficult to collect large area of the membranes under ambient conditions, because the material tends to form clumps over time.

Fig.4.26 FESEM images of PSSLi with different EtOH/ H₂O ratios (a) 70/30, (b) 60/40, (c) 50/50 and (d) 40/60

High electrolyte uptake (Fig.4.27) was shown by the membranes when activated with the solvent mixture. It was seen that the membranes with rounded fiber structure show higher uptake than the flat ribbon like fibers. It was seen that the highest uptake of 200% is obtained for the membrane with solvent ratio 40/60 EtOH/H₂O. The uptake of the electrospun P(VdF-*co*-HFP) membranes was 400%. It was seen that the uptake was slow when compared to the electrospun P(VdF-*co*-HFP), and the uptake was much lower. The lower uptake can be attributed to the fact that PSSLi is not soluble in the organic solvent and thus it has lower affinity to the mixture. The electrospun PSSLi merely acts as a porous matrix into which the solvent was absorbed, rather than forming a gel phase like the P(VdF-*co*-HFP) GPEs. The lower uptake also suggests that this solvent blend was not the ideal choice for forming high ionic conducting gel phase.

Fig.4.27 Electrolyte uptake of PSSLi with different EtOH/H₂O ratios

The temperature dependent ionic conductivity of PSSLi GPEs is shown in Fig.4.28. The ionic conductivity of the activated membranes was studied in the temperature range of 20 to 70 °C. The ionic conductivity was directly proportional to the uptake of the solvents. The ionic conductivity of the membrane with solvent ratio 40/60 EtOH/ H₂O showed the highest room temperature ionic conductivity. The ionic conductivity (mS/cm) at 30 °C followed the order of the EtOH/H₂O solvent ratio; 70/30 (0.02) < 60/40 (0.032) < 50/50 (0.044) < 40/60 (0.06).

It was seen that the ionic conductivity of the electrospun PSSLi membranes was almost linear and it followed the Arrhenius law. Upon introduction of the solvent, the dissociated lithium ions diffuse through the solvent, which forms the fast ion conduction channel. It was seen that the ionic conductivity of electrospun membranes was more than two orders of magnitude

higher than the pelletized samples. The improved ionic conductivity is because of the diffusion controlled ion transport.

Fig.4.28 Temperature dependent ionic conductivity of PSSLi GPEs with different EtOH/H₂O ratios

However, it was seen that the conductivity was an order of magnitude lower than the P(VdF-*co*-HFP) GPEs. The difference in conductivity was attributed to two reasons. Firstly, since only lithium ions were mobile, the number of charge carriers was lower. Secondly since a gel phase was not formed, the total amount of conducting phase was lower in the case of PSSLi. The ionic conductivity of the electrospun PSSLi was too low for practical testing at room temperature. Therefore, to further enhance the ionic conductivity, the solvent content was increased by preparing PSSLi gels. PSSLi was dissolved in DMSO, to study the effect of the effect of increased solvent and improved diffusion. The low enhancement in ionic conductivity by the use of electrospinning coupled with the practical difficulties in the experiment; make the study of PSSLi gels more

attractive as a way to improve its ion transport properties. The dissolution of the polymer matrix in DMSO increases the solvent content of the system and therefore the lithium ions can diffuse faster leading to improved ionic conductivity.

The ionic conductivity of the PSSLi gels with varying PSSLi concentration was studied from room temperature to 70 °C and the results are shown in Fig.4.29. It was seen that all the samples show linear enhancement with increasing temperature. The gels follow Arrhenius function suggesting that the ionic conduction has been decoupled from chain segmental motion. However for the sample with 25 wt.% PSSLi, a slight curve was seen indicating that at higher PSSLi content the chain segmental motion begins to affect the ion transport process.

From Fig.4.29, it was seen that the ionic conductivity was strongly dependent on the concentration of PSSLi. The ionic conductivity increased with increasing PSSLi content till 15 wt.% and after that the conductivity begins to drop steeply. The drop in conductivity when the concentration increases beyond 20 wt.% was significant. This trend suggests that increasing lithium ion concentration does not necessitate an increase in ionic conductivity. It was seen that beyond 15 wt.%, increase in total PSSLi content results in a decrease in polyelectrolyte gel conductivity, despite the increase in absolute lithium ion concentration [180].

Fig.4.29 Temperature dependent ionic conductivity of PSSLi gels with varying PSSLi concentration

The decrease in conductivity can also be attributed to the increasing viscosity with increasing PSSLi content. The high viscosity leads to a more entangled network of the polymer chains, which when combined with the repulsion between adjacent lithium ions leads to lowered diffusion. According to Einstein–Stokes equation, mobility is inversely proportional to the micro-viscosity of the system [180]. The viscosities of the PSSLi gels are tabulated in Table 4.4

Table 4.4 Viscosity of PSSLi gels

PSSLi content (wt.%)	Viscosity (mPas)
5	250
10	315
15	340
20	370
25	425

Another reason for this behaviour is the screening effect of the SO_3^- ions present in the vicinity of the lithium ions, which effectively neutralize the charge of the lithium ions. With increasing concentration, stronger screening occurs accompanied by more coiled chain conformation, and consequently a lower conductivity [180]. Therefore the decreased ion diffusion with increasing lithium ion concentration can be attributed to the combined effect of increased viscosity, decreased chain flexibility, increased screening and ion-ion repulsion [180]. The highest room temperature ionic conductivity was obtained for the sample with 15 wt.% PSSLi at 1.4 mS/cm. The conductivity is an order of magnitude higher than the electrospun samples and four orders of magnitude higher than the bare pelletized sample. The conductivity of the PSSLi gel is of the same order of conductivity as the electrospun P(VdF-*co*-HFP) GPE.

To further investigate the reason for the reduction in ionic conductivity beyond 15 wt.% PSSLi content, pfg-NMR was used to measure the ^7Li diffusion coefficient. The diffusion coefficients of the DMSO (^1H) were also measured. The temperature dependent diffusion coefficients of ^1H and ^7Li are shown in Fig.4.30.

It was seen that the diffusion coefficients follow the same trend as ionic conductivity with highest diffusion coefficient observed for the 15 wt.% sample. The diffusion coefficient begins to drop with further increase in lithium ion concentration. This implies that even though the number of ions was higher, the presence of shielding effect leads to lowered diffusion. Also the presence of ion-ion repulsion leads to a coiled conformation of the chains leading to a more tortuous path for ion diffusion. The diffusion coefficient of DMSO was also

measured using ^1H spectrum to see the extent of association or dissociation in the PSSLi systems. It was seen that, the average diffusion coefficient of the solvent is higher than Li, implying presence of ion pairs and bound lithium.

Fig.4.30 Diffusion coefficients of PSSLi gels by NMR (^1H and ^7Li) with varying PSSLi concentration

4.3 Effect of fillers and blends on the electrochemical performance of gel polymer electrolytes

4.3.1 P(VdF-*co*-HFP) based composites and blends

The section discusses composite and blend GPEs based on P(VdF-*co*-HFP). Each subsection discusses one composite/blend in detail. Section 4.3.1.1 discusses P(VdF-*co*-HFP)-clay composites. The effect of reduced ion coupling on the ionic conductivity, due to the presence of clay is examined. Section 4.3.1.2 discusses P(VdF-*co*-HFP)-BDN composites. The effect of increased ion dissociation and improved lithium diffusion on the ionic conductivity, due to the presence of BDN is examined. Section 4.3.1.3 discusses P(VdF-*co*-HFP)-LAGP composites. The combined effect of reduced ion coupling and increased lithium concentration on ionic conductivity is discussed. Section 4.3.1.4 discusses P(VdF-*co*-HFP)/PEO blends. The effect of increased chain segmental motion on the ionic conductivity, due to the presence of PEO is examined. Section 4.3.1.5 discusses in-situ porosity generated P(VdF-*co*-HFP)-LAGP/PEO composites. The effect of further increased lithium ion concentration on the ionic conductivity is examined. The effect of the fillers and blends on the physical and electrochemical properties of the GPEs is discussed.

4.3.1.1 P(VdF-*co*-HFP)-clay composites

The effect of reduced ionic coupling/ion pair formation was studied using P(VdF-*co*-HFP)-clay composite GPEs. The structure of the clay used in the current study is shown in Fig.4.31.

Fig.4.31 Structure of clay [123]. Reprinted with permission from publisher

Clay has a plate like structure with ~ 1 nm thick aluminosilicate layers, substituted with metal cations and stacked in ~ 10 μm -sized stacks. It consists of octahedral aluminum oxide layers sandwiched between two tetrahedral silicon oxide layers. To create defects in the structure, the aluminum atoms which sit atop the silicate layers were replaced with iron, magnesium or lithium ions [181]. The

absence of ionic bonding between the anionic defects in the aluminum oxide layer and the cations on the silicate layer, allows for exchange of the cations with other similar charge bearing cationic functional groups. This ion exchange is necessary because clay is hydrophilic, while P(VdF-*co*-HFP) is hydrophobic and without this treatment, only dispersion (micro-composite) can be formed. As mentioned previously in Chapter 3, the clay in this study has been treated with quaternary amines [123,141]. The presence of the cationic functional groups offers the possibility of a Lewis acid-base interaction between the clay platelets and the polymer chain or the anion, thereby lowering the ionic coupling between lithium ions and the anion/polymer chain, promoting lithium ion diffusion.

Sonication of clay in DMAc was done for 48 h to exfoliate the clay. Three types of composites can be formed by the interaction of clay and P(VdF-*co*-HFP) as shown in Fig.4.32. In the microcomposite, the interlayer space between the clay platelets is not sufficient for the polymer chains to intercalate between them. In the intercalated composite, the interlayer distance is sufficiently high for the polymer chains to insert themselves between the clay platelets, but the clay platelets still have a well-defined spatial attraction to each other. In the exfoliated composite, the clay platelets have no spatial attraction to each other. They are completely separated from each other and well dispersed throughout the matrix leading to the formation of complete interface polymer-clay composite [123,141]. Exfoliated composites offer the highest surface area for Lewis acid-base interactions between the platelets and the polymer.

The exfoliated clay dispersion was used as stock solution. In the following pages, the bare electrospun membrane will be referred to as P(VdF-co-HFP)-clay(x%)-ESM and the GPE after activation will be referred to as P(VdF-co-HFP)-clay(x%)-GPE ($x = 1-2$ wt.%). The effect of decreased ionic coupling by varying the clay content on the electrochemical and mechanical properties of the composites was studied.

Fig.4.32 Effect of ultra-sonication on composite formation [141]. Reprinted with permission from publisher

The surface morphology of the electrospun composite membranes are shown Fig.4.33. It was seen that by optimizing spinning condition, a uniform multilayered three dimensional network of ultrathin fibers with bead free morphology was obtained [141]. The membranes with clay exhibits comparatively uniform fiber diameter and pore structure, with high surface roughness [141].

Fig.4.33 Surface morphology of P(VdF-*co*-HFP)-clay(x%) ESM ;(a) x=1% and (b)x= 2% [141]

The effect of clay and relationship between AFD and porosity is shown in Fig.4.34. The AFD is highly dependent on solution viscosity. Low viscosity polymer solution makes thinner jet, resulting the loose packing of fibers on the collection drum [141]. This leads to membranes with lower AFD and higher porosity [141].

Fig.4.34 Effect of clay content on the average fiber diameter and porosity

AFD is also influenced by the conductivity of the spinning solution. Increasing conductivity of the solution leads to deposition of thinner fibers with lower AFD. It was seen that the AFD of the bare P(VdF-co-HFP) ESM was 1.5 μm . AFD of P(VdF-co-HFP)-clay(1%)-ESM and P(VdF-co-HFP)-clay(2%)-ESM was 1.3 and 2.3 μm respectively [141]. With increasing clay content, the viscosity increases, because the P(VdF-co-HFP) chains associate with the platelets to establish a highly entangled network [141]. The AFD of 1 wt.% composite ESM shows the optimum balance of viscosity and conductivity leading to thinner fibers with narrow and uniform fiber diameter distribution [141]. The porosity followed the same trend as AFD. P(VdF-co-HFP)-clay(1%)-ESM showed the highest porosity (87%), while bare P(VdF-co-HFP)-ESM and P(VdF-co-HFP)-clay(2%)-ESM showed porosity of 83 and 80%, respectively [141].

Fig.4.35 shows the EDX spectrum of P(VdF-co-HFP)-clay(2%)-ESM. The presence of the peaks corresponding to Al and Si for the clay and C and F for the

polymer proves that the clay has been uniformly dispersed in the polymer matrix.

It also confirms the presence of clay in the ESM.

Fig.4.35 EDX of P(VdF-*co*-HFP)–clay(2%)–ESM [141]. Reprinted with permission from publisher

The DSC curves of the electrospun membranes are shown in Fig.4.36. The presence of an intense melting peak indicates the semi-crystalline nature of the composites [141]. The crystallinity was calculated from the heat of fusion, which was obtained from the endotherm area bounded by the melting curve and the base line [141]. The crystallinity values are tabulated in Table.4.5. The decreasing crystallinity with increasing clay content can be attributed to the following reasons; (i) presence of a disordered exfoliated structure and crystal transformation from α to β phase, (ii) decreasing crystallinity with increasing clay content, attributed to steric hindrance and Lewis acid–base interaction between polymer chains and clay tactoids, and (iii) slowdown of crystallization kinetics caused by the clay platelets [141]. The decrease in crystallinity is beneficial for ion conduction.

Fig.4.36 DSC of P(VdF-co-HFP)-clay composites [141]. Reprinted with permission from publisher

The TGA curves of the electrospun membranes are shown in Fig.4.37. The observed char yield at 800 °C is 20, 24 and 28% for bare P(VdF-co-HFP)-ESM, P(VdF-co-HFP)-clay(1%)-ESM and P(VdF-co-HFP)-clay(2%)-ESM, respectively. Higher char yield indicates improved thermal stability with increasing clay content.

The improved thermal stability can be attributed to the following factors. Firstly, higher thermal energy is required to initiate chain scission due to the restricted chain motion in the confined composite morphology [141]. Secondly, the exfoliated and well dispersed high aspect ratio clay platelets may hinder the outward diffusion of decomposed volatile products and act as an insulating surface. This may slow down the degradation of the underlying material and weight loss of decomposed materials [141].

Fig.4.37 TGA of P(VdF-*co*-HFP)-clay composites [141]. Reprinted with permission from publisher

The XRD patterns of the membranes and clay before sonication is shown in Fig.4.38. The characteristic peak at $2\theta = 6.9^\circ$ in Fig.4.38 (a), corresponds to (001) plane of clay with a basal spacing of 1.3 nm. In the P(VdF-*co*-HFP)-clay composites, no characteristic peak was seen in the 2θ range of $2-10^\circ$. The absence of the peak confirms the exfoliation of clay [141]. From Fig.4.38 (b), it was seen that PVdF predominantly has α crystals with characteristic 2θ peaks at 17.9° (α (020)), 18.4° (α (100)), 19.9° (α (110)), 20.1° (β (200)/ β (110)) and 26.1° (α (021)). With increasing clay content, the intensities of α (020), β (200)/ β (110) and α (021) diminished. This suggests that the clay probably acts as a nucleation centre for the transformation of non-polar α to polar β phase crystals [123]. The increased polarity due to this crystal transformation is beneficial for increasing the ion dissociation [182]. The widening of the peaks further supports the reduction of crystallinity observed from the DSC data.

Fig.4.38 (a) Small angle and (b) Wide angle XRD pattern of P(VdF-co-HFP)-clay composites [141]. Reprinted with permission from publisher

The TEM image of the P(VdF-co-HFP)-clay composites is shown in Fig. 4.39. It was seen that the clay platelets are well dispersed in the polymer matrix. The absence of long distance ordering of the clay particles was observed in both

the compositions, with the silicate layers having no spatial attraction to each other. The silicate layers appear to exist as single and double layers with no stacking [183].

Fig. 4.39 TEM image of P(VdF-co-HFP)-clay(x%) ESM ;(a) x=1% and (b)x= 2%

The mechanical strength of the membranes was studied and the results are tabulated in Table.4.5. It was seen that the mechanical properties showed an increasing trend with increasing clay content [141]. The ultimate tensile strength and Young's modulus increase with increasing clay content, due to the reinforcing nature of the clay platelets. Increasing tensile strength with clay content indicates that uniformly dispersed clay tactoids inhibits stress concentration and improves the load bearing capacity of composite membranes [141].

Table.4.5.Properties of P(VdF-*co*-HFP)-clay composites

Clay content (wt.%)	Crystallinity (%)	Tensile Strength (MPa)	Young's modulus (MPa)	Electrolyte uptake (%)	Retention ratio	Ionic conductivity at 30 °C (mS/cm)	Transference number (T_{Li^+})
0	43	4.5±0.3	9.2±0.3	400	0.90	2.9	0.42
1	40	8.2±0.3	10.4±0.3	456	0.92	5.5	0.57
2	38	9.1±0.3	11.1±0.3	474	0.92	4.1	0.51

The electrolyte uptake of the GPEs is shown in Fig.4.40 and the values tabulated in Table.4.5.

Fig.4.40 Electrolyte uptake of P(VdF-*co*-HFP)-clay GPEs [141]. Reprinted with permission from publisher

It was seen that the uptake process was rapid and was almost stabilized in 15 min [141]. The electrolyte uptake increased with increasing clay content. The electrolyte retention characteristics were studied and it was seen that all the membranes maintain their gel structure with storage time. The retention ratios of the GPEs are tabulated in Table.4.5. The high retention of the composite GPEs showed that a stable low leak gel was formed by the incorporation of clay. The high porosity, fast uptake, affinity of the polymer and clay to the electrolyte leads to a stable gel formation.

Temperature dependent ionic conductivity of GPEs was determined in the -20 to 70 °C temperature range and the results are shown in Fig.4.41.

Fig.4.41 Temperature dependent ionic conductivity of P(VdF-*co*-HFP)-clay composite GPEs [141]. Reprinted with permission from publisher

The $\log \sigma$ vs $1000/T$ curves were plotted to see if conductivity follows Arrhenius function of VTF function. The curvature of the $\log \sigma$ vs $1000/T$ plot (Fig.4.41), suggests that the ionic conductivity follows the VTF function [138]. The ionic conductivity obtained from the impedance data was fitted using nonlinear least square fitting and the results are shown in Fig.4.41. The parameters are tabulated in Table 4.6. It was seen that a good fit was obtained for all the GPEs. The ionic conductivity at 30 °C (mS/cm) for the composite GPEs is calculated and tabulated in Table.4.5. The ionic conductivity increased with increasing clay content upto 1 wt.% clay content.

Table 4.6 VTF parameters of P(VdF-*co*-HFP)-clay composite GPEs

Clay content (wt.%)	σ_0 (S/cm/K)	E_a (eV)	T_o (°C)
0	0.19	0.08	109
1	0.124	0.058	111
2	0.116	0.067	114

Three types of possible complex formations in the P(VdF-*co*-HFP)-clay composite based GPEs are shown in Fig.4.42 [141]. In bare P(VdF-*co*-HFP) GPE, only possibility is the formation of Complex I [141]. Complex III may form within the clay phase and Complex II at the interphase of P(VdF-*co*-HFP) and clay [141]. The extent of formation of Complexes II and III greatly depends on the amount of clay in the composite and extent of exfoliation of the clay [141]. Presence of excess clay platelets or insufficient exfoliation may lead to reduced ionic conductivity. In the P(VdF-*co*-HFP)-clay composite GPEs, the cationic charges on the surface of clay tactoids act as Lewis acid centers and compete with

Li^+ cations to form complexes i.e. II and/or III. This leads to lowered ion coupling between lithium ions and the polymer chain/ the PF_6^- anions. This may cause the structural modification and promotion of Li^+ conducting pathways at the surface of the clay tactoids [141].

Fig.4.42 Complex formation (a) Complex I, (b) Complex II, and (c) Complex III

[141]. Reprinted with permission from publisher

The improved ionic conductivity of the P(VdF-*co*-HFP)-clay composite GPEs can also be attributed to the higher electrolyte uptake and lowered crystallinity. The higher uptake of the P(VdF-*co*-HFP)-clay composite membranes leads to an increase in the number of charge carriers and therefore an increase in ionic conductivity. The decreased crystallinity due to the presence of exfoliated clay platelets also contributes towards increasing ionic conductivity.

Compared to P(VdF-*co*-HFP)-clay(1%)-GPE, ionic conductivity of P(VdF-*co*-HFP)-clay(2%)-GPE is lower, even though it shows higher electrolyte uptake. This phenomenon may be due to the fact that excess clay platelets may clutch the Li^+ ions tightly, and thus restrict the mobility of cations and decreasing the conductivity. Also the extent of complex III formation may be higher leading to lower interaction with the polymer chains. The ionic conductivity of P(VdF-*co*-HFP)-clay(1%)-GPE is 90% higher than the bare P(VdF-*co*-HFP) GPE.

The initial interfacial resistance between the GPE and lithium metal is plotted in Fig.4.43. It was seen that impedance spectrum shows a distorted semi-circle in the middle frequency range. The expansion with storage time indicates the formation and growth of passivation layer at the GPE and lithium metal interface [141]. The real axis intercept at the high frequency end of the spectrum denotes the R_b of the polymer electrolyte and the real component of the impedance at the lowest frequency is representative of the Li/electrolyte interfacial resistance (R_f). The low R_b values (magnified region of Fig.4.43) follows the same trend as the ionic conductivity, with P(VdF-*co*-HFP)-clay(1%)-GPE having the lowest value. The lower interfacial resistance (R_f) of the

composite GPEs is due the better adhesion of the GPE with lithium metal, owing to the increased surface roughness. Presence of exfoliated clay tactoids with high aspect ratio on fiber surface forms a barrier layer at the electrode. This barrier effectively impedes the formation of passivation layer on the electrode leading to reduced interfacial resistance [87].

Fig.4.43 Initial interfacial resistance of P(VdF-co-HFP)-clay composite GPEs [141]

The interfacial resistance (R_f) of the GPEs over time is shown in Fig.4.44. The R_f increases with time. This increase in R_f with storage time is associated with the growth of passivation layer on the lithium electrode surface and degradation of physical contact between the electrode and GPE [141]. After one day of storage, all the GPEs showed significant increase in R_f , which was about 100 to

135% higher than the initial value [141]. The R_f for the composite GPEs gets stabilized after storage time of 6 days. The R_f for the bare P(VdF-*co*-HFP) GPE increases even after 8 days. After 10 days of storage, R_f for P(VdF-*co*-HFP)-clay(1%)-GPE and P(VdF-*co*-HFP)-clay(2%)-GPE was observed to be 104 and 129 Ω respectively, while R_f for bare P(VdF-*co*-HFP) GPE was 268 Ω . Thus, the presence of intercalated/exfoliated clay platelets effectively reduces the time needed for stabilization of the passivation layer on the lithium surface. It also prevents any undesirable interaction between electrolyte and lithium electrodes.

Fig.4.44 Time dependent interfacial resistance of P(VdF-*co*-HFP)-clay composite GPEs

The lithium transference number (T_{Li}^+) was measured using DC polarization technique. The values are tabulated in Table.4.5. It was seen that T_{Li}^+ of the P(VdF-*co*-HFP)-clay(2%)-GPE was lower than P(VdF-*co*-HFP)-clay(1%)-GPE. The T_{Li}^+ follows the same trend of ionic conductivity. This further supports

the hypothesis that the excess clay platelets may clutch the lithium ions, thereby leading to lower number of charge carriers.

The cycling stability of the Li/LiFePO₄ cells over 50 cycles at 0.1C was studied and the results are shown Fig.4.45. The cycling stability was also compared with the commercial Celgard separator. The cell with P(VdF-*co*-HFP)-clay(1%)-GPE and P(VdF-*co*-HFP)-clay(2%)-GPE delivered an initial discharge capacity of 160 and 154 mAh/g respectively. The cell with bare P(VdF-*co*-HFP) GPE and Celgard shows an initial discharge capacity of 149 and 132 mAh/g.

After 50 cycles, the cell with P(VdF-*co*-HFP)-clay(1%)-GPE and P(VdF-*co*-HFP)-clay(2%)-GPE delivered a discharge capacity of 147 and 140 mAh/g. The cell with bare P(VdF-*co*-HFP) GPE and Celgard delivered 136 and 124 mAh/g. The discharge capacity delivered by the cell with composite GPEs was 2-8% higher than cell comprising bare P(VdF-*co*-HFP) GPE [141]. The capacity of the composite GPEs was 12-18% higher than the cell with Celgard. The capacity retention of all the electrospun GPEs was higher than the cell with Celgard. This can be attributed to the formation of low leak stable gel. Slight capacity fade observed for the electrospun GPEs may be due to the progressive decomposition and/or leakage of the electrolyte. Also the structural characteristics and composition of cathode materials play a vital role on the capacity of the cell and cycling performance [141]. The capacity retention ratio of the cell with P(VdF-*co*-HFP)-clay(1%)-GPE after 50 cycles was observed to be ~92% (calculated based on initial discharge capacity).

Fig.4.45 Cycling properties of Li/ LiFePO₄ cells with P(VdF-*co*-HFP)-clay composite GPEs [141]

The performance of the cells at various current densities was evaluated and the results are shown in Fig.4.46. The cells were cycled between 0.1 and 3C-rate and back to 0.2C-rate for 10 cycles each continuously. The cells showed good discharge capacity and cycling performance even at higher C-rate and retain similar capacity after the current density is changed back to 0.2C-rate after 40 cycles, which clearly demonstrates high capacity retention of the cells [141]. The lower capacity at high current densities can be attributed to the nature of the cathode material. The LiFePO₄ cathode material is known to suffer the limitation of lower performance at higher C-rate and reduced temperatures due to slow Li⁺ ion diffusion at the solid, two-phase boundary of LiFePO₄/FePO₄ [184].

Fig.4.46 Rate capability of Li/LiFePO₄ cells with P(VdF-*co*-HFP)-clay composite GPEs [141]. Reprinted with permission from publisher

4.3.1.2 P(VdF-*co*-HFP)-BDN composite GPE

The effect of increased lithium salt dissociation and increased charge carrier mobility was studied using P(VdF-*co*-HFP)-BDN composite GPEs. Reported BDN-salt electrolytes conduct only in the plastic phase (between -38 and 58 °C) due to presence of trans-gauche isomerism involving rotation of molecules about the central C–C bond [138]. The trans isomer is an impurity phase which results in enhancement of lattice defects and lowering of activation energy for ionic conduction, thereby directly affecting the ionic conductivity [185]. BDN has high dielectric constant ($\epsilon=55$) and therefore, it leads to increased lithium salt dissociation. The effect of increased salt dissociation by adding different amounts of BDN to the polymer on the electrochemical and mechanical properties was examined. The presence of active ion hopping centres on BDN increases the

lithium ion mobility in the system [186–188]. The scheme for the preparation of the composite membrane is shown in Fig.4.47. In the following pages, the membranes are designated as ESM-01, ESM-02 and ESM-03 respectively for electrospun membrane based on P(VdF-co-HFP) with BDN content (wt.%) 3, 6 and 9 to highlight their composition.

Fig.4.47 Scheme for preparation of BDN composite membranes by electrospinning

The surface morphology of the membranes was studied with FE-SEM. Fig.4.48 shows the FE-SEM images of P(VdF-co-HFP)-BDN composite membranes. It was seen that the membranes exhibit three dimensional network of fibers, with large number of fully interconnected pores formed by the interlaying of fibers [138]. This indicates that fast evaporation of solvent takes place during electrospinning. The interlaying of fibers impart sufficient mechanical strength to the membrane and fully interconnected micron-sized pores in the membranes make them an ideal host matrix for preparing gel polymer electrolytes [138].

The average fiber diameter was measured to be 1.9, 1.7 and 0.7 μm for ESM-01, ESM-02 and ESM-03 respectively. It was seen that average fiber diameter (AFD) decreases with increasing BDN content. Compared to ESM-02 and ESM-03, ESM-01 showed relatively higher AFD. The decrease in AFD with increasing BDN content can be attributed to the reduced viscosity and increased dielectric constant of the spinning solution [138]. Compared to other membranes, ESM-03 showed narrow fiber distribution and more uniform fibers. This can be attributed to the synergetic effect of viscosity and conductivity of the solution [138].

Fig.4.48 Surface morphology of (a) ESM-01, (b) ESM-02 and (c) ESM-03 [138]

As mentioned previously, ionic conductivity and cycle performance of GPEs greatly depends on the amount of liquid electrolyte encapsulated in the polymer matrix, which is primarily determined by porosity of the membrane [138]. Higher porosity of the membrane can increase the contact area between the polymer and liquid electrolyte. Increased surface area leads to increases retention of the electrolyte in the polymer. Thus higher amount of gel phase is formed, which is the high conduction channels for GPEs [127,138]. The values of porosity are tabulated in Table.4.7. Higher porosity for ESM-03 is due to the lower AFD, which results in loose packing of fibers and thereby higher porosity [138].

Table.4.7.Properties of P(VdF-*co*-HFP)-BDN composites

Membrane	Crystallinity (%)	Porosity (%)	Tensile strength (Mpa)	Young's modulus (MPa)	Ionic conductivity at 30 °C (mS/cm)	Lithium transference number (T_{Li}^+)
P(VdF- <i>co</i> -HFP)	43	80	4.5 ± 0.3	9.2 ± 0.3	2.9	0.42
ESM-01	35	82	4.1 ± 0.3	8.8 ± 0.3	4.1	0.47
ESM-02	32	85	3.5 ± 0.3	8.3 ± 0.3	5.0	0.48
ESM-03	30	88	2.8 ± 0.3	7.7 ± 0.3	6.3	0.49

The degree of crystallinity of the membranes was evaluated from DSC thermograms shown in Fig.4.49. The values are tabulated in Table.4.7. It was also observed that incorporation of BDN reduces the crystallinity of P(VdF-*co*-HFP) from 43 to 30% [138].

Fig.4.49 DSC of P(VdF-*co*-HFP)-BDN composites [138]. Reprinted with permission from publisher

The TGA profiles of ESM-01, 02 and 03 is compared with P(VdF-*co*-HFP) membrane and the results are shown in Fig.4.50.

Fig.4.50 TGA of P(VdF-*co*-HFP)-BDN composites [138]

It was seen that decomposition was almost over by 485 °C, after which the rate of decomposition slows down rapidly. The observed weight loss at 485 °C was 26, 29 and 31% for ESM-03, ESM-02 and ESM-01 respectively. The char yield at 700 °C was 19, 21 22 and 21% for ESM-03, ESM-02, ESM-01 and P(VdF-*co*-HFP) respectively.

Fig.4.51 shows the comparison of electrolyte uptake of P(VdF-*co*-HFP)-BDN composite GPEs with bare P(VdF-*co*-HFP) GPE. The uptake of all samples was very fast and reached equilibrium state in about 15 min. The electrolyte uptake (%) of P(VdF-*co*-HFP)-BDN composite membranes was in the order of ESM-03 > ESM-02 > ESM-01 > P(VdF-*co*-HFP) GPE.

Fig.4.51 Electrolyte uptake of P(VdF-co-HFP)-BDN composite GPEs [138].

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It was observed that electrolyte uptake increases with increasing BDN content, which shows that BDN has good affinity to the polar organic solvent. The higher uptake of the composite membranes can be attributed to the polarity of host matrix, presence of BDN, low average fiber diameter, interconnected pore structure, porosity and partial gelation of the membranes [120,133,137,138].

The electrolyte retention properties of the composite GPE were evaluated. The relative retention ratio R , which is the ratio of liquid electrolyte retained in the GPE over time, is shown in Fig.4.52. Higher retention ratio indicates lower leakage and formation of a more stable gel. It was observed that leakage characteristics tend to reach an equilibrium state within 2 h [138]. It was seen that the composite GPEs show lower retention when compared to P(VdF-co-HFP) GPE. However, the electrolyte retention properties of the GPEs are comparable to those reported for P(VdF-co-HFP) fibers with AFD $\sim 1.2 \mu\text{m}$ [79]. The electrolyte retention in this study was lower than the membranes with clay. The greater

leakage compared to bare P(VdF-*co*-HFP) GPE indicates the formation of a less stable gel.

Fig.4.52 Electrolyte retention of P(VdF-*co*-HFP)-BDN composite GPEs [138]

The mechanical stability of the GPEs was studied. The tensile strength and Young's modulus values are tabulated in Table.4.7. It was seen that ultimate tensile strength and Young's modulus decreased with increasing BDN content. A reduction of 20-40% in mechanical properties was seen by the addition of BDN. This can be attributed to the plastic, waxy nature of BDN. BDN retains its solid waxy state only till 57 °C.

The temperature dependent ionic conductivity of the GPEs in the temperature range -20 to 70 °C was studied. The $\log \sigma$ vs $1000/T$ curves were plotted to see if the conductivity resembles Arrhenius function or VTF function. The curves are shown in Fig.4.53. The curvature in the $\log \sigma$ vs $1000/T$ plot (Fig.4.53) indicates that the ionic conductivity follows the VTF function [138].

The ionic conductivity at 30 °C (mS/cm) calculated from Fig.4.53 is tabulated in Table.4.7.

Fig.4.53 Temperature dependent ionic conductivity of P(VdF-co-HFP)-BDN composite GPEs [138]. Reprinted with permission from publisher

The ionic conductivity obtained from the impedance data was fitted using nonlinear least square fitting and the results are shown in Fig.4.53. The parameters are tabulated in Table 4.8. It was seen that a good fit was obtained for all the GPEs. The activation energy decreases with increasing BDN content, further supporting the increased ionic conductivity.

Table 4.8 VTF parameters of P(VdF-co-HFP)-BDN composite GPEs

GPE	σ_0 (S/cm/K)	E_a (eV)	T_o (°C)
P(VdF-co-HFP)	0.19	0.08	109
ESM-01	0.124	0.056	108
ESM-02	0.116	0.052	106
ESM-03	0.110	0.048	104

Ionic conductivity of ESM-03 is 117% higher than the pristine P(VdF-*co*-HFP) GPE [138]. The observed high values of ionic conductivity of the composite GPEs can be attributed to the synergistic effect of high electrolyte uptake, lower crystallinity and increased charge carrier concentration [56,185]. The most significant factor affecting ionic conductivity in the P(VdF-*co*-HFP)-BDN composites is however the increased lithium salt dissociation and increased mobility.

Decrease in crystallinity increases the chain flexibility of the polymer and reduces the lattice-like rigidity of BDN. This results in enhancement of rate of transition from gauche to trans state. The increased amount of trans phase (impurity phase) leads to increased ionic conductivity [188]. The increased amount of trans phase coupled with the high dielectric constant of BDN, leads to increased dissociation of lithium. The increased charge carrier concentration leads to increased ionic conductivity.

From Fig.4.53, it was seen that the conductivity sharply decreases below 0 °C (3.6K^{-1}), due to the freezing property of carbonate solvents in the electrolyte solutions [84]. However the conductivity is still comparatively high here because of the presence of BDN which acts as a good solvating medium above -38 °C [188]. BDN exists in plastic phase between -38 °C and 58 °C. Both gauche and trans (low energy, high defect state of BDN) isomers exist in this temperature range [56,185,189]. At temperature above 0 °C, gauche to trans transformation takes place and the concentration of the defect rich state increases. This in turn reduces the activation energy for ion transport, thereby improving ionic

conductivity [189]. Thus compared with the GPE based on pristine P(VdF-*co*-HFP), the incorporation of BDN greatly enhances the ionic conductivity of the GPE especially at low temperature. At -20°C , the ionic conductivity of ESM-03 was 1.5 mS/cm, which is 3 times higher than GPE based on pristine P(VdF-*co*-HFP) (0.5 mS/cm).

The lithium transference number (T_{Li}^{+}) of the composite GPEs was measured and the results tabulated in Table.4.7. It was seen that there was no significant difference in the T_{Li}^{+} values of ESM-01, 02 and 03. The values were slightly higher than that of the bare P(VdF-*co*-HFP) GPEs.

The time dependent interfacial resistance R_f of the GPEs is presented in Fig.4.54. The cells with P(VdF-*co*-HFP)-BDN GPEs showed an interfacial resistance (R_f) $< 65\ \Omega$ initially, whereas GPE based on pristine P(VdF-*co*-HFP) showed R_f value of 94 Ω . The initial R_f of the cell was observed to be 46, 50, 65 and 94 Ω respectively for the GPEs with BDN content of 3, 6 9 and 0 wt.%. The R_f for all GPEs increased slightly with storage time, but the increase for ESM-01,02 and 03 was lower than that of bare P(VdF-*co*-HFP) GPE [138]. After 7 days of storage the cell with pristine P(VdF-*co*-HFP) showed R_f value of 268 Ω , which is 88-147% higher than P(VdF-*co*-HFP)-BDN GPE. It was observed that R_f of ESM-01, 02 and 03 gets stabilized within 4 days. But the R_f of bare P(VdF-*co*-HFP) GPE increases slightly upon storage even after 7 days. The increase in interfacial resistance with storage time may also be associated with degradation of physical contact between the electrode and GPE.

Fig.4.54 Time dependent interfacial resistance of P(VdF-co-HFP)-BDN composite GPEs

The electrochemical stability studies (Fig.4.55) show that by the incorporation of BDN in the polymer matrix, the electrochemical stability of composite GPEs was enhanced to >4.7 V [138] .

Fig.4.55 Electrochemical stability window of P(VdF-co-HFP)-BDN composite GPEs

The stability of the GPE without BDN was 4.6 V. The voltage corresponding to the onset of a steady and continuous increase of current indicates the electrochemical stability limit of the electrolyte [179]. Thus, the composite GPEs electrolytes have good anodic stability versus Li/Li^+ , i.e., sufficient to be compatible with most of the common cathode materials used for lithium ion batteries. A good interface with lithium is a very important necessity for electrolytes in Li metal batteries. A good SEI layer formation indicates good cycling without capacity fading.

Fig.4.56 shows the cycling stability of the GPEs at 0.1 C rate over 50 cycles [138]. A cell with commercial separator (Celgard) was also included for comparison.

Fig.4.56 Cycling properties of Li/LiFePO₄ cells with P(VdF-co-HFP)-BDN composite GPEs [138]

The cell with ESM-01, ESM-02 and ESM-03 showed initial discharge capacity of 152, 155 and 160 mAh/g which corresponds to 90-94% of the

theoretical capacity (170 mAh/g) of the active material [138]. The cell with Celgard showed an initial discharge capacity of ~130 mAh/g [138]. After 50 cycles the cells with the electrospun GPEs exhibit capacity retention of 94%, calculated based on the initial discharge capacity. The cell with Celgard has a lower retention (91%). The higher capacity fade may be due to the leakage of electrolyte [138].

Owing to the better ionic conductivity and cycling stability of ESM-03, when compared to ESM-02 and ESM-01, the rate capability of ESM-03 was compared with bare P(VdF-*co*-HFP) GPE and Celgard, at different current densities and shown in Fig.4.57. The cells were cycled between 0.1 and 3C-rate and back to 0.2C-rate for 10 cycles each continuously. The cells showed good discharge capacity and cycling performance even at higher C-rate and retain similar capacity after the current density is changed back to 0.2C-rate after 40 cycles, which clearly demonstrates high capacity retention of the cells.

The capacity was normalized by the capacity obtained at 0.1 C rate to study the effect of porosity. The nature of the porous membrane has a poor effect on the cycling test performances at low rate [190,191]. At high C rates, the effect of the membrane morphology is observed [190,191]. At low C rates, it is seen that both Celgard and the electrospun GPEs have similar capacities. But at 3 C rate, ESM-03 shows much higher capacity compared to the Celgard membrane. The capacity of the bare P(VdF-*co*-HFP) GPE is also slightly lower than ESM-03 at 3C rate. The lower capacity of Celgard is attributed to the fact that, at a fixed thickness, a less conductive electrolyte results in an increase of the ohmic drop

and ion concentration gradient in the electrolyte leading to lower capacity [138,190,191]. The lower interfacial resistance, higher ionic conductivity, porosity, electrolyte uptake and pore structure of the composite GPE are responsible for the higher normalized capacity.

Fig.4.57 Normalized rate capability of Li/LiFePO₄ cells with P(VdF-*co*-HFP)-BDN composite GPEs [138]. Reprinted with permission from publisher

4.3.1.3 P(VdF-*co*-HFP)-LAGP composite GPEs

The combined effect of decreased ion coupling and increased charge carrier concentration was studied using P(VdF-*co*-HFP)-LAGP composite GPEs. LAGP combines the advantages of clay and BDN. Lithium aluminum germanium phosphate (LAGP) is a glass ceramic belonging to the NASICON family. It crystallizes in a rhombohedral NASICON-type structure, consisting of an open three-dimensional framework of GeO₆ octahedra, sharing all corners with PO₄

tetrahedra. Both units are linked by their corners to form a three dimensional network structure. Al replaces part of the Ge to form $\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$ [192]. The substitution decreases the unit cell dimension, which in turn enhances the ionic conductivity by more than two orders of magnitude [193]. This structure results in cavities, where lithium ions reside and bottlenecks, through which they move.

LAGP is a fast single ion conductor with good mechanical strength, thermal and chemical stability [192]. The advantage of using LAGP as a filler in P(VdF-*co*-HFP) based GPEs is two-fold. Firstly, it acts as any other ceramic filler to improve the mechanical properties and reduce ion coupling by the formation of Lewis acid-base complex with the polymer. Secondly, being a fast lithium ion conductor, it acts as a source of lithium ions and increases the number of mobile charge carriers in the system. Owing to the unity lithium transference number it also leads to an increase in transference number of the resulting composite GPE. The LAGP content was varied between 3 and 15 wt.% to study the effect of increased lithium ion concentration and reduced ionic coupling with increasing LAGP content on the composite GPEs. The membranes and the GPEs in this section will be referred to as P(VdF-*co*-HFP)-LAGP(x%)-ESM and P(VdF-*co*-HFP)-LAGP(x%)-GPE (x represents the wt.% of LAGP).

The LAGP synthesized via solid state and sol gel were characterized using Rietveld Refinement and the results are shown in Fig.4.58. The refinement shows significant improvement of LAGP phase employing sol gel methodology with close to 100 % phase purity obtained as compared to LAGP synthesized from

solid state. The LAGP prepared by solid state had only 71.71 wt.% of LAGP with impurities such as GeO_2 20.44 wt.% and AlPO_4 7.85 wt.%. For the sample prepared by sol gel process, no resistive oxide phases were seen.

Fig.4.58 Rietveld refinement of (a) solid state sample, and (b) sol gel sample

For ionic conductivity measurement, the sintered LAGP was pressed into pellets of thickness 1 mm using a pressure of 10 tonnes. A thin layer of gold was sputter coated on both sides of the pellet. The pellet was then assembled in SS/LAGP/SS configuration and the temperature dependent ionic conductivity measured in the same way as the GPE samples.

Ionic conductivity of LAGP synthesized by solid state and sol gel methodologies was measured. The ionic conductivity at 25 °C for the solid state sample was 3 mS/cm and the ionic conductivity of the sol gel sample was 4.82 mS/cm respectively. The higher ionic conductivity of the sol gel sample can be attributed to the lesser amount of the resistive impurity phase as discussed above. The higher ionic conductivity may also be due to smaller particle size of the LAGP particles synthesized by sol gel method, when compared to solid state method. Due to its superior ionic conductivity and purity, the LAGP prepared by sol gel method was chosen for further study.

The morphology of the composite membranes was studied using FESEM. The FESEM images are shown in Fig.4.59. It was seen that the membranes consist of a three dimensional network of fibers with multiple layers. The fibers in the multiple layers were interconnected with a large number of pores between them. The membranes show uniform fiber diameter and pore structure without the presence of any beading. The membranes displayed sufficient mechanical integrity.

Fig.4.59 Morphology of membranes with varying LAGP content (wt.%) (a) 0 (b) 3 (c) 6 (d) 9 (e)12 and (f) 15

The fiber distribution histograms of the membranes are shown in Fig.4.60.

Fig.4.60 Histograms of membranes with varying LAGP content (wt.%) (a) 0 (b) 3 (c) 6 (d) 9 (e)12 and (f) 15

The changes in fiber diameter and diameter distribution can be attributed to the altered surface tension, electrostatic repulsion and viscoelastic force caused by the presence of lithium-ion conducting LAGP particles [179,193]. It was seen

that as LAGP content increases, the fiber distribution histogram becomes narrower, with more fibers exhibiting uniform and closer diameter. The porosity of the composite membranes follows the order P(VdF-*co*-HFP)-LAGP(15%)-ESM > P(VdF-*co*-HFP)-LAGP(12%)-ESM > P(VdF-*co*-HFP)-LAGP(9%)-ESM > P(VdF-*co*-HFP)-LAGP(6%)-ESM > P(VdF-*co*-HFP)-LAGP(3%)-ESM > bare P(VdF-*co*-HFP) ESM.

The electrolyte uptake of the porous membrane as mentioned greatly depends on the porosity and pore structure of the membranes. Fig.4.61 shows the comparison of electrolyte uptake of the P(VdF-*co*-HFP)-LAGP composite electrospun membrane with varying LAGP content.

Fig.4.61 Electrolyte uptake of P(VdF-*co*-HFP)-LAGP composite GPEs

By adding 15 wt.% LAGP, the electrolyte uptake increased from 400% to 527%. The electrolyte uptake follows the order P(VdF-*co*-HFP)-LAGP(15%)-GPE > P(VdF-*co*-HFP)-LAGP(12%)-GPE > P(VdF-*co*-HFP)-LAGP(9%)-GPE >

$P(\text{VdF-co-HFP})\text{-LAGP}(6\%)\text{-GPE} > P(\text{VdF-co-HFP})\text{-LAGP}(3\%)\text{-GPE} > \text{bare } P(\text{VdF-co-HFP}) \text{ GPE}$. The high electrolyte uptake with addition of LAGP can be attributed to the increased porosity, surface roughness, higher dielectric constant and lower AFD.

To test the stability of the GPE to retain the absorbed liquid electrolyte, the electrolyte retention characteristics were studied. The electrolyte retention ratio of the membranes is shown in Fig.4.62. It was seen that all the membranes have high retention ratio, which means that leakage was minimal.

Fig.4.62 Electrolyte retention of $P(\text{VdF-co-HFP})\text{-LAGP}$ composite GPEs

It was observed that leakage characteristics tend to reach an equilibrium state within 2 h. The highly interconnected pore structure of the membranes makes it an efficient matrix to soak up the electrolyte, and maintain the gel nature even upon application of external force. Thus a stable, low leak gel (no free flowing liquid electrolyte was formed when the membranes are activated with liquid electrolyte.

The degree of crystallinity for the composites membranes was evaluated from the heat of fusion, obtained from DSC and the values are tabulated in Table.4.9. It was observed that incorporation of LAGP reduces the crystallinity of P(VdF-*co*-HFP) from 43 to 31%. The decrease in crystallinity with the addition of LAGP confirms that addition of LAGP slows down and inhibits the crystallization kinetics [138]. This in turn increases the amorphous content of the polymer, thereby leading to higher ionic conductivity.

Fig.4.63 shows the TGA curves of both the pristine membrane and the membranes with LAGP.

Fig.4.63 TGA of P(VdF-*co*-HFP)-LAGP composites

The onset decomposition temperature is tabulated in Table.4.9. The initial onset decomposition temperatures of the membranes follows the order P(VdF-*co*-HFP)-LAGP(15%)-ESM > P(VdF-*co*-HFP)-LAGP(12%)-ESM > P(VdF-*co*-HFP)-LAGP(9%)-ESM > P(VdF-*co*-HFP)-LAGP(6%)-ESM > P(VdF-*co*-HFP)-LAGP(3%)-ESM > bare P(VdF-*co*-HFP). Shift of thermal decomposition

temperature towards higher temperature range for P(VdF-*co*-HFP)-LAGP membranes confirms enhancement in thermal stability.

The observed char yield at 800 °C follows the order P(VdF-*co*-HFP)-LAGP(15%)-ESM > P(VdF-*co*-HFP)-LAGP(12%)-ESM > P(VdF-*co*-HFP)-LAGP(9%)-ESM > P(VdF-*co*-HFP)-LAGP(6%)-ESM > P(VdF-*co*-HFP)-LAGP(3%)-ESM > bare P(VdF-*co*-HFP). Higher char yield indicates improvement in thermal stability which can be attributed to higher thermal energy is required to initiate chain scission and the higher melting point of LAGP.

Mechanical strength of membranes was studied and the results are tabulated in Table.4.9.

Table.4.9.Properties of PVdF-*co*-HFP)-LAGP composites

LAGP content(wt.%)	Porosity(%)	Crystallinity (%)	Onset decomposition temperature (°C)	Young's Modulus (MPa)	Tensile strength (MPa)	Ionic conductivity at 30 °C (mS/cm)	Lithium transference number (T _{Li} ⁺)
0	80	43	400	9.2	4.5± 0.3	2.9	0.42
3	81	41	420	10.3	7.1± 0.3	4.6	0.52
6	83	39	424	11.1	7.9± 0.3	5.4	0.59
9	85	37	424	12.6	9.1± 0.3	6.3	0.63
12	87	34	425	14.2	10.9± 0.3	7.0	0.66
15	89	31	426	16.2	12.4± 0.3	8.3	0.68

Both ultimate tensile strength and Young's modulus increased with increasing LAGP content. This can be attributed to reinforcing inorganic component dispersed in the polymer. The incorporation of LAGP improves the load bearing capacity of the membranes. The increasing mechanical strength improves the handleability of the composite membrane.

Ionic conductivity of the GPEs was measured by AC impedance in the temperature range -20 to 70 °C. The $\log \sigma$ vs $1000/T$ curves were plotted to see if the conductivity resembles Arrhenius function or VTF function. It was seen that in the temperature range -20 to 70 °C the $\log \sigma$ vs $1000/T$ curves for all the GPEs are slightly curved, hence the activation energy for ionic conduction E_a can be obtained using the Vogel-Tamman-Fulcher (VTF) model $\{ \sigma = \sigma_0 T^{-1/2} \exp [(-E_a/R(T-T_0))]\}$. This indicates that the conduction mechanism not only involves the increasing dissociation of lithium salt and lowering of ionic coupling but also the segmental motion of the polymer chains.

The ionic conductivity obtained from the impedance data was fitted using nonlinear least square fitting and the results shown in Fig.4.64. The parameters are tabulated in Table 4.10. It was seen that a good fit was obtained for all the GPEs. The activation energy decreases with increasing LAGP content, further supporting the increased ionic conductivity. An enhancement in conductivity with increasing temperature was observed in Fig.4.64. The ionic conductivity at 30 °C was calculated and the values are tabulated in Table.4.9. The ionic conductivity follows the same trend as the electrolyte uptake. The observed high values of ionic conductivity of the P(VdF-co-HFP)-LAGP GPEs can be attributed to the

combined effect of high electrolyte uptake, lower crystallinity, increased charge carrier concentration and reduced ion coupling.

Fig.4.64 Temperature dependent ionic conductivity of P(VdF-co-HFP)-LAGP composite GPEs

As seen previously, with increasing LAGP content, the crystallinity decreases, leading to increased amorphous content and gel phase. Also because of the presence of ceramic particles on the surface of the fiber, weakening of the polymer cation association takes place [194]. The hydroxyl groups on the surface of the sol gel synthesised LAGP can compete with the F atom of the polymer to form complexes with lithium. This results in weakening of polymer-Li ion complex and reduced of ion coupling. The reduced ion coupling leads to increased number of lithium ions.

Table 4.10 VTF parameters of P(VdF-*co*-HFP)-LAGP composite GPEs

LAGP content (wt.%)	σ_0 (S/cm/K)	E_a (eV)	T_0 (°C)
0	0.19	0.08	109
3	0.119	0.058	111
6	0.116	0.054	112
9	0.114	0.050	112
12	0.109	0.046	116
15	0.100	0.041	117

As mentioned previously, LAGP by itself has a high ionic conductivity (4.82 mS/cm). The high ionic conductivity of LAGP may contribute to the overall conductivity. The presence of LAGP in the composite increases the lithium ion concentration of the system, while also improving the lithium ion transference number. The increment in ionic conductivity is attributed to the combined effect of two factors-decreased ionic coupling and increased lithium ion concentration. It is seen that an increment of ~190% when compared to the bare P(VdF-*co*-HFP) GPE, is seen by the combined effect.

The transference number T_{Li}^+ of the composite GPEs was measured by DC Polarization and the values are tabulated in Table.4.9. It was seen that T_{Li}^+ increased with increasing LAGP content.

The stability of GPEs against lithium metal was studied by evaluating its interfacial properties. The final interfacial resistance (R_f) with storage time is plotted in Fig.4.65.

Fig.4.65 Time dependent interfacial resistance of P(VdF-co-HFP)-LAGP composite GPEs

It was seen that the R_f for all the GPEs increased with storage time, denoting the growth and stabilization of the SEI layer. But the increase was very low as compared to other GPEs based on electrospun PVdF [137] or P(VdF-co-HFP) [195]. For the composite GPEs, after the initial enhancement in impedance, the layer characteristics get stabilized within 6 days. For the bare P(VdF-co-HFP) GPE, it was seen that the R_f continued to increase even after 8 days. After 12 days of storage, the R_f value of the P(VdF-co-HFP)-LAGP(15%)-GPE was 86 Ω which is 210% lower than that of the bare P(VdF-co-HFP) GPE. The better stability of the composite GPEs when compared to the bare P(VdF-co-HFP) GPE can be attributed to the LAGP particles, which act as surface stabilizers [179,193].

Owing to the better ionic conductivity and interface properties of the composite with 15 wt.% LAGP when compared to the other compositions, it was

chosen for further evaluation. The electrochemical stability window of the P(VdF-*co*-HFP)-LAGP(15%)-GPE was compared with bare P(VdF-*co*-HFP) GPEs and the results are shown in Fig.4.66. The electrochemical stability studies shows that polymer electrolyte based on pristine P(VdF-*co*-HFP) exhibits an anodic stability up to 4.6 V. By the incorporation of LAGP in the polymer matrix, the electrochemical stability of GPEs is enhanced to >5.1 V. The high anodic stability can be attributed to the excellent affinity of the composite membrane to the carbonate based liquid electrolyte solution. The surface roughness of the fibers with the addition of LAGP may also lead to better adhesion of the electrolyte to lithium surface which also leads to better anodic stability. The LAGP particles also can act as a surface stabilizer and enhance the electrochemical oxidation stability of the composite [179,193].

Fig.4.66 Electrochemical stability window of P(VdF-*co*-HFP)-LAGP composite GPEs

The galvanostatic charge discharge characteristics of the P(VdF-*co*-HFP)-LAGP(15%)-GPE was studied and compared with bare P(VdF-*co*-HFP) GPE and Celgard. Fig.4.67 shows the discharge capacity vs cycle number for the Li/LiFePO₄ cells, cycled at 0.1 C rate for 50 cycles. The cell with P(VdF-*co*-HFP)-LAGP(15%)-GPE showed an initial discharge capacity of 166 mAh/g, which corresponds to 97% of the theoretical capacity (170 mAh/g) of the active material.

Fig.4.67 Cycling properties of Li/LiFePO₄ cells with P(VdF-*co*-HFP)-LAGP composite GPEs and Celgard

The higher discharge capacity can be attributed to higher electrolyte uptake, ionic conductivity and better compatibility with lithium. The initial discharge capacity of the cell with bare P(VdF-*co*-HFP) GPE was 150 mAh/g, which is 10% lower compared to the cell with composite GPE. The initial discharge capacity of Celgard is 128 mAh/g which is 12% lower than the cell with

bare P(VdF-*co*-HFP) GPE. After 50 cycles a discharge capacity fade of 2% was observed (over initial capacity) for the cell with P(VdF-*co*-HFP)-LAGP(15%)-GPE, while a capacity fade of 7% was seen for the cell with Celgard. The better cycling stability implies the formation of a stable leak proof gel.

To test the suitability of the P(VdF-*co*-HFP)-LAGP(15%)-GPE at higher temperatures, it were activated with an ionic liquid (1M LiTFSI in EMITSFI). The charge-discharge properties were evaluated at 80 °C and compared with bare P(VdF-*co*-HFP) GPE. The results are shown in Fig.4.68.

Fig.4.68 High temperature cycling properties of Li/LiFePO₄ cells with P(VdF-*co*-HFP)-LAGP composite GPEs

The commercial liquid electrolyte is not stable beyond 60 °C and therefore an ionic liquid has been chosen to study the battery performance at 80 °C. The initial discharge capacity of the bare GPE and the P(VdF-*co*-HFP)-LAGP(15%)-GPE was 159 and 166 mAh/g. After 50 cycles a discharge capacity fade of 4-6%

was seen for both the GPEs. After 50 cycles the discharge capacity of the bare GPE and the P(VdF-*co*-HFP)-LAGP(15%)-GPE were 149 and 159 mAh/g. This shows that the GPEs show good performance at high temperature. It also proves that the composite membrane can be used as a separator cum electrolyte at various temperatures by carefully choosing the activating solution.

The rate capability of the P(VdF-*co*-HFP)-LAGP(15%)-GPE, at different current densities was evaluated and compared with bare P(VdF-*co*-HFP) GPE. The results are shown in Fig.4.69. The cells were cycled between 0.1 and 2C-rate and back to 0.1C-rate for 10 cycles each continuously. All the cells showed good discharge capacity and cycling performance even at higher C-rate and retain similar capacity after the current density is changed back to 0.1C-rate after 40 cycles, which clearly demonstrates high capacity retention of the cells.

Fig.4.69 Rate capability of Li/LiFePO₄ cells with P(VdF-*co*-HFP)-LAGP composite GPEs

At 2C the cells with P(VdF-*co*-HFP)-LAGP(15%)-GPE delivered a discharge capacity of ~102 mAh/g, which is ~67% of the theoretical capacity of LiFePO₄. At 2C the cell comprising bare P(VdF-*co*-HFP) GPE showed a discharge capacity of ~88 mAh /g which is about 16% less than the cell with P(VdF-*co*-HFP)-LAGP(15%)-GPE. The incorporation of LAGP improves the performance of the GPE at all the studied current densities.

4.3.1.4 P(VdF-*co*-HFP)/PEO blend GPE

Based on the curvature of ionic conductivity curves of the GPEs, it was seen that chain segmental mobility also affects the performance of GPEs. PEO has ether linkages, with oxygen atoms present at a suitable inter-atomic separation to allow segmental motion of the polymeric chain which is beneficial for facile ionic conduction [22]. To study the effect of increased chain segmental motion, P(VdF-*co*-HFP)/PEO blend GPEs were studied. The presence of PEO in the blend will improve the local chain mobility and increase amorphous content leading to improved lithium ion transport. The effect of increased chain segmental motion on the electrochemical and mechanical properties of the blend GPEs was studied by varying the concentration of PEO in the blend. The membranes and GPEs are labelled as ESM-A, B and C based on the P(VdF-*co*-HFP)/PEO ratio (wt.%) of 95/5, 90/10 and 80/20 respectively in the following pages.

The morphology of the membranes was examined using FE-SEM and the images are shown in Fig.4.70. The membranes consist of multilayered, three dimensional network of fine fibers with uniform non-beaded morphology and high surface roughness. It was seen that the amount of PEO blended into the

composite has an effect on the average fiber diameter of the membranes. With increasing PEO content in the composite, the fiber diameter increased slightly.

The AFD of the ESM membranes was 1.9, 2.3 and 2.7 μm for ESM-A, ESM-B and ESM-C respectively. This can be attributed to the higher voltage used to electrospin the membranes, because of the increased viscosity, by the addition of PEO [139]. The higher applied voltage ejects more fluid in the jet, which leads to deposition of fibers with larger diameter [86]. The interlaying of the fibers generates porous structure in the electrospun membrane. The porosity was 78, 80 and 83% for ESM-A, ESM-B and ESM-C respectively. The higher porosity with increasing PEO content can be attributed to the higher voltage used for electrospinning. The usage of a higher voltage leads to a more compact packing of fibers leading to higher porosity.

Fig.4.70 Surface morphology of (a) ESM-A, (b) ESM-B and (c) ESM-C

The electrolyte uptake characteristics were studied and the results are shown in Fig.4.71. It was seen that the electrolyte uptake follows the same trend as porosity. This supports the argument that increased porosity leads to availability of higher surface area for liquid uptake.

Fig.4.71 Electrolyte uptake of P(VdF-co-HFP)/PEO GPEs

PEO has good affinity to liquid electrolyte, therefore increasing concentration of PEO leads to increased electrolyte uptake. It was seen that uptake process is rapid and gets stabilized within 15 min [139]. The electrolyte uptake of the membranes follow the order ESM-C>ESM-B>ESM-A. The uptake was higher than the bare P(VdF-co-HFP) membrane having similar porosity. This is due to the increased polarity of the matrix by the addition of PEO and the affinity of PEO to the carbonate based solvents.

The electrolyte retention characteristics were studied and the results are shown in Fig.4.72. The electrolyte retention of ESM-A, ESM-B and ESM-C was lower than bare P(VdF-co-HFP) GPE. This can be attributed to the solubility of PEO in the organic solvents. The GPEs with increased PEO concentration formed a more stable gel, owing to the higher degree of interconnectivity of the pores and

the increased surface area. The formation of a leak proof gel is advantageous for shape flexibility of the battery.

Fig.4.72 Electrolyte retention of P(VdF-co-HFP)/PEO GPEs

The effect of blending low melting point PEO with P(VdF-co-HFP) on the thermal stability of the electrospun membrane was studied using TGA and DSC. Fig.4.73 shows the TGA plot of both the polymers and the blended electrospun membranes. The ESM membranes showed intermediate thermal stability compared to the component polymers. It was seen that TGA curve of ESM membranes showed a characteristic two step weight loss, with the first short peak at a temperature 347 °C and longer peak at 418 °C, corresponding to the decomposition temperature of PEO and P(VdF-co-HFP) respectively [139]. At a temperature of 412 °C, pristine PEO was completely decomposed.

Fig.4.73 TGA of P(VdF-co-HFP)/PEO membranes

At 700 °C, a char yield of 17,18 and 19% was observed for ESM-A, ESM-B and ESM-C respectively, which is about 85%-95% char yield of pristine P(VdF-co-HFP), proving that the prepared electrospun membranes have good thermal stability [139].

Similar to the TGA curve, DSC curve (Fig.4.74) also shows the characteristic peaks of both the constituent polymers. The melting endotherm at 65 °C and 147 °C corresponds to PEO and P(VdF-co-HFP) respectively. PEO exhibits a crystalline melting transition, starting at 50 °C, with a melting peak (T_m) at 65 °C [139]. ESM-B and ESM-C have two T_m at 61 and 146 °C, corresponding to the melting temperatures of PEO and P(VdF-co-HFP). ESM-A on the other hand, shows only one melting temperature at 146 °C. This implies that microphase separation was accomplished in the syringe, when the composite solution

containing higher PEO content (≥ 10 wt.%) was kept without stirring for long time while spinning [196].

Fig.4.74 DSC of P(VdF-co-HFP)/PEO membranes

The endotherm corresponding to PEO was very shallow when compared to pristine PEO, implying that crystallinity has been marginally reduced by blending. The crystallinity of the membranes was calculated from the heat of fusion, and the values are tabulated in Table.4.11. The crystallinity increased with increasing PEO content, owing to the high crystallinity of PEO.

The mechanical strength of the ESM membranes was studied. The tensile strength and the Young's modulus were measured and the values are tabulated in Table.4.11. It was seen that both tensile strength and Young's modulus increase with increasing crystallinity and PEO content.

Table.4.11.Properties of the P(VdF-*co*-HFP)/PEO blends

Membrane	Crystallinity (%)	Tensile strength (MPa)	Young's modulus (MPa)	Ionic conductivity at 30 °C (mS/cm)	Lithium transference number $T_{(Li^+)}$
ESM-A	40	4.9±0.3	7.4±0.3	3.6	0.42
ESM-B	41	5.8±0.3	8.1±0.3	4.4	0.43
ESM-C	43	6.4±0.3	9.4±0.3	5	0.43

The temperature dependent ionic conductivity of the GPEs between -20 and 70 °C was studied. The curves are shown in Fig.4.75.

Fig.4.75 Temperature dependent ionic conductivity of P(VdF-*co*-HFP)/PEO GPEs

The ionic conductivity of the GPEs follow the order ESM-C>ESM-B>ESM-A. It was seen that ionic conductivity follows the same trend as porosity. Higher porosity leads to higher electrolyte uptake which results in higher ionic conductivity. Higher swelling implies larger number of free charge carriers

translating to higher ionic conductivity. Also the presence of PEO improves the chain segmental motion of the GPE, which leads to improved ion dissociation.

The ionic conductivity of the ESM membranes at 30 °C was calculated and the values are tabulated in Table.4.11. Compared to P(VdF-*co*-HFP) GPE which shows a conductivity of 2.9 mS/cm at 30 °C, the higher conductivity of ESM membranes is associated with the PEO crystalline-amorphous phase transition. The transition enhances the ion mobility and segmental motion of the polymer chains. Hence the Li⁺ ions coordinated with the 'O' atoms of PEO segments could be freed partially or fully which could lead to larger number of charge carriers with improved charge migration.

From literature, it was observed that polymer blend containing higher PEO content (30%) has higher ionic conductivity [196]. It was seen that within the temperature range -20 to 70 °C, log σ vs 1000/T curves for all the GPEs shows three linear regions (Arrhenius behaviour) with change in slope. This indicates the three different activation energies involved for the ion transport as function of temperature. The three slopes were observed between 3.9 to 3.6, 3.6 to 3.3 and 3.3 to 2.9 K⁻¹ in Fig.4.75 [139].

The transition temperature 25 °C (3.3 K⁻¹) and 40 °C (3.19 K⁻¹) found by intercepting the two linear portions, corresponds to the freezing point of carbonate solvents in the electrolyte and melting of crystalline phase of PEO respectively [139]. The sharp decrease in conductivity below 10 °C (3.53 K⁻¹) is due to the freezing property of carbonate solvents in the electrolyte solution. The decrease in

activation energy together with significant rise in conductivity (at or above 40 °C) can be attributed to the softening and melting of crystalline phase of PEO near 60 °C making the GPE fully amorphous[139]. This amorphous structure facilitates the fast lithium ion motion in the polymer network, by providing higher free with increasing temperature [139]. The ionic conductivity is however; lower than the clay, BDN and LAGP composite GPEs.

The transference number T_{Li}^{+} of the ESM GPEs was measured by DC Polarization and the values are tabulated in Table.4.11. It was seen that there was no significant change in T_{Li}^{+} for the three compositions

The formation of a stable solid electrolyte interface on the lithium metal that can conduct lithium ions freely and simultaneously avert any undesirable interaction between the electrolyte components and lithium is crucial for achieving good cycle performance. Fig.4.76 (a) and (b) shows the complex impedance response of Li/GPE/Li symmetric cells and their impedance initially, and after 12 days storage measured at ambient temperature. Impedance spectrum shows a distorted semi-circle in the middle frequency range. Its expansion with storage time indicates the formation and growth of passivation layer at the interface of GPE and lithium metal. The growth of passivation layer is associated with the decomposition of the electrolyte or the reaction between the electrolyte and the Li-metal electrode [11,12,15]. The initial R_f values follow the order ESM-C<ESM-B<ESM-A.

Fig.4.76 AC impedance behaviors of P(VdF-co-HFP)/PEO GPEs: (a) initial impedance and (b) impedance after 12 days of storage

The time dependent interfacial resistance (R_f) with storage time is shown in Fig.4.77.

Fig.4.77 Time dependent interfacial resistance of P(VdF-co-HFP)/PEO GPEs

After one day of storage all the GPEs showed significant increase in R_f , which is about 100 to 135% higher than the initial value. The R_f for all the GPEs increased with storage time, denoting the growth and stabilization of the SEI layer. After the initial enhancement in impedance, the layer characteristics get stabilized within 8 days. After 12 days the R_f values follow the order ESM-C<ESM-0B<ESM-A in the close range of 163 to 220 Ω .

The electrochemical stability of ESM GPEs against lithium metal was studied using linear sweep voltammetry. The LSV sweep of the GPEs is shown in Fig.4.78.

Fig.4.78 Electrochemical stability window of P(VdF-co-HFP)/PEO GPEs

It was seen that the GPEs exhibit good anodic stability with stability window in a close range of 4.8-5.0V. The formation of a low leak stable gel with increased surface roughness and surface area leads to good adhesion between the GPE and lithium metal. This improved adhesion leads to the formation of a good

interface resulting in high electrochemical stability. The high stability implies that the GPE can be used with high voltage cathode materials, without electrolyte degradation or capacity fading. The formation of a stable solid electrolyte interface with lithium metal is beneficial for achieving good electrochemical stability.

The GPEs were tested in Li/LiFePO₄ cells to test the galvanostatic charge discharge performance of the GPEs. Fig.4.79 shows the charge discharge characteristics of the cells for 90 cycles.

Fig.4.79 Cycling properties of Li/GPE/LiFePO₄ cells with P(VdF-co-HFP)/PEO GPEs

The cells with ESM-A, ESM-B and ESM-C deliver initial discharge capacities of 153, 155 and 158 mAh/g respectively, which corresponds to 90-93% of the theoretical capacity. The high capacity can be attributed to the high ionic

conductivity. The higher ionic conductivity leads to faster lithium ion transportation between the cathode and anode leading to higher capacity. After 100 cycles, a discharge capacity fade of 2% was observed over initial capacity for the cell with ESM-C. The observed capacity fade may be due to the progressive decomposition and/or leakage of the electrolyte. Also as mentioned previously the structural characteristics and composition of cathode materials play a vital role on the capacity of the cell and cycling performance [184,197].

The electrochemical performance of Li/LiFePO₄ cells with the ESM GPEs at different current densities is shown in Fig.4.80. It was seen that with increasing C rate the difference in discharge capacities of the GPEs begin to increase. At low C rates (0.1-0.6 C), it was seen that all the GPEs have similar capacities. But at higher C rates (1.5-3.0 C), the difference in capacity between ESM-C and ESM-A was more prominent. This is because at a fixed thickness, a less ionically conducting electrolyte results in an increased ohmic drop and the ion concentration gradient in the electrolyte leading to lower capacity [190,191]. The lower interfacial resistance, higher electrolyte uptake and ionic conductivity of the ESM-C are responsible for the higher capacity. It was seen that all the cells showed good discharge capacity and cycling performance even at higher C-rate and retain similar capacity after the current density is changed back to 0.2 C-rate after 40 cycles, which clearly demonstrates high capacity retention of the cells with ESM GPEs.

Fig.4.80 Rate capability of Li/ LiFePO₄ cells P(VdF-*co*-HFP)/PEO GPEs

4.3.1.5 In-situ porosity generated P(VdF-*co*-HFP)-LAGP/PEO blend

The effect of blending PEO with P(VdF-*co*-HFP) to improve the chain segmental motion and thereby improving the electrochemical performance of the resulting GPE has been explored in the previous section. It was seen that the addition of PEO helps to improve the segmental motion, but its effect on improving the ionic conductivity was much lower than the previous cases. Therefore, to identify the most critical factor influencing ionic conductivity, a preferential polymer dissolution process was adopted. PEO was isolated and removed from the composite polymer membrane to generate in-situ porosity on the electrospun PEO/P(VdF-*co*-HFP)-LAGP composite. The in-situ porosity generation helps to increase the electrolyte absorption capability and swelling ability of the membrane. The presence of 6 wt.% LAGP maintains the thermal stability and mechanical stability [198,199]. The incorporation of LAGP into the polymer also

increases the lithium ion concentration in the system [198]. By keeping the LAGP content constant and varying the amount of PEO, the effect of in-situ porosity generation on the ionic conductivity and electrochemical properties was studied. In the following pages, the in-situ porosity generated membranes are designated as IPG-01 and IPG-02 for membranes based on PEO blended with P(VdF-*co*-HFP)-LAGP composite with PEO content (wt.%) 5 and 10 to highlight their respective composition.

Fig.4.81 (a) and (b) shows the surface morphology of IPG-01 and IPG-02. It was seen that the amount of PEO blended into the composite has an effect on the average fiber diameter of the membranes. With increasing PEO content in the composite, the fiber diameter increased slightly. This can be attributed to the higher voltage used to electrospin the membranes and the increased viscosity due to the addition of PEO [139]. The AFD of IPG-01 and IPG-02 was 2.0 and 2.4 μm respectively.

The magnified images (Fig.4.81 (c) and (d)) show that pores are uniformly distributed on the surface of the fibers, with IPG-02 having a more porous surface, attributed to the higher PEO content in the blend [199]. The uniformly distributed pores on the fiber surface indicate that blending results in a uniform solution. The presence of large number of pores on the surface of the fiber confirms that PEO has been successfully leached out from the membrane by the preferential dissolution process. It was observed that the surface roughness of the membranes is enhanced by in-situ porosity generation. This increased surface

roughness and porosity is beneficial for higher electrolyte uptake and enhanced electrochemical properties.

Fig.4.81 Surface morphology of (a) IPG-01, (b) IPG-02, (c) magnified image of IPG-01 and (d) magnified image of IPG-02

It was observed that the porosities of both the membranes before in-situ porosity generation were $88 \pm 5\%$. The narrow range of porosity of the membranes is attributed to the close similarities in the membrane morphologies and interlaying of fibers. After in-situ porosity generation, the membranes showed higher porosity which depended on the amount of PEO present in the original blend [199]. The porosities are tabulated in Table.4.12.

The electrolyte uptake of the IPG membranes was studied for a period of 1 h and the results are shown in Fig.4.82.

Table.4.12. Properties of IPG composites

Membrane	Porosity (%)	Crystallinity (%)	Ionic conductivity at 30 °C (mS/cm)	Lithium transference number (T_{Li^+})
IPG-01	87	38	8.4	0.64
IPG-02	91	39	9.6	0.65

Fig.4.82 Electrolyte uptake of IPG GPEs

The electrolyte uptake is strongly dependent on porosity, pore size, pore volume and pore density. It was seen that the electrolyte uptake follows the same trend as porosity, with IPG-02 having the highest electrolyte uptake. The high uptake can be attributed to the high porosity and surface roughness of the IPG membranes. The electrospun membrane displays sufficient mechanical strength and easy handleability even after activation with electrolyte. The electrolyte uptake of IPG-01 and IPG-02 was 575 and 640% respectively. The increased

uptake can be attributed to the increased surface roughness and porosity by the preferential polymer dissolution process [199].

The retention characteristics are shown in Fig.4.83. It was seen that the membranes show high retention with IPG-01 and IPG-02 showing leakage of <14%. The retention is slightly lower than the clay (0.92) and LAGP system (0.94), which is attributed to the increased porosity by the in-situ porosity generation process. The retention ratio was however higher than the blend system (0.86) implying that the IPG membranes for a stable low leak GPE.

Fig.4.83 Electrolyte retention of IPG GPEs

The thermal properties of the IPG membranes were studied using TGA and DSC. The crystallinity was calculated from the heat of fusion, obtained from DSC curves and the values are tabulated in Table.4.12. It was seen that the crystallinity increases with increasing PEO content. The crystallinity is however

lower than the bare P(VdF-*co*-HFP) membranes, which exhibits a crystallinity of 43%. The lowered crystallinity can be attributed to the presence of LAGP [199]. It was seen that the crystallinity of the composite membranes increased with increasing PEO content. The composite membrane shows lower crystallinity than P(VdF-*co*-HFP)/PEO blend membrane without LAGP (Table.4.11.) [139].

The observed difference in the crystallinity arises from the inhibition of crystallization by the LAGP glass ceramic during the solidification process of the fiber, which reduces the volume fraction of the crystalline phase in the fiber [198,199]. The surface charges on the ceramic particles also contribute to increasing the amorphous phase of the polymer as a result of higher nucleation rate during the solidification process by acting as facile nucleation centers [200]. The increase of amorphous regions in the polymer is beneficial for achieving a higher ionic conductivity [86,87,140].

The TGA curves of the IPG membranes are shown in Fig.4.84.

Fig.4.84 TGA of IPG membranes

A slight decomposition peak at $\sim 360^{\circ}\text{C}$ observed for the membranes may be due to the presence of negligible amount of PEO traces in the membrane after in-situ porosity generation process [199]. The onset decomposition shifts slightly to the right when compared to the bare P(VdF-*co*-HFP) membranes (400°C). This shift toward higher temperature range suggests enhancement in thermal stability of the composite [178,198].

The lowered crystallinity and increased porosity of the IPG membranes leads to doubts on the mechanical stability of the membranes. Mechanical strength of IPG-02 was compared with electrospun P(VdF-*co*-HFP)/PEO (80:20 w/w) blend membrane with and without 6 wt.% LAGP. The values are tabulated in Table.4.13.

Table.4.13.Mechanical properties of IPG membranes

Membrane	Young's modulus (MPa)	Tensile strength (MPa)
P(VdF- <i>co</i> -HFP)/PEO (80:20 w/w) blend	8.1 ± 0.3	5.8 ± 0.3
P(VdF- <i>co</i> -HFP)/PEO (80:20 w/w) blend with 6wt.% LAGP	9.4 ± 0.3	6.9 ± 0.3
IPG-01	10.2 ± 0.3	7.6 ± 0.3
IPG-02	10.0 ± 0.3	7.8 ± 0.3

It was found that incorporation of LAGP enhances both ultimate tensile strength and Young's modulus of the membranes, which is attributed to reinforcing effect of inorganic component dispersed in the polymer matrix [86]. The blend membranes without LAGP showed a Young's modulus which was

about 25% lower than the IPG membranes. Similarly, the ultimate tensile strength of IPG membranes was 34% higher than blend membrane without LAGP. Thus it was confirmed that incorporation of LAGP into the composite membrane contributes towards improving the mechanical properties.

The temperature dependent ionic conductivity of the IPG-01 and IPG-02 GPE in the temperature range of -20 and 70 °C was studied. The $\log \sigma$ vs $1000/T$ curves were plotted, to see if the conductivity resembles Arrhenius function or VTF function. The curves are shown in Fig.4.85. It was seen that in the temperature range -20 to 70 °C the $\log \sigma$ vs $1000/T$ curves for all the GPEs are slightly curved, hence the activation energy for ionic conduction E_a can be obtained using the Vogel-Tamman-Fulcher (VTF) model $\{ \sigma = \sigma_0 T^{-1/2} \exp [(-E_a/R(T-T_0))]\}$ [199]. The ionic conductivity follows the same order as electrolyte uptake, IPG-02 > IPG-01. The ionic conductivity at 30 °C was calculated and the values are tabulated in Table.4.12.

The ionic conductivity obtained from the impedance data was fitted using nonlinear least square fitting and the results shown in Fig.4.85. The parameters are tabulated in Table 4.14. It was seen that a good fit was obtained for all the GPEs. The activation energy decreases with increasing in-situ generated porosity further supporting the increased ionic conductivity. The higher ionic conductivity, with higher uptake is attributed to the lower crystallinity and higher electrolyte uptake. Ionic conductivity is related to the number of active charge carriers by the equation $\sigma = \sum N_i R_i \dot{E}_i$, where N_i , R_i and $\dot{E}_i$ are number of charge carriers, ionic charge and ionic mobility, respectively [199]. When the content of LAGP was

constant, it was seen that increased uptake leads to increased ionic conductivity because of the presence of larger number of charge carriers. Thus, the effect of increased lithium concentration was more pronounced than the reduced ionic coupling by the presence of LAGP.

Fig.4.85 Temperature dependent ionic conductivity of IPG GPEs

Table 4.14 VTF parameters of IPG GPEs

GPE	σ_0 (S/cm/K)	E_a (eV)	T_0 (°C)
IPG-01	0.115	0.038	104
IPG-02	0.110	0.034	107

In the IPG GPEs, the high ionic conductivity is also due to the presence of LAGP. LAGP acts as a source of lithium ions thereby increasing the number of active charge carries, also the presence of Lewis acid-base interactions reduces the ion-ion coupling, leading to increased lithium ion dissociation [86,140]. The surface functional groups (O/OH) of LAGP can compete with the F atoms of

PVdF to form Lewis acid-base complexes with Li ion. This leads to the weakening of the complexation between Li ions and F atoms of the PVdF chain thereby promoting Li ion diffusion [82,199,201]. The sharp decrease in conductivity seen in Fig.4.85, below 10 °C (3.6 K⁻¹) is due to the freezing property of carbonate solvents in the electrolyte solution (EC:DEC) [139].

The transference number of the IPG GPEs was measured by DC polarization. The values are tabulated in Table.4.12. It was seen that there was no significant difference in the T_{Li}^{+} values of the two GPEs. The T_{Li}^{+} was higher than the bare P(VdF-*co*-HFP) GPE, which showed a T_{Li}^{+} of 0.42. The increased T_{Li}^{+} can be attributed to the presence of unity transference number LAGP.

The formation of a stable SEI layer which passivates the interface between the GPE and lithium metal is important for good electrochemical properties. The stability of the GPEs against lithium metal was studied using AC impedance. The initial impedance behavior and the impedance behavior after 12 days of storage are shown in Fig.4.86. Impedance spectrum showed a distorted semi-circle in the middle frequency range. Its expansion with storage time indicates the formation and growth of passivation layer at the interface of GPE and lithium metal [199]. The growth of passivation layer can be associated with the decomposition of the electrolyte or the reaction between the electrolyte and the Li-metal electrode [11,12,15]. The real axis intercept at the high frequency end represents the bulk electrolyte resistance (R_b) while the intercept at the low frequency end represents the charge transfer kinetics and the growth of the SEI layer [199]. The intercept at

the lower frequency end (R_f) is the resistance of the interface between lithium and the electrolyte.

Fig.4.86 Interfacial resistance of IPG GPEs :(a) initial impedance and (b) impedance after 12 days storage

The initial R_f values follow the order IPG-01 > IPG-02. The initial R_f values of IPG-01 and IPG-02 was 22 and 18 Ω respectively. The change in R_f is attributed to the formation of SEI layer. After a period of 12 days storage the R_f value (Ω) follows the order IPG-02 (51) < IPG-01 (57).

The interfacial resistance with storage time was monitored and the results are shown in Fig.4.87. The R_f for both GPEs increased with storage time, denoting the growth and stabilization of the SEI layer. Although the R_f value increases initially due to the growth of the passivation layer, the layer characteristics were stabilized within 8 days. The low increase in R_f proves that a high ionic conducting GPE with low leakage was formed by activating the IPG membranes.

The higher amorphous content due to lowered crystallinity and higher electrolyte uptake; and increased surface roughness due to the in-situ porosity generation helps improve the electrochemical stability of the resulting GPEs [199].

Fig.4.87 Time dependent interfacial resistance of IPG GPEs

To further test the stability of the GPEs against lithium metal, the LSV was studied and the results are shown in Fig.4.88.

Fig.4.88 Electrochemical stability window of IPG GPEs

The electrochemical stability window is an important factor which determines the suitability of electrolytes to be used with various cathodes and anodes. It was seen that both IPG-01 and IPG-02 have anodic stability $> 5\text{V}$, rendering them suitable for use with most of the common cathode materials used in lithium ion batteries.

The high anodic stability can be attributed to a combination of factors. The excellent affinity of the electrospun membranes to the carbonate based liquid electrolyte which partially swells the fibers, leads to better contact with lithium. The increased surface roughness of the fibers due to in-situ porosity generation also leads to better contact of the electrolyte to lithium surface which leads to better anodic stability. It is reported that LAGP particles can act as a surface stabilizer and enhance the electrochemical oxidation stability [179,193]. Therefore, presence of LAGP can also improve the anodic stability [199].

The GPEs were tested in $\text{Li}/\text{LiFePO}_4$ cells to demonstrate their performance in a lithium battery. The discharge capacity vs. cycle number for the cells based on IPG membranes cycled at 0.1 C is shown in Fig.4.89. The discharge capacity of the cells follows the same order as ionic conductivity. A higher conducting electrolyte results in more efficient transfer of lithium ions between the cathode and the lithium reservoir, which results in higher discharge capacity [199]. It was observed that all the cells show relatively stable performance without significant capacity fading for 50 cycles.

The initial discharge capacity of the cell with IPG-01 was 159 mAh/g , while the corresponding capacity of the cell with IPG-02 was 164 mAh/g . The

cells show 93-97% of theoretical capacity. After 50 cycles the cells with IPG 02 and IPG-01 deliver discharge capacities of 163 and 156 mAh/g respectively. The cells show good capacity retention with a capacity loss of 1-3 mAh/g. The observed capacity fade may be due to the progressive decomposition and/or leakage of the electrolyte. The relatively stable performance with good capacity retention proves the suitability of the IPG GPEs for application in LIBs.

Fig.4.89 Cycling properties of Li/LiFePO₄ cells with IPG GPEs

The electrochemical performance of Li/LiFePO₄ cells with the IPG electrolytes at different current densities was studied and the results are shown in Fig.4.90. The cells were cycled between 0.1 and 3 C-rate for 10 cycles each continuously and then at 0.2C rate for 10 cycles. All the cells showed good discharge capacity and cycling performance even at higher C-rate. The cells retain similar capacity after the current density is changed back to 0.2 C-rate after 40 cycles, which clearly demonstrates high capacity retention of the cells. The

capacity was normalized by the capacity obtained at 0.1 C rate, to study the effect of the porous morphology. The nature of the porous membrane has a poor effect on the cycling test performances at low rate [190,191]. At high C rates, the effect of the membrane morphology is observed [190,191].

At low C rates (0.1-0.6 C), it was seen that both the GPEs have similar capacities, but at 1.5C and 3C rate, IPG-02 has a higher capacity when compared to IPG-01. The lower interfacial resistance, higher porosity, electrolyte uptake, pore structure and ionic conductivity of the IPG-02 GPE is responsible for the higher normalized capacity. At a fixed thickness, a less conductive electrolyte results in an increase of the ohmic drop and the ion concentration gradient in the electrolyte leading to lower capacity [138,190,191].

Fig.4.90 Normalized rate capability of Li/LiFePO₄ cells with IPG GPEs

4.3.2 PSSLi based composites and blends

The section discusses PSSLi based composites and blends. The effect of processing method on the ionic conductivity of the composites and blends is evaluated by comparing thin film, pelletized and gel samples. Each subsection discusses one composite/blend in detail. Section 4.3.2.1 discusses PSSLi/ PEO blends. The effect of increased chain segmental motion on the ionic conductivity is discussed. Section 4.3.2.2 discusses PSSLi-BDN composites. The effect of increased ion dissociation and improved lithium diffusion, on the ionic conductivity due to the presence of BDN is examined. Section 4.3.2.3 discusses PSSLi-SiO₂ composites. The effect of reduced ion coupling on ionic conductivity is discussed.

4.3.2.1 PSSLi/PEO blends

To prepare a free standing film and study the effect of increased chain segmental motion, PEO was blended with PSSLi in different concentrations and the solution was cast on the Teflon plate. A free standing film was formed by the incorporation of PEO into PSSLi. The ionic conductivity of the resulting films at 90 °C is shown in Table.4.15. It was seen that the ionic conductivity of the bare PSSLi is lower than that of the blended samples. The presence of the ether linkages with oxygen atoms at a suitable distance to allow the chain segmental motion is beneficial for the ion transport in PSSLi, because of increased lithium solvation. It was seen that with increasing PSSLi content, the ionic conductivity drops. It was expected that an increase in lithium ion concentration would lead to an increase in ionic conductivity, however the reverse happens. This can be

attributed to the fact that with increasing PSSLi content, the lithium ions on the styrene units begin to repel each other leading to a more coiled and tortuous path for ion transport. The styrene unit in PSSLi may impede ion motion by acting as an insulator leading to decreased ionic conductivity.

Table.4.15.Ionic conductivity of PEO/PSSLi composites

Sample	Ionic conductivity(mS/cm) at 90 °C
Bare PSSLi	2.1×10^{-4}
90/10 PEO/PSSLi	1.6×10^{-3}
80/20 PEO/PSSLi	1.1×10^{-3}
70/30- PEO/PSSLi	0.5×10^{-3}

For testing the PSSLi blends in a device, the ionic conductivity has to be of the order of atleast 0.1 mS/cm. To further improve the ionic conductivity of the PSSLi/PEO blend, BDN was used as filler to improve lithium dissociation. The reaction scheme is presented in Fig.4.91.

Fig.4.91 Schematic of PSSLi/PEO/BDN blends

The ionic conductivities of the resulting films at 90 °C are shown in Table.4.16. In the samples containing BDN, it was seen that the addition of BDN improves the ionic conductivity. This increment may be due to the presence of the

active ion hopping nitrile centers on BDN, which may increase the dissociation of the SO_3Li bond. It was seen that even with the presence of BDN, increasing PSSLi content leads to decreasing ionic conductivity, though the effect was not as prominent as the case without BDN. This difference may be due to the reduced crystallinity due to the addition of BDN. The effect of BDN incorporation on the blend was more significant than the incorporation of PEO due to the combined action of reduced crystallinity and increased lithium ion dissociation rate.

Table.4.16.Ionic conductivity of PSSLi/PEO/BDN blends

Sample	Ionic conductivity(mS/cm) at 90 °C
Bare PSSLi	2.1×10^{-4}
80/10/10 PEO/BDN/PSSLi	2.3×10^{-3}
70/20/10 PEO/BDN/PSSLi	3.6×10^{-3}
70/10/20 PEO/BDN/PSSLi	2.2×10^{-3}
60/10/30 PEO/BDN/PSSLi	1.3×10^{-3}
60/30/10 PEO/BDN/PSSLi	5.3×10^{-3}

The ionic conductivity was still too low for application in a practical device. To further improve the ionic conductivities, PSSLi/PEO gels were prepared. Based on the results obtained for bare PSSLi (Section 4.2.2), the blends were gelled using DMSO to form a gel. Based on the optimum concentration of 15 wt.% obtained for the bare PSSLi gels, similar concentration was used to prepare the blend gels.

The DSC curves of the blend gels are shown in Fig.4.92. It was seen that the DSC curves are a combination of the patterns of bare PSSLi and PEO, with the second peak corresponding to PEO.

Fig.4.92 DSC of PSSLi/PEO gels

The melting temperatures and the heat of fusion are tabulated in Table.4.17. The heat of fusion increased with increasing PEO content. The heat of fusion of both the peaks increases with increasing PEO content. The melting temperature of the second peak decreases very slight with increasing PEO content. It was seen that the samples are phase separated and the heat of fusion increases with increasing PEO content. The incorporation of PEO does not suppress the crystallization of the solvent and hence does not lead to reduced crystallinity.

Table.4.17.Melting temperature and heat of fusion of PSSLi/PEO blends

Composition	Melting temperature (°C)	Heat of fusion (J/g)
Bare PSSLi	10	54.3
10 wt.% PEO	9	57.6
20 wt.% PEO	9	62.6
50 wt.% PEO	12	64.4
70 wt.% PEO	13	71.8

The ionic conductivity of the blend gels was studied between 25 and 70 °C. The $\log \sigma$ vs $1000/T$ curves were plotted and the curves are shown in Fig.4.93. It was seen that the gels display Arrhenius behavior over the entire temperature range. It was seen that ionic conductivity decreases with increasing PEO content, as opposed the results obtained for the pelletized samples. The decreasing conductivity can be attributed to the increasing crystallinity. It was seen that the ether linkages in PEO were not effective in improving the ion transport properties. This can be attributed to the lowered lithium ion dissociation with increasing PEO content. Strong association exists between the ether oxygen of PEO with lithium ions, which leads to the charge carriers remaining associated with the PEO chains rather than being solvated in the solvent.

In the pelletized samples, the solvation resulted in improved ion transport because of the involvement of chain mobility. In the gel samples, the mechanism is diffusion and hence association was detrimental to ion mobility. Another reason for the decreasing ionic conductivity with increasing PEO content may be the increasing micro-viscosity of the gel. According to Einstein–Stokes the mobility

of the lithium-ion is inversely proportional to the micro-viscosity of the system [180], therefore with increasing viscosity the mobility of lithium ions is lowered.

Fig.4.93 Temperature dependent ionic conductivity of PSSLi/PEO gels

It was seen that the ionic conductivity of the blend GPE is lower than the bare PSSLi gel proving that increased chain segmental motion is not effective in improving the ion transport properties of PSSLi gels. The combined effect of increased viscosity and association between lithium and oxygen leads to reduced ionic conductivity.

4.3.2.2 PSSLi-BDN composites

Based on the presence of active ion hopping centres in BDN and the ability of BDN to improve the lithium ion dissociation, BDN was used as filler with PSSLi as the polymer matrix. It was seen that a free standing film was not formed in the absence of PEO. An attempt was made to crosslink PSSLi units using BDN as the crosslinking agent and potassium peroxydisulfide as the initiator. It was seen that

crosslinking did not lead to the formation of a free standing film, which may be due to the poor mechanical properties of BDN. The ionic conductivity of these samples was studied after pelletizing. The ionic conductivity of the PSSLi-BDN composites and PSSLi samples crosslinked with BDN is tabulated in Table.4.18.

Table.4.18.Ionic conductivity of PSSLi-BDN composites at 90 °C

Sample	Ionic conductivity(mS/cm) at 90 °C
90:10 PSSLi:BDN	1.8×10^{-3}
80:20 PSSLi:BDN	2.1×10^{-3}
70:30 PSSLi:BDN	2.5×10^{-3}
50:50 PSSLi:BDN	3.3×10^{-3}
30:70 PSSLi:BDN	5.1×10^{-3}
20:80 PSSLi:BDN	8.5×10^{-3}
10:90 PSSLi:BDN	2.1×10^{-2}
PSSLi crosslinked with 5 % BDN	1.7×10^{-3}
PSSLi crosslinked with 10% BDN	0.8×10^{-3}
PSSLi crosslinked with 20 % BDN	1.6×10^{-4}

It was seen that crosslinking did not improve the ionic conductivity. The ionic conductivity drops with increased crosslinking. Higher degree of crosslinking may lead to the formation of more branches in the ion conduction pathway. This may lead to the ions getting stuck in the nitrile chains or in the induced defects rather than having a linear, less tortuous path for ion transport. The presence of a highly tortuous path for ion conduction leads to lowered ion diffusion, resulting in lower ionic conductivity. It was seen that the composites have higher ionic conductivity when compared to the cross linked samples. It was

seen that just like in the case of the thin film samples in Table.4.16., increase in the concentration of PSSLi leads to a decrease in ionic conductivity of the composite samples.

The BDN composites follow the same trend as the PEO blends, but the reduction in ionic conductivity of the PEO composites was more significant when compared to the BDN samples. The longer polymer chain length of PEO may lead to coiling up of the ends of the PEO chains due to the ionic repulsion between the lithium ions on the styrene units. This results in a highly tortuous path for ion conduction. It was seen that the increase/decrease in ionic conductivity of all the samples was very small. This small change is attributed to the action of two opposing forces; increasing lithium ion concentration due the increase in PSSLi content and increased repulsion and lowered lithium ion mobility due to the increased PSSLi concentration. It was seen that the highest obtained ionic conductivity for the BDN composites or crosslinked samples was 0.02 mS/cm, which is more than two orders of magnitude lower than that required for a practical device. More importantly the lack of mechanical stability of the resulting material is a critical issue.

The ionic conductivity of the BDN composites was still too low for application in a practical device. Based on the results obtained for bare PSSLi, the blends were gelled using DMSO. Based on the optimum concentration of 15 wt.% obtained for the bare PSSLi gels, similar concentration was used to prepare the composite gels.

The DSC curves of the composite gels are shown in Fig.4.94.

Fig.4.94 DSC of PSSLi-BDN composite gels

It was seen that the incorporation of BDN does not change the glass transition temperature or the melting temperature significantly. This implies that the dynamics of the polymer have not undergone any significant change with addition of BDN [111].

The melting temperature and the heat of fusion values are tabulated in Table.4.19. It was seen that the heat of fusion decreases with increasing concentration of BDN, upto 20 wt.% BDN. The decreasing heat of fusion indicates that the incorporation of BDN hinders the crystallization of the solvent. It was seen that beyond 20 wt.% BDN, the peak corresponding to the solid state transition of BDN at -32 °C reappears, indicating the presence of inactive BDN [187]. The reduction in crystallinity is beneficial for increasing ionic conductivity.

Table.4.19.Melting temperature and heat of fusion of PSSLi-BDN composites

Composition	Melting temperature (°C)	Heat of fusion (J/g)
Bare PSSLi	10	54.3
10 wt.% BDN	8	52.1
20 wt.% BDN	7	50.8
50 wt.% BDN	6	57.6

The ionic conductivity of the blend gels was studied between 25 and 70 °C. The $\log \sigma$ vs $1000/T$ curves were plotted and the curves are shown in Fig.4.95. It was seen that the gels display Arrhenius behavior over the entire temperature range, indicating that ion motion has been decoupled from chain segmental mobility. It was seen that ionic conductivity increases with BDN incorporation till 20 wt.% BDN. Beyond 20 wt.% BDN, the ionic conductivity begins to drop. This behavior can be attributed to the decrease in lithium ion concentration with increased BDN content and the presence of inactive BDN which may lower ionic conductivity.

Fig.4.95 Temperature dependent ionic conductivity of PSSLi-BDN composite gels

4.3.2.3 PSSLi-SiO₂ composites

To study the effect of decreased ionic coupling due to Lewis acid-base interactions between surface functional groups of SiO₂ and the SO₃⁻ group on the ionic conductivity, PSSLi-SiO₂ composites were studied. SiO₂ was generated in-situ and used as a ceramic filler to improve the mechanical properties of PSSLi. The reaction scheme is presented in Fig.4.96.

Fig.4.96 Reaction scheme for PSSLi-SiO₂ composites

It was seen that even with the addition of ceramic filler, free standing films were not obtained. The ionic conductivity of the in-situ SiO₂ generated composites is tabulated in Table.4.20. As mentioned earlier, these samples also could not be obtained as a free standing thin film and therefore, they were pelletized for ionic conductivity measurement.

The in-situ generated samples were compared with samples prepared by using commercial SiO₂ as the inert filler. It was seen that in-situ SiO₂ generation offers a distinct advantage over adding SiO₂ to prepare the composite. The ionic conductivity of the in-situ generated samples was higher than the externally added SiO₂. This may be due to a more uniform dispersion of SiO₂ in the polymer matrix due to the SiO₂ being generated in-situ. The ionic conductivity increases with

increasing SiO₂ concentration, reaching a maximum at 6 wt.% SiO₂, after which it begins to reduce on further addition of SiO₂. The same trend was observed for both the sets of samples.

Table.4.20.Ionic conductivity of PSSLi-SiO₂ composites at 90 °C

Sample	Ionic conductivity(mS/cm) at 90 °C
97:3 PSSLi:SiO ₂	2.3×10^{-3}
94:6 PSSLi:SiO ₂	3.2×10^{-3}
91:9 PSSLi:SiO ₂	2.1×10^{-3}
88:12 PSSLi:SiO ₂	1.8×10^{-3}
85:15 PSSLi:SiO ₂	1.1×10^{-3}
97:3 PSSLi:SiO ₂ (Commercial)	2.1×10^{-3}
94:6 PSSLi:SiO ₂ (Commercial)	2.5×10^{-3}
91:9 PSSLi:SiO ₂ (Commercial)	1.9×10^{-3}
88:12 PSSLi:SiO ₂ (Commercial)	1.4×10^{-3}
85:15 PSSLi:SiO ₂ (Commercial)	9.4×10^{-4}

The ceramic particles exhibit saturation effect. This is a commonly reported phenomenon in polymer composite electrolytes [17]. This saturation takes place because the filler particles agglomerate leading to reduced surface area which hinders the conduction process. At low filler concentrations, dilution effect is compensated by the Lewis acid-base interactions. At high filler concentrations due to the decreased surface area, dilution effect predominates the surface specific interactions, leading to reduced ionic conductivity [111,202].

Just like the PEO blends and BDN composites, the ionic conductivity of the SiO_2 samples is too low for further testing. Therefore, PSSLi- SiO_2 gels in DMSO were prepared. The dissolution of the polymer matrix in DMSO increases the solvent content of the system and therefore the lithium ions can diffuse faster leading to improved ionic conductivity. The effect of incorporation of SiO_2 to create more defects and improve the ionic conductivity of PSSLi gels was studied. Based on the optimum concentration of 15 wt.% obtained for the bare PSSLi gels, similar concentration was used to prepare the composite gels.

The DSC curves of the composite gels are shown in Fig.4.97.

Fig.4.97 DSC of PSSLi- SiO_2 composite gels

It was seen that the incorporation of SiO_2 does not change the glass transition temperature or the melting temperature significantly. This implies that the dynamics of the polymer have not undergone any significant change with addition of SiO_2 [111]. The slight increase in T_g with increasing SiO_2 content can

be attributed to the reduction in flexibility due to the presence of the ceramic particles [198].

The melting temperature and heat of fusion of the composites is tabulated in Table.4.21. It was seen that the heat of fusion decreases with increasing SiO_2 content till 6 wt.%, but increases thereafter. This can be explained by the steric hindrance caused by PSSLi and SiO_2 , which induces creation of crystalline sites in the polymer [97]. The sample with 6 wt.% SiO_2 content has lower melting temperature and heat of fusion when compared to all the samples. The reduction in heat of fusion implies lower degree of crystallinity, is beneficial for increasing ionic conductivity.

Table.4.21.Melting temperature and heat of fusion of PSSLi- SiO_2 composites

Composition	Melting temperature (°C)	Heat of fusion (J/g)
Bare PSSLi	10	54.3
3 wt.% SiO_2	10	49.5
6 wt.% SiO_2	11	47.2
9 wt.% SiO_2	12	51.6
12 wt.% SiO_2	13	52.3
15 wt.% SiO_2	13	53.8

The ionic conductivity of the composite gels is shown in Fig.4.98. It was seen that the ionic conductivity increases with increasing SiO_2 concentration upto 6 wt.% SiO_2 content, beyond that conductivity begins to drop.

Fig.4.98 Temperature dependent ionic conductivity of PSSLi-SiO₂ composite gels

The ionic conductivity follows the same trend as DSC. It was seen that ionic conductivity increases with decreasing heat of fusion. Also the presence of Lewis acid- base interactions between the surface functional groups of SiO₂ and –SO₃ group can weaken the interaction between the sulfonate group and lithium leading to an increase in dissociation of lithium ions [111].

The increased dissociation of lithium ions leads to increased number of charge carriers and thereby higher ionic conductivity. The increased number of charge carriers in this case, is in the solvent and therefore there is no shielding effect or lithium condensation effect which leads to coiling up of the polymeric chain [111]. The ionic conductivity of the 6 wt.% composite gel is 1.3 times that of the bare PSSLi gel. The enhancement of ionic conductivity by the addition of fillers is seen at all temperatures. The decrease in ionic conductivity beyond 6

w.t% SiO₂ content may be due to the agglomeration of SiO₂ particles leading to reduction of surface area [111].

5 Chapter 5 Cross examination and comparison of the various studied systems and Discussion of fundamental mechanism study

5.1 Influence of polymer structure on the electrochemical performance of GPEs

As seen from the results section, the polymer structure plays an important role in the ion transport mechanism of the GPEs. The mechanism of ion conduction in the fluorinated polymer is very different from the mechanism of ion conduction in the lithiated polymer. In P(VdF-*co*-HFP) GPEs, the source of lithium ions is the electrolyte solution and hence the focus is on increasing the electrolyte uptake. In the lithiated polymer, the source of lithium ions is the polymer itself and therefore the focus is on improving the dissociation of the SO₃Li bond and preventing screening and charge repulsion.

The fluorinated GPEs have higher ionic conductivity when compared to the lithiated polymers. The best performing PSSLi GPE (EtOH/H₂O ratio 40/60) and PSSLi gel (15 wt.%) were compared with bare P(VdF-*co*-HFP) GPE. The temperature dependent ionic conductivity comparison between P(VdF-*co*-HFP) GPE, PSSLi gel and PSSLi GPE is shown in Fig.5.1. It was seen that P(VdF-*co*-HFP) GPE has a slight curvature, while the PSSLi GPE and gels showed a linear Arrhenius behavior. The ionic conductivity of P(VdF-*co*-HFP) GPE, PSSLi gel and PSSLi GPE was 2.9, 1.4 and 0.05 mS/cm at 30 °C. The ionic conductivity of PSSLi GPE was two orders of magnitude lower than the P(VdF-*co*-HFP) GPE, due to the number of charge carriers being halved. The ionic conductivity of the

PSSLi gel was 48% of the ionic conductivity of P(VdF-*co*-HFP) GPE. The difference in ionic conductivity is due to the difference in ion conduction mechanism between the three systems. In the P(VdF-*co*-HFP) GPE, there are three phases-solid polymer matrix, gelled polymer phase and absorbed liquid electrolyte. The solid polymer matrix offers mechanical integrity to the microporous membranes, while the latter two phases significantly contribute towards ionic conductivity. Thus an increase in the amount of gel phase and the absorbed liquid electrolyte lead to an increase in ionic conductivity.

Fig.5.1 Comparison of temperature dependent ionic conductivity of lithiated and fluorinated GPEs

Electrospun PSSLi on the other hand, merely acts as a porous matrix into which the solvent was absorbed, rather than forming a gel phase. It was seen that the ionic conductivity of the electrospun PSSLi GPE was linear and it follows the Arrhenius law rather than the VTF function. Upon introduction of the solvent, the

dissociated lithium ions diffuse through the solvent, which forms the fast ion conduction channel. In the PSSLi GPE although the lithium ions are dissociated, the poor affinity of the polymer to the solvents and the lack of formation of gel phase results in the lower ionic conductivity.

In the PSSLi gel, dissolution of PSSLi in the solvent leads to the formation of a stable gel. The ionic conductivity increases by two orders of magnitude when compared to the PSSLi GPE, due to the increased gel phase and optimized lithium concentration. The optimized composition for achieving best ionic conductivity was found to be 15 wt.% PSSLi. Beyond the optimum composition, it was seen that ionic conductivity begins to drop. Thus, it was seen an increase in gel phase does not necessitate and increase in ionic conductivity as in the case of the P(VdF-*co*-HFP) GPE. A balance between the concentration of lithium, viscosity of the gel, ion-screening effect and dissociation of the SO₃Li bond was necessary to obtain optimum performance. Although the ionic conductivity was an order of magnitude higher than the PSSLi GPE, the ionic conductivity was lower than the P(VdF-*co*-HFP) GPE due to the lower number of charge carriers.

The effect of polymer structure on the transference number was studied. Transference number measured by DC Polarization method and NMR and compared in Table.5.1. It was seen that the values are in close agreement with the NMR values. It was seen that PSSLi gel exhibits unity transference number, while the P(VdF-*co*-HFP) GPE exhibits a transference number of 0.4 which implies that 60% of the current is being carried by the anions.

Table.5.1.Comparison of transference number of lithiated and non-lithiated GPE

Electrolyte	T_{Li^+} (DC polarization)	T_{Li^+} NMR
P(VdF- <i>co</i> -HFP) GPE	0.42	0.51
PSSLi gel	0.93	0.97

This clearly proves that the lower ionic conductivity of PSSLi gel is due to the lower number of charge carriers. However, because of the higher T_{Li^+} , it is expected that PSSLi gel would deliver higher discharge capacities at high current densities. To study the effect of increased T_{Li^+} on the discharge capacity, the normalized rate capability of PSSLi gel and P(VdF-*co*-HFP) GPE was compared. PSSLi gel was chosen over PSSLi GPE owing to its higher ionic conductivity. The results are shown in Fig.5.2. The capacity was normalized using the capacity obtained for the individual cells at 0.1 C rate. The lack of mechanical stability of PSSLi gel necessitates the use of Celgard as a separator. The use of Celgard adds to the ohmic drop of the cell.

Fig.5.2 Comparison of rate capability of lithiated and non-lithiated GPE

As mentioned in chapter 4, increase in ohmic drop leads to a lower capacity at high C rates, but in this case, it was seen that there was no significant difference at high rates. This can be attributed to the lack of concentration gradients in the cell with PSSLi gel. Although the capacity of the cell with PSSLi was lower than the cell with P(VdF-*co*-HFP) GPE, the exclusion of concentration polarization in the cell leads to improved cycling at high C-rates. In the P(VdF-*co*-HFP) GPE, the bulk of the current is still being carried by the anions, this leads to anions diffusing faster due to the concentration gradient and forming a layer on the electrode which acts as a barricade. Thus lithium is no longer able to access the active material beyond this layer and this leads to lower performance especially at high C rates. But in PSSLi gel, since only lithium ions are mobile, this polarization effect is absent. Although the capacity at all the studied rates is lower for the PSSLi gel, there is no significant difference in the normalized capacity.

5.2 Effect of fillers and blends on the electrochemical performance of P(VdF-*co*-HFP) GPEs

As seen from Chapter 4, the nature of the filler/ polymeric blend is very important for the electrochemical performance of the fluorinated GPE. The fillers influence porosity, uptake, crystallinity and ion transport. The nature of the interactions between the filler and the polymeric surface are instrumental in altering the ion transporting properties and transference number of the GPEs. The basic reason for incorporation of fillers is that they improve the thermal, mechanical and ion conducting properties by altering the ion transport pathway in different ways. The results for each individual composite/blend were presented in Chapter 4. The best

performing GPEs from each system were compared, to understand the effect of the fillers and the mechanism by which they improve the electrochemical properties of GPEs. P(VdF-*co*-HFP)-clay(1%) GPE, ESM-03 (9 wt.% BDN), P(VdF-*co*-HFP)-LAGP(15%) GPE, ESM-C (P(VdF-*co*-HFP)/PEO ratio (wt.%) of 80/20) and IPG-02(P(VdF-*co*-HFP)-LAGP composite with PEO content 10 wt.%) were compared.

The electrolyte uptake of the GPEs was compared and the results are shown in Fig.5.3.

Fig.5.3 Comparison of electrolyte uptake of composite and blend GPEs

It was seen that electrolyte uptake is strongly dependent on the nature of the filler. BDN, PEO and LAGP exhibit greater affinity to the carbonate based solvents when compared to clay. The electrolyte uptake of the IPG GPE was higher than the other GPEs owing to the higher porosity and presence of LAGP. Electrolyte uptake is strongly dependent on the polarity of the composite. The

increase in polarity of the polymer matrix by the addition of BDN and LAGP leads to increased electrolyte uptake. In the blend GPE, the presence of ether oxygen bonds and the solubility of PEO in EC:DEC (1:1 w/w) leads to formation of higher amount of gel phase, leading to higher uptake. The lower uptake of the P(VdF-*co*-HFP)-clay(1%) GPE was due to the lower polarity of the composite. The electrolyte uptake of the GPEs followed the order P(VdF-*co*-HFP)-clay(1%) GPE < ESM-03 < P(VdF-*co*-HFP)-LAGP(15%) GPE < ESM-C < IPG-02.

The stability of the GPEs was compared by studying their retention characteristics (Fig.5.4). It was seen that the P(VdF-*co*-HFP)-LAGP(15%) GPE shows lowest leakage with a leakage of < 8% over 2 h and ESM-C shows highest leakage with a leakage of 13% over 2 h.

Fig.5.4 Comparison of electrolyte retention of composite and blend GPEs

The difference in retention properties results from the difference in mechanical stability of the GPEs. It was seen that the retention of the IPG-02 was

higher than ESM-C and ESM-03, although it shows much higher porosity and therefore a much higher amorphous content. This increase in retention was due to the presence of LAGP. It was seen the presence of clay leads to a formation of a stable with leakage $< 10\%$, suggesting that the presence of high surface area clay tactoids on the surface of the GPE results in the formation of a low leak gel. The low leakage implies that the GPEs are capable of maintaining their good electrochemical properties with storage.

It was seen that the stability of the gel was directly linked to the mechanical stability of the membranes which were activated to form the GPE. The mechanical properties of the GPEs were compared and the values are tabulated in Table.5.2. It was seen that the LAGP and clay composites displayed best mechanical properties.

Table.5.2.Mechanical properties of composites and blends

Membrane	Tensile strength (MPa)	Young's modulus (MPa)
P(VdF- <i>co</i> -HFP)	4.5 ± 0.3	9.2 ± 0.3
P(VdF- <i>co</i> -HFP)-clay(1%)	8.2 ± 0.3	10.4 ± 0.3
ESM-03	2.8 ± 0.3	7.7 ± 0.3
P(VdF- <i>co</i> -HFP)- LAGP(15%)	12.4 ± 0.3	16.2 ± 0.3
ESM-C	6.4 ± 0.3	9.4 ± 0.3
IPG-02	7.8 ± 0.3	10.0 ± 0.3

The effect of the composites/blends on the thermal properties was compared and the results are shown in Fig.5.5. The values of the onset decomposition temperature and char yield are tabulated in Table 5.3. It was seen that P(VdF-*co*-HFP)-LAGP(15%) shows highest thermal stability. The order of onset decomposition temperature was P(VdF-*co*-HFP)-LAGP(15%) > IPG-02 > P(VdF-*co*-HFP)-clay(1%) > ESM-C > ESM-03. ESM-C, however shows two onset decomposition temperatures corresponding to onset for PEO and P(VdF-*co*-HFP).

Fig.5.5 TGA of composite and blend membranes

The char yield followed the almost the same trend with the exception of ESM-C and ESM-03. It was seen that ESM-C shows the lowest char yield. This was because PEO was completely decomposed by 412 °C and therefore the blend showed the lowest char yield. The onset decomposition temperature of all the membranes except ESM-03 was higher than pristine P(VdF-*co*-HFP) (400 °C), due to the presence of either high melting point reinforcing ceramics or

interactions between P(VdF-*co*-HFP) and PEO. The low melting point of BDN coupled with the higher amorphous content leads to a reduction in thermal stability of the composite.

Table 5.3. Thermal properties of composite and blend GPEs

Membrane	Onset decomposition temperature (°C)	Char yield at 500 °C (%)
P(VdF- <i>co</i> -HFP)	400	35
P(VdF- <i>co</i> -HFP)-clay(1%)	418	38
ESM-03	407	28
P(VdF- <i>co</i> -HFP)-LAGP(15%)	426	43
ESM-C	418	25
IPG-02	424	34

The effect of nature of filler/blend on the crystallinity was compared, and the results are shown in Table.5.4. It was seen that that addition of clay, LAGP and BDN resulted in reduced crystallinity when compared to bare P(VdF-*co*-HFP). The addition of PEO leads to increased crystallinity due to the higher crystallinity of PEO. It was seen that the melting temperature was hardly influenced by fillers or blends [203]. BDN and LAGP are most successful in inhibiting the crystallization of P(VdF-*co*-HFP). The difference in crystallinity between the IPG-02 and the P(VdF-*co*-HFP)-LAGP(15%) membrane is attributed to the difference in concentration of LAGP.

Table.5.4.Comparison of crystallinity and melting temperatures of composite and blend membranes

Membrane	Melting temperature (T_m)(°C)	Crystallinity (%)
P(VdF- <i>co</i> -HFP)	146	43
P(VdF- <i>co</i> -HFP)- clay(1%)	146	38
ESM-03	146	30
P(VdF- <i>co</i> -HFP)- LAGP(15%)	145	31
ESM-C	146	43
IPG-02	146	39

It was seen that the electrolyte uptake of the ESM-C (Fig.5.3) was high even though the membrane is more crystalline, which can be attributed to the solubility of PEO in the organic solvent mixture. It was seen that the uptake values are in line with the crystallinity values, proving that increased amorphous phase leads to higher uptake and larger number of charge carriers

The effect of the nature of the filler or polymeric blend, on the ionic conductivity of the GPEs was compared. The results are shown in Fig.5.6. The electrolyte uptake values and the ionic conductivity calculated at 30 °C are tabulated in Table.5.5. It was seen that the ionic conductivity does not follow the same trend as electrolyte uptake, implying that apart from higher uptake, there are other factors which contribute to improving the ionic conductivity of the GPEs. As mentioned earlier ionic conductivity is influenced by different factors.

Fig.5.6 Comparison of ionic conductivity of composite and blend GPEs

The important factors which influence the ionic conductivity are reduced ionic coupling/ ion pair formation, increased lithium salt dissociation and increased segmental chain motion leading to better lithium diffusion. It was seen that although the ESM-C shows higher uptake compared to P(VdF-co-HFP)-LAGP(15%) GPE, ESM-03 and P(VdF-co-HFP)-clay(1%) GPE, the ionic conductivity was lower. This is because of the different mechanisms by which these fillers and blends affect lithium ion conduction.

In the P(VdF-co-HFP)-clay(1%) GPE, the layered structure of clay provides an opportunity for exfoliation of the platelets and the intercalation of polymer chains between the platelets [123,141,204]. This intercalated structure offers a two-fold advantage; one is the reduction of crystallinity which translates to higher ionic conductivity and two a Lewis acid-base complex formation. The

positive charges on the surface of the clay platelets compete with lithium ions to form complexes with the polymer. This leads to a reduction in ionic coupling between Li^+ and PF_6^- and Li^+ and the polymeric chain, thereby offering alternate pathways for ion motion [205]. The main reason for the improvement in ionic conductivity of P(VdF-*co*-HFP)-clay GPE is the reduced ion coupling or reduced ion pair formation.

Table.5.5.Electrolyte uptake and ionic conductivity of composite and blend GPEs

GPE	Electrolyte uptake (%)	Ionic conductivity at 30 °C (mS/cm)
P(VdF- <i>co</i> -HFP)	400	2.9
P(VdF- <i>co</i> -HFP)-clay(1%)	456	5.5
ESM-03	477	6.3
P(VdF- <i>co</i> -HFP)-LAGP(15%)	527	8.3
ESM-C	599	5.0
IPG-02	634	9.6
P(VdF- <i>co</i> -HFP)-LAGP)/PEO	532	7.0

In ESM-03, the presence of BDN which has high dielectric constant ($\epsilon = 55$) and good solvating ability, helps in improving the lithium salt dissociation capability [187,206]. Unlike clay which increases the conductivity of GPEs by reducing the formation of ion pairs, BDN actively participate in ion conduction mechanism and is directly involved in increasing ionic conductivity [186–188]. The presence of the active ion hopping centers (nitrile bond) in BDN leads to

faster lithium ion diffusion [186–188]. Also the high polarity of the matrix leads to increased lithium salt dissociation. The ionic conductivity of ESM-03 was 14% higher than that of P(VdF-co-HFP)-clay (1%) GPE. Therefore, it was seen that the effect of increased lithium salt dissociation on ion conduction was more critical than reduced ionic coupling.

In ESM-C, the presence of PEO improves the chain segmental motion of the polymeric chains. The transport of Li^+ ions in ESM-C is a combination of the lithium ion diffusion in the gel phase and motion of the complexed Li^+ , due the local relaxation and segmental motion of the amorphous regions in the PEO chains [139]. The higher conductivity of ESM-C when compared to bare P(VdF-co-HFP) GPE is associated with the PEO crystalline-amorphous phase transition, which enhances the ion mobility and segmental motion of the polymer chains. It was seen that the shape of the curve of the blend GPE was significantly different from the other GPEs. The significant rise in conductivity of the blend GPE above 40°C (3.19 K^{-1}) was due to the softening and melting of crystalline phase of PEO near 60°C making the polymer electrolyte fully amorphous and hence the conductivity enhancement. However, it was seen that the ionic conductivity of ESM-C was lower than all the composite GPEs at all temperatures. This implies that the increased segmental motion was not as significant in improving ion motion as increased lithium salt dissociation of reduced ionic coupling. Although the electrolyte uptake of the ESM-C was high, the association of lithium ions with the O atoms of PEO leads to motion of lithium ions by the local segmental motion

of the PEO chains. This process is very slow compared to the lithium diffusion though the gel phase.

In the P(VdF-*co*-HFP)-LAGP(15%) GPE, the presence of LAGP which is a fast single ion conductor with good mechanical strength, thermal and chemical stability leads to a two-fold advantage [192]. The use of LAGP combines the effects of using clay and BDN by reducing the ion pair formation and increasing the lithium ion concentration. The presence of hydroxyl groups on the surface of the LAGP which can compete with the F atom of the polymer to form complexes with lithium, results in weakening of polymer-Li ion complex. This leads to reduction of ion coupling, thereby leading to increased ionic conductivity. Being a lithium ion conductor and carrier, it increases the concentration of lithium ions in the system. The ionic conductivity of P(VdF-*co*-HFP)-LAGP(15%) GPE was 36% higher than ESM-03 and 51% higher than P(VdF-*co*-HFP)-clay(1%) GPE. This implies that combined effect of increased lithium ion concentration and decreased ionic coupling is more significant than each individual factor. The ionic conductivity of P(VdF-*co*-HFP)-LAGP(15%) GPE was 66% higher than that of ESM-C proving that improved chain segmental motion has a lower effect on ionic conductivity.

In IPG-02, the preferential polymer dissolution leads to higher porosity, leading to increased electrolyte uptake. The increased uptake, leads to an increase in the gelled polymer phase and absorbed liquid electrolyte encapsulated in the pores. Due to the presence of LAGP the effect of decreased ionic coupling was also present. It was seen that the ionic conductivity of the IPG-02 was higher than

that of P(VdF-*co*-HFP)-LAGP (15%) GPE. This implies that when the effect of decreased ionic coupling was constant, further increasing the number of lithium ions leads to an increase in ionic conductivity. This implies that increasing lithium salt dissociation and number of lithium ions has a more pronounced effect on the ionic conductivity of GPEs. The ionic conductivity of the IPG-02 was 16% higher than the conductivity of P(VdF-*co*-HFP)-LAGP(15%) GPE.

For comparison P(VdF-*co*-HFP-LAGP)/PEO GPE, which has the same composition as IPG-02; but where PEO was not washed off, was also studied. The ionic conductivity of P(VdF-*co*-HFP-LAGP)/PEO GPE was 40% higher than ESM-C. This difference can be attributed to the presence of LAGP in the P(VdF-*co*-HFP-LAGP)/PEO GPE. However, the conductivity was lower than the IPG GPEs. This further proves that, the effect of increased chain segmental motion (by addition of PEO) was lower than the effect increased lithium ion concentration (electrolyte uptake and lithium ion concentration and decreased ion coupling (by incorporation of LAGP and also increased lithium ion concentration). The ionic conductivity of P(VdF-*co*-HFP-LAGP)/PEO GPE was 37% lower than IPG-02 GPE.

Therefore the order in which the factors influence ionic conductivity was; increased lithium ion concentration > decreased ionic coupling > increasing chain segmental motion. However the first two factors have a more pronounced effect on the ion transport mechanism when compared to the third factor.

The transference number of the composite and blend GPEs measured by DC polarization were compared and the results shown in Fig.5.7.

Fig.5.7 Transference number of composite and blend GPEs by DC polarization (a) Initial impedance (b) steady state impedance and (c) initial to steady state current response

The effect of the fillers/polymeric blends on the transference number was compared and the values are tabulated in Table.5.6.

Table.5.6.Comparison of transference number of composite and blend GPE

GPE	D_{Li} (*10 ⁷ cm ² /s) (30 °C)	D_F (*10 ⁷ cm ² /s) (30 °C)	T_{Li+} (DC polarization)	T_{Li+} NMR
P(VdF- <i>co</i> -HFP)	9	9	0.42	0.50
P(VdF- <i>co</i> -HFP)- clay(1%)	15	9	0.57	0.62
ESM-03	17	13	0.49	0.56
P(VdF- <i>co</i> -HFP)- LAGP(15%)	20	9	0.68	0.71
ESM-C	7	9	0.43	0.49
IPG-02	22	12	0.65	0.70

It was seen that the incorporation of clay, BDN and LAGP lead to an increase in transference number of the GPE. However in ESM-C, the incorporation of PEO leads to a negligible change in transference number because of complexation of lithium with the O atoms in PEO. The increase in transference number was most significant for the P(VdF-*co*-HFP)-LAGP(15%) GPE. This can be attributed to the presence of LAGP which is a pure lithium conductor and hence has a lithium transference number of 1. It was seen that the maximum transference number of 0.68 was obtained for P(VdF-*co*-HFP)-LAGP(15%) GPE, which was 61% higher than the pristine P(VdF-*co*-HFP) GPE. It was seen that the

IPG-02 has a slightly lower transference number compared to P(VdF-*co*-HFP)-LAGP(15%) GPE. This can be attributed to the higher uptake, which leads to larger number of PF_6^- anions and thereby leading to a slight decrease in lithium transference number

The stability of the composite and blend GPEs against lithium metal was compared and the results are shown in Fig.5.8. The equivalent circuit simulating the EIS data is also shown in Fig.5.8.

Fig.5.8 Time dependent interfacial resistance of composite and blend GPEs and inset equivalent circuit for the EIS data

It was seen that IPG-02 was the most stable while ESM-C was least stable. The stability of the GPE is dependent on the electrolyte retention. High retention ensures that high conductivity is maintained and a stable SEI layer is formed. The interfacial resistance of all the GPEs stabilizes within 5 days. The presence of

LAGP which acts a surface stabilizer is responsible for the good stability of the IPG-02 and P(VdF-*co*-HFP)-LAGP(15%) GPE. The presence of high surface area clay tactoids which stabilize the interface between lithium metal and P(VdF-*co*-HFP)-clay(1%) GPE, is responsible for its high stability. The lower stability of the ESM-03 and ESM-C is due to higher leakage which leads to loss of conductivity over time.

The equivalent circuit shown in Fig.5.8 consists of three elements, R_s which represents the bulk resistance connected in series to the parallel combination of a constant phase element (CPE) accounting for the double layer formation and R_{ct} , which represents the interface resistance (charge transfer) [207–209]. The values obtained from the fitting of the equivalent circuit for the final interfacial resistance are tabulated in Table 5.7. It was seen that the measured values and the fitted values follow the same trend, with IPG-02 showing the lowest bulk and interface resistance.

Table 5.7. Equivalent circuit fitting parameters for interfacial resistance

Cell	R_s (Ω)	R_{ct} (Ω)
P(VdF- <i>co</i> -HFP)-clay(1%)	5	102
ESM-03	6	144
P(VdF- <i>co</i> -HFP)-LAGP(15%)	4	92
ESM-C	5	170
IPG-02	3	64

The stability of the GPEs against lithium metal was further studied using LSV to understand their electrochemical stability window. The results are shown in Fig.5.9

Fig.5.9 Electrochemical stability window of composite and blend GPE

It was seen that the LSV curves follow the same trend as the interfacial resistance. The lower stability of ESM-03 and ESM-C can be attributed to poor adhesion to lithium metal and the leakage of electrolyte, which leads to increased resistance.

The stability of the composite and blend GPEs to the reductive condition was studied using continuous cyclic voltammetry. The CV profiles are shown in Fig.5.10. It was seen that all the GPEs showed well defined anodic and cathodic peaks. There was no significant difference in the oxidation and reduction peaks of the composite and blend GPEs. It was seen that all the GPEs exhibit high reversibility with constant oxidation and reduction peaks over continuous cycling

[178]. The composite and blend GPEs exhibit slightly higher reversibility compared to the bare GPE as seen by the shape of the reduction scan in Fig.5.10.

Fig.5.10 CV scans of GPEs (a) P(VdF-co-HFP), (b) PVdF-co-HFP-clay (1%), (c) ESM-03, (d) ESM-C, (e) P(VdF-co-HFP)-LAGP(15%) and (f) IPG-02

The charge discharge curves of the Li/LiFePO₄ cells with composite and blend GPEs at 0.1C rate for the first cycle and the 50 th cycle are shown in

Fig.5.11. It was seen that all the GPEs show good capacity retention and a flat plateau at 3.4 V characteristic of LiFePO_4 . It was seen that the discharge capacities of all the cells were lower in the 50 th cycle when compared to the first cycle. However, the capacity loss was lower for P(VdF-*co*-HFP)-LAGP (15%) and IPG-02 GPE owing to higher ionic conductivity and better utilization of active material [133].

Fig.5.11 Charge discharge curves of cells with composite and blend GPEs

The impedance response of the $\text{Li}/\text{LiFePO}_4$ cells with the composite and blend GPEs were studied before and after cycling. The EIS plots which have been fitted using nonlinear least square fitting are shown in Fig.5.12. It was seen that the impedance follows the same trend as ionic conductivity and discharge capacity. The cell with IPG-02 GPE showed the lowest impedance further

supporting its high ionic conductivity. The impedance of all the cells increased with cycling, indicating the formation and stabilization of the SEI layer.

Fig.5.12 EIS of Li/LiFePO₄ cells before and after cycling

The equivalent circuit used to simulate the EIS is shown in Fig.5.13 and the fitting parameters are tabulated in Table 5.8. The equivalent circuit consists of a resistance (R_s) which represents the bulk resistance of the electrolyte, R_{SEI} which represents the resistance of the interface between the GPE and LiFePO₄, R_b , which represents the resistance to ion transport within the electrode and Warburg element (W), which represents the lithium ion diffusion. The circuit also consists of two constant phase elements representing the formation of the SEI layer [207–209].

Fig.5.13 Equivalent circuit used to fit EIS data

Table 5.8. Equivalent circuit fitting parameters of Li/LiFePO₄ cells before and after cycling

GPE	R_s (Ω)	R_{SEI} (Ω)	R_b (Ω)
P(VdF- <i>co</i> -HFP)-clay(1%) before	5	53	143
P(VdF- <i>co</i> -HFP)-clay(1%) after	10	98	276
ESM-03 before	5	55	140
ESM-03 after	12	141	295
P(VdF- <i>co</i> -HFP)-LAGP(15%) before	4	51	132
P(VdF- <i>co</i> -HFP)-LAGP(15%) after	9	72	274
ESM-C before	4	53	148
ESM-C after	12	165	269
IPG-02 before	3	49	141
IPG-02 after	8	66	252

It was seen that the measured values and the fitted values match well. It was seen that the R_s values for the cells with ESM-03 and ESM-C increased more significantly during cycling, when compared to the other composites. This can be attributed to the lower electrolyte retention, which leads to loss of conductivity. The R_{SEI} values of all the cells increased with time, with the values following the same trend as the interfacial resistance.

The cycling stability of Li/LiFePO₄ cells with composite and blend GPEs at 0.1C rate is compared. The results are shown in Fig.5.14. It was seen that all cells show good capacity retention with a capacity fade <4 mAh/g over 50 cycles. The discharge capacity follows the same order as ionic conductivity. A lower resistive gel phase leads to a better transport of lithium and a faster diffusion of lithium ions between cathode and anode. IPG-02 and P(VdF-*co*-HFP)-LAGP (15%) GPE show slightly higher capacity compared to other composite and blend GPEs, due to the higher ionic conductivity.

Fig.5.14 Comparison of cycling stability of composite and blend GPEs

The rate capability of the composite and blend GPE was compared. The results are shown in Fig.5.15. The capacity was normalized with the capacity obtained for the individual cells at 0.1C rate, to study the effect of the morphology of the GPE. At 3C rate, the high porosity and conductivity of IPG-02, leads to a smaller ohmic drop leading to a higher capacity. At other C rates, no significant

difference was seen in the capacities of the cells. All the cells maintain good capacity retention even after the cell is returned back to 0.2C rate after 50 cycles.

Fig.5.15 Comparison of rate capability of composite and blend GPE

The charge discharge curves of the Li/LTO cells with composite and blend GPEs at 0.1C rate for the first cycle are shown in Fig.5.16. It was seen that all the GPEs show good capacity retention and a flat plateau at 1.5 V characteristic of LTO. It was seen that the discharge capacities follow the same trend as the Li/LiFePO₄ cells. It was seen that the P(VdF-co-HFP)- LAGP (15%) and IPG-02 GPE show better performance owing to higher ionic conductivity and better utilization of active material [210].

Fig.5.16 Initial charge/discharge of Li/LTO cells with composite and blend GPEs

The cycling stability of Li/LTO cells with composite and blend GPEs at 0.1C rate is compared and the results shown in Fig.5.17.

Fig.5.17 Comparison of cycling stability of Li/LTO cells composite and blend GPEs

It was seen that all cells show good capacity retention with a capacity fade <9 mAh/g over 50 cycles. The discharge capacity follows the same order as ionic conductivity. A lower resistive gel phase leads to a better transport of lithium and a faster diffusion of lithium ions between cathode and anode. IPG-02 and P(VdF-*co*-HFP)-LAGP (15%) GPE show slightly higher capacity compared to other composite and blend GPEs, due to the higher ionic conductivity.

5.3 Effect of fillers and blends on the electrochemical performance of PSSLi gels

As mentioned previously, unlike the P(VdF-*co*-HFP) based GPEs increased lithium concentration does not result in improved ionic conductivity of the PSSLi system. Ionic conductivity is mainly influenced by the number of lithium ions which are dissociated in the solvent, because the high conduction pathway is the diffusion of lithium through the solvent. The ion hopping mechanism is too slow, and the repulsion between adjacent lithium ions due to condensation effect leads to loss of ionic conductivity.

The effect of fillers and polymeric blends on the ionic conductivity of PSSLi gel was compared and the results are shown in Fig.5.18. It was seen that the incorporation of BDN and SiO₂ results in increasing the dissociation of lithium ions leading to a higher ionic conductivity. On the other hand, addition of PEO results in increased viscosity and formation of complexes between lithium and ether oxygen of PEO leading to lower ionic conductivity.

Fig.5.18 Comparison of temperature dependent ionic conductivity of composite and blend PSSLi gels

5.4 Fundamental studies on ion transport mechanism in PSSLi gels

To further understand the ion transport mechanism in the PSSLi gels, the lithium diffusion coefficients were studied. Ion conduction in PSSLi gels is predominantly by diffusion through the solvent (DMSO). The effect of PSSLi concentration on the lithium ion diffusion coefficient is discussed. The effect of fillers/blends and PSSLi concentration on the lithium ion diffusion is discussed by comparing values calculated from ionic conductivity by Nernst Einstein equation and diffusion coefficients measured by NMR.

5.4.1 Effect of PSSLi concentration on lithium diffusion

Ionic conductivity is dependent on two opposing factors- (i) increased dissociated lithium ions and (ii) reduced mobility with increasing lithium content. Therefore a balance between the two is necessary for optimum ionic conductivity.

It was seen from Chapter 4, that ionic conductivity of the PSSLi gel is strongly dependent on increasing the lithium dissociation and diffusion and not merely increasing lithium content. Therefore, the effect of PSSLi composition on the diffusion of lithium was studied. The diffusion coefficients were calculated from the ionic conductivity data using the Nernst Einstein equation,

$$D^{\sigma} = \frac{\sigma_{dc}KT}{Nq^2}$$

where $K = 1.3806505 \times 10^{-23} \text{ J/K}$, T is the absolute temperature in Kelvin, N is the particles density of the charge carriers and q is the charge in coulomb. The diffusion coefficients obtained from ionic conductivity are representative of only the mobile lithium ions in the system. The log diffusion coefficient (D) versus $1000/T$ plot is shown in Fig.5.19. Almost linear curves were obtained and therefore diffusion coefficients also follow Arrhenius fit just like ionic conductivity.

For the sample with 25wt.% PSSLi, a slight curvature is seen, indicating that it follows VTF function. This indicates that, beyond optimum concentration, the motion of the bound lithium ions begin to influence the diffusion process and the chain segmental motion is also involved. It was seen that the diffusion coefficients follow the same trend as ionic conductivity with highest diffusion coefficient observed for the 15 wt.% sample. The diffusion coefficient begins to drop with further increase in lithium ion concentration. This implies that even though the number of ions was higher, the presence of shielding effect leads to

lowered diffusion. Also the presence of ion-ion repulsion may lead to a coiled conformation of the chains, thereby creating to a more tortuous path for ion diffusion. This leads to lowered diffusion coefficient.

Fig.5.19 Temperature dependent lithium diffusion coefficients of PSSLi gels with varying PSSLi concentration

The diffusion coefficients of the 15 wt.% PSSLi gel was calculated from ionic conductivity and compared with that measured by NMR. The PSSLi gel with 15 wt.% PSSLi was chosen, because it displayed the highest ionic conductivity, which implies it has the largest number of mobile lithium ions. The results are shown in Fig.5.20. It was seen that the diffusion coefficient from NMR resembled the calculated values, indicating that the conduction process resembles the lithium diffusion process.

Fig.5.20 Temperature dependent diffusion coefficients of 15 wt.% PSSLi gels by NMR and AC impedance

The diffusion coefficients measured by NMR was a degree higher than that calculated from AC impedance. The difference in diffusion coefficients can be attributed to the nature of measurement. Ionic conductivity measurements measure the diffusion of the charged species (isolated ions) and therefore, this is a measure of the free dissociated lithium ions in the system [157]. NMR measures the total diffusion of lithium ions in the system, both paired and isolated charges. In general, both isolated and paired charges are present in the system and a rapid exchange between the two states takes place. [107,157,180].

The difference in the two diffusion coefficients indicates that there is significant ion coupling and association in the PSSLi gel. Although by introducing DMSO into PSSLi, lithium solvation increases, bound lithium ions are still present in the system. However, it was seen that the trend of the measured

values are the same as that calculated from AC impedance proving that PSSLi gel is a good lithium ion transport medium.

5.4.2 Effect of fillers and blends on lithium diffusion

To better understand the effect of fillers on the lithium ion diffusion, the diffusion coefficients were measured using pfg-NMR and compared with the values calculated from AC Impedance. To further investigate the effect of SiO₂ in increasing lithium ion dissociation, the lithium diffusion coefficient was calculated using Nernst-Einstein equation and the results are shown in Fig.5.21. The log diffusion coefficient (D) versus 1000/T plot is shown in Fig.5.21. Linear plots were obtained and therefore diffusion coefficients also follow Arrhenius law just like ionic conductivity.

Fig.5.21 Temperature dependent lithium diffusion coefficients of PSSLi-SiO₂ composite gels

It was clearly seen that the presence of SiO₂ increases the diffusion coefficient of the free lithium ions, implying that it is an active agent in increasing the dissociation of lithium ions from the sulfonate group. The presence of larger number of free lithium ions, leads to the higher diffusivity and therefore higher conductivity of the composite gels. The diffusion coefficient begins to decrease beyond 6 wt.% SiO₂, implying that the aggregation of particles reduces the interaction between SiO₂ and the polymer leading to lower conductivity compared to the bare sample.

The temperature dependent lithium diffusion coefficients measured by NMR are plotted in Fig.5.22.

Fig.5.22 Temperature dependent ⁷Li diffusion coefficient of PSSLi-SiO₂ composite gels

It was seen that the values are more than an order of magnitude higher than the calculated values. It was seen that the diffusion coefficients increase upto

6 wt.% SiO₂, after which they begin to fall steeply, which is consistent with the ionic conductivity data.

The measured and calculated diffusion coefficients of 6 wt.% SiO₂ gel, which has the highest ionic conductivity was compared with bare PSSLi gel. The results are shown in Fig.5.23.

Fig.5.23 Comparison of diffusion coefficients of 6wt.% SiO₂ gels

Similar to the bare PSSLi gel, it was seen that the measured values were an order of magnitude higher than the calculated values. This implies that ion pairing is still present in the SiO₂ gels. The increased ionic conductivity is due to the slight increase in the diffusion coefficients of the free lithium ions due to the Lewis acid-base interactions which reduce ion coupling. The difference in the measure and calculated values is also slightly lower for the 6 wt.% SiO₂ gel.

To further understand the effect of BDN, diffusion coefficients of the composite gels were calculated from AC impedance spectroscopy and compared with that measured by NMR. The Haven ratio, which is a measure of the degree of dissociation of the system, was calculated using the equation

$$H = \frac{D^{\text{NMR}}}{D^{\sigma}} \quad (14)$$

where H is the Haven ratio, D^{NMR} is the diffusion coefficient of all the lithium ions in the system (both bound and free) and D^{σ} is the diffusion coefficients of only the free lithium ions.

The comparison of diffusion coefficients with BDN content at room temperature is shown in Fig.5.24. The diffusion coefficients follow the same trend as ionic conductivity. It was seen that as expected, the diffusion coefficients of the free lithium ions increases with increasing BDN content upto 20 wt.% BDN and then decreases. However, for the gel with 50 wt.% PSSLi, it was seen that the difference between the two values continued to decrease. This implies that although the diffusion coefficients of the free lithium ions decreases with increasing BDN content for the composites with BDN content > 20 wt.%, the Haven ratio was closer to one. This implies that the degree of dissociation continues to increase with increasing BDN content. The decrease in ionic

conductivity can thus be attributed to the decreased number of charge carriers in the system [113].

The ionic conductivity is governed by both the number of charge carriers and the increased ion mobility. In general, increased lithium ion concentration leads to lowered ionic mobility and hence a balance between the two is necessary. The sample with 20 wt.% BDN shows the optimum value with an ionic conductivity increment by a factor of 3. This clearly indicates that for achieving optimum ionic conductivity, a balance between the number of charge carriers and the number of dissociated lithium ions (free charge carriers) has to be achieved.

Fig.5.24 Room temperature lithium diffusion coefficients with varying BDN content

To understand the effect of PEO, the diffusion coefficients were calculated using the Nernst-Einstein equation. The log diffusion coefficient (D) versus $1000/T$ plot is shown in Fig.5.25.

Fig.5.25 Temperature dependent lithium diffusion coefficients of PSSLi-PEO gels

Linear plots were obtained and therefore diffusion coefficients also follow Arrhenius law just like ionic conductivity. It was seen that the diffusion coefficients follow the same trend as ionic conductivity implying that the presence of PEO does not increase the dissociation of lithium. The mobility of lithium ions reduces because of the increased crystallinity and increased microviscosity, which leads to a more tortuous path for ion conduction. The number of free charge carriers in the system decreases with increasing PEO content.

To further understand the effect of PEO addition on the dissociation of lithium, the Haven ratio was calculated and compared. The comparison of calculated and measured diffusion coefficients at room temperature is shown in Fig.5.26. It was seen that the ratio is constant showing no dependency on PEO content. The number of free lithium ions (D^0) in PEO blend gels was lower than the bare PSSLi gel. The presence of PEO therefore has a negative effect on the

solvation of lithium ions. The difference in the measured and calculated diffusion coefficients of the blend gels was slightly higher than the bare PSSLi gels. This implies that the presence of PEO increases lithium association due to the presence of two competing groups for solvation.

Fig.5.26 Room temperature lithium diffusion coefficients with varying PEO content

The room temperature ^1H diffusion coefficient of DMSO and ^7Li of the composite and blend gels with highest ionic conductivity (6 wt.% SiO_2 , 20 wt.% BDN and 10 wt.% PEO) is shown in Fig.5.27. The constant ^1H diffusion coefficient implies that the composite formation affects the mobility of only lithium, and not the solvent. It was seen that increasing dissociation of lithium ions into the solvent results in an increase in ion diffusion which leads to high ionic conductivity. Therefore, it was seen that BDN was most effective in increasing the dissociation of lithium, while PEO was least effective. The presence of PEO leads to formation of more ion pairs leading to lower lithium

diffusion. SiO₂ is also effective in increasing the lithium ion dissociation though it is not as effective as BDN. The difference is because of the high dielectric constant and polarity of BDN.

Fig.5.27 ¹H and ⁷Li diffusion coefficients of PSSLi gels

6 Chapter 6 Conclusions

This thesis explored P(VdF-*co*-HFP) gel polymer and PSSLi gels for application as electrolytes in lithium batteries. P(VdF-*co*-HFP) membranes were prepared by phase inversion method and electrospinning. Electrospinning was found to be a better processing method to obtain better electrochemical properties. Various characterization methods like FE-SEM, TGA, DSC, AC Impedance and galvanostatic charge discharge were used to understand the electrochemical properties of the GPEs.

Effect of polymer composition on the electrochemical performance of GPEs, electrospun PVdF and P(VdF-*co*-HFP) GPEs were studied and compared. The electrochemical properties of P(VdF-*co*-HFP) GPE were found to be better than PVdF based GPEs. The P(VdF-*co*-HFP) GPE displayed good thermal and mechanical properties with a conductivity of 2.9 mS/cm at 30 °C and a transference number of 0.42.

Three different approaches were taken to improve the ion transport properties without compromising the mechanical stability. Fillers and blends were appropriately chosen to target one of the factors affecting ionic conductivity. The effect of fillers and blends on the electrochemical properties of P(VdF-*co*-HFP) GPEs was examined. Each of the fillers/blends affects one or more factors influencing ionic conductivity. The factor that has the most influence on ionic conductivity was identified.

The effect of decreased ion coupling on the ionic conductivity was studied. Exfoliated P(VdF-*co*-HFP)-clay composites were prepared using electrospinning. The P(VdF-*co*-HFP)-clay composite GPE with 1 wt.% clay exhibited the best electrochemical properties. The ultimate tensile strength of the P(VdF-*co*-HFP)-clay composite GPE with 1 wt.% clay improved by 87% compared to the bare P(VdF-*co*-HFP) GPE. The ionic conductivity of the P(VdF-*co*-HFP)-clay composite GPE with 1 wt.% clay increased by 90% compared to the bare P(VdF-*co*-HFP) GPE. The transference number of the composite improved to 0.57 from 0.42.

The effect of increased lithium dissociation was studied using BDN as the filler. The ionic conductivity improved to 6.3 mS/cm at 30 °C by the addition of 9 wt.% BDN, which was 14% higher than the P(VdF-*co*-HFP)-clay composite GPE with 1 wt.% clay and 117% higher than the bare P(VdF-*co*-HFP) GPE. It was seen that the effect of increased lithium dissociation on the ionic conductivity was more pronounced than reduced ion coupling.

The combined effect of increasing the lithium charge carrier concentration and reducing ionic coupling was studied using LAGP as the filler. The ultimate tensile strength increased by 175% when compared to the bare P(VdF-*co*-HFP) GPE. The ionic conductivity of the P(VdF-*co*-HFP)-LAGP GPE with 15 wt.% LAGP at 30 °C was 8.3 mS/cm, which was 32% higher than the P(VdF-*co*-HFP)-BDN GPE with 9 wt.% BDN. It was seen that the combined effect of both the factors on the ionic conductivity was more prominent than each individual factor.

The effect of improved local segmental chain motion was studied using P(VdF-*co*-HFP)/PEO blend GPEs. The ionic conductivity was 72% higher than the pristine P(VdF-*co*-HFP) GPE. The ionic conductivity of the P(VdF-*co*-HFP)/PEO blend GPE with 20 wt.% PEO content was 5 mS/cm at 30 °C which was 10-26% lower than the P(VdF-*co*-HFP)-BDN composite and the P(VdF-*co*-HFP)-clay composite GPE. Thus, it was seen that the effect of increased chain segmental motion on the ionic conductivity was less pronounced than reduced ion coupling and increased lithium dissociation.

The effect of increased charge carrier concentration was compared with effect of constant reduced ionic coupling. P(VdF-*co*-HFP)-LAGP/PEO blended membranes with constant LAGP content and varying PEO content were prepared. The membranes were subjected to a preferential polymer dissolution process to wash off the PEO to generate porosity in-situ. The increased porosity led to increased electrolyte uptake, with the uptake 230% more than the pristine P(VdF-*co*-HFP) GPE and 35% higher than P(VdF-*co*-HFP)/PEO blend with 20 wt.% PEO. The ionic conductivity at 30 °C for the P(VdF-*co*-HFP)-LAGP/PEO blended GPEs with 20 wt.% PEO was 9.1 mS/cm, which was 82% higher than the P(VdF-*co*-HFP)/PEO blend GPE with 20 wt.% PEO and 10% higher than the P(VdF-*co*-HFP)-LAGP GPE with 15 wt.% LAGP. Thus increased lithium charge carrier concentration was identified as most critical for improving the ionic conductivity of GPEs.

To further confirm the argument, P(VdF-*co*-HFP)-LAGP/ PEO membranes with 10 wt.% PEO content was compared, before and after in-situ

porosity generation. The ionic conductivity of the P(VdF-*co*-HFP)- LAGP/PEO GPE with 10 wt.% PEO content at 30 °C was 6.9 mS/cm, which was 32% lower than the GPE after in-situ porosity generation and 38% higher than P(VdF-*co*-HFP)/PEO blend with 10 wt.% PEO content without LAGP. Thus, amongst the factors which affect ion transport, improved chain segmental motion was least important while increased charge carrier concentration was most important.

The effect of unity transference number on the electrochemical performance was studied using the PSSLi system. PSSLi was pelletized, electrospun and gelled in DMSO and their electrochemical properties were compared. Gelling in DMSO was found to be the best method for achieving improved electrochemical properties.

The lithium concentration necessary for best ionic conductivity was optimized. It was seen that contrary to the P(VdF-*co*-HFP) based GPEs, increase in lithium ion concentration did not lead to increased ionic conductivity in PSSLi system. It was seen that increasing the lithium content in the gel beyond 15 wt.% led to a drop in conductivity. The effect of fillers and blends on the ionic conductivity of PSSLi gels was studied.

The effect of reduced ion coupling on the ionic conductivity by the incorporation of SiO₂ was studied. The ionic conductivity of the PSSLi-SiO₂ gel with 6 wt.% SiO₂ at 30 °C was 1.8 mS/cm which was 20% higher than the bare PSSLi gel. The effect of increased lithium dissociation by the incorporation of BDN was studied. The ionic conductivity of the PSSLi gel with 20 wt.% BDN at

30 °C improved by 38% compared to PSSLi-SiO₂ composite gel. However, beyond 20 wt.%, BDN the conductivity drops. The effect of improved local chain segmental motion by the incorporation of PEO was studied. The ionic conductivity of the PSSLi/PEO blend gels was lower than the bare PSSLi gel.

From the comparison of P(VdF-*co*-HFP) GPEs and PSSLi gels, it was seen that the mechanism of ion transport was very different in the two systems. An increase in lithium content (dissociated or associated) resulted in an increase in ionic conductivity in the P(VdF-*co*-HFP) GPE. In the PSSLi system, such a clear trend was not observed.

To further understand the mechanism of ion conduction in PSSLi gels, the lithium diffusion coefficients for AC impedance and NMR were compared. It was seen that beyond the 15 wt.% PSSLi, the diffusion coefficient of the free lithium ions begins to drop. The value of diffusion coefficient measured by NMR was an order of magnitude higher than the values calculated from AC impedance, implying the presence of large number of bound lithium ions. Therefore to improve the ionic conductivity, the number of mobile lithium ions needs to be increased.

For the PSSLi composite and blends systems, the same trend was observed. Therefore, to achieve optimum performance a balance between concentration of lithium and number of dissociated lithium ions is needed.

The cycling performance of a cell based on PSSLi gel was demonstrated for the first time. Celgard was used to physically separate the cathode and anode to

prevent shorting of the cell. The cell showed comparable capacity as P(VdF-*co*-HFP) GPE at high current rates, proving that the added resistance due to Celgard is compensated by the unity transference number of PSSLi. The cycling stability demonstrates the feasibility of PSSLi gel as an electrolyte for lithium ion batteries.

Based on the study, it was seen that in order to achieve alternate flexible, mechanically stable, high ionic conductivity and high transference number electrolytes, more than one factor needs to be considered. For both P(VdF-*co*-HFP) based GPEs and PSSLi gels, the mechanical and ion transporting abilities needs to be optimized by proper addition of fillers. The main significance of the work done in this thesis was the formulation of the selection criterion for choosing appropriate fillers and blends to achieve optimum performance and a better understanding of the parameters to be taken into consideration while exploring other lithiated structures for application in LIBs.

Based on the results and analysis conducted in this work, it was seen that the ideal filler for a non lithiated GPE was a lithium containing active ceramic filler, which not only serves as a reinforcing component, but also participates in the ion transport process and improves the transference number. For a lithiated GPE, it was seen that the ideal filler was a high dielectric constant material, which can also increase the diffusion rate.

Based on the various experiments conducting in this thesis, it was seen that a careful balance between the number of charge carriers and the ionic

conductivity was most critical in the lithiated electrolytes. The outcome of the experiments suggests that the best structure for achieving high transference number electrolytes which are flexible would be a copolymer structure of a lithiated monomer with another monomer which has high local segmental mobility. The copolymer would ensure that the lithium ions are sufficiently separated, so that repulsion and screening effects are minimal. By a proper choice of monomers, a high molecular weight flexible structure can be developed, which when gelled would show sufficiently stable mechanical properties.

Thus through the work carried out in this thesis, it was concluded that the future direction of research for developing alternate electrolytes based on P(VdF-co-HFP) GPE and PSSLi gel was the identification of additional fillers based on the criterion formulated in this work and the synthesis of copolymer structures based on the optimized lithium concentration obtained in this work.

6.1 Novel contributions from this thesis

Based on the studies carried out in this thesis, the scientific and technological contributions are summarized below

6.1.1 Scientific contributions

- Electrospun P(VdF-co-HFP) based composite and blend GPEs which demonstrate improved electrochemical performance, transference number, flexibility and mechanical stability
- Preferential polymer dissolution process to improve uptake and ionic conductivity

- Investigation of the mechanism by which the composite and blend improves the electrochemical performance and determination of most critical factor
- Optimization of lithium ion concentration for achieving best electrochemical performance in PSSLi gels
- Synthesis of PSSLi composites and blends and study of effect of morphology on electrochemical performance
- Fundamental studies on ion transport mechanism in PSSLi composites and blends by comparison of diffusion coefficients calculated from AC Impedance and measured by NMR

6.1.2 Technological significance

- Demonstration of cycling performance of PSSLi gel in lithium ion battery
- Demonstration of high temperature performance of P(VdF-*co*-HFP) composite GPEs by using ionic liquid.

7 Chapter 7 Recommendations for future work

7.1 Fundamental studies on P(VdF-*co*-HFP) composites and blends

Since the electrochemical performance of GPEs is dependent on a number of factors, a more in-depth study of these factors will be interesting. In this thesis, the effect of various factors on the ion transporting ability of GPEs was studied using a combination of AC Impedance and NMR. To further understand the mechanism by which composites improve the electrochemical performance, the mechanism of gel phase formation can be studied by using pfg-NMR. The diffusion coefficients can be measured at different points of time, to understand the optimum activation time to achieve best electrochemical performance. Also the stability of the composite and blended GPEs, measured by the time taken to form the GPE from NMR can be compared to the pristine GPE, to further understand the effect of the filler on the stability of the GPE. To further improve the mechanical and thermal properties of the composite GPEs, hot/cold pressing can be explored. This will also improve the high temperature performance of the GPEs. To further improve the transference number of P(VdF-*co*-HFP), it can be partially sulfonated to introduce lithium on the polymeric backbone, which will lead to increased number of lithium charge carriers. An optimization of the degree of sulfonation can be done using diffusion coefficients measured from NMR.

7.2 Fundamental studies on PSSLi gels

In this thesis, an effort was made to make free standing films using PSSLi. PSSLi was electrospun, but it has poor ionic conductivity when compared to the PSSLi gel. A co-polymer of PSSLi with a unit containing ether oxygen can be designed

and synthesized. The presence of ether oxygen will provide a good solvation medium for lithium, leading to increased number of mobile lithium ions [211]. The ratios can be manipulated so that the lithium ions are spaced out and therefore do not repel each other [104]. This use of a high molecular weight monomer to co-polymerize with styrene will result in good mechanical properties and a free standing flexible film. Such a polymer can be electrospun to prepare a porous matrix, and an ionic liquid can be used to activate the matrix. The monomer that can be co-polymerized with styrene can resemble the structure below

The presence of two electron withdrawing benzene rings can help reduce the bonding between O and Li, leading to an increase in free lithium ion concentration. Also fillers can be incorporated to improve the mechanical properties. The free standing film will eliminate the need for Celgard, which will lead to higher capacities at high C rates. The higher capacity can be attributed to the lack of the extra ohmic drop due to the presence of non-conducting Celgard.

7.3 Investigation of PSSLi in full cell

Based on the promising half-cell result for the PSSLi gel, a full cell can be constructed using LiFePO_4 and LTO, to study the effect of increased transference number on the performance of a full cell at varying current rates.

8 Bibliography

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Appendix

Fig. S1. Storage modulus of composite and blend GPEs

Table S1- Storage modulus of composite and blend GPEs at 25 °C

GPE	Storage modulus (GPa)
P(VdF- <i>co</i> -HFP)	0.696
P(VdF- <i>co</i> -HFP)- clay (1%)	0.794
ESM-03	0.633
P(VdF- <i>co</i> -HFP)- LAGP(15%)	0.823
ESM-C	0.697
IPG-02	0.743

List of publications

1. **N. Shubha**, R. Prasanth, H.H. Hng, M. Srinivasan, Dual phase polymer gel electrolyte based on non-woven poly(vinylidene fluoride)-layered clay nanocomposite porous membranes for lithium ion polymer batteries, *Material Research Bulletin*.48 (2013), 528-537
2. **N. Shubha**, R. Prasanth, H.H. Hng, M. Srinivasan, Plastic crystalline-semi crystalline polymer composite gel electrolyte based on non-woven poly(vinylidene fluoride-co-hexafluoropropylene) porous membranes: Novel soft matter polymer gel electrolyte for lithium ion batteries, *Electrochimica Acta*, 125 (2014), 362-370.
3. **N. Shubha**, R.Prasanth, H.H.Hng, M. Srinivasan, Study on effect of poly(ethylene oxide) addition and in-situ porosity generation on poly(vinylidene fluoride)-glass ceramic composite membranes for lithium polymer batteries, *Journal of Power sources*, 267(2014), 48-57.
4. R. Prasanth, **N. Shubha**, H.H. Hng and M. Srinivasan, Preparation and electrochemical characterization of polymer gel electrolyte based on poly(vinylidene fluoride)-layered clay nanocomposite porous membranes for lithium ion polymer batteries, *European polymer journal*,49 (2013),307-318.
5. R. Prasanth, **N. Shubha**, H.H. Hng and M. Srinivasan, Effect of poly(ethylene oxide) on ionic conductivity and electrochemical properties of poly(vinylidene fluoride) based polymer gel electrolytes prepared by

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- electrospinning for lithium ion batteries, *Journal of Power Sources*, 245, (2014) , 283-291.
6. V.Aravindan, **N.Shubha**, Yan L. Cheah, R.Prasanth, W. Chuiling, Rajiv Ramanujam Prabhakar, S. Madhavi, Extraordinary long-term cyclability of TiO₂-B nanorods as anodes in full cell assembly with electrospun PVdF-HFP membranes, *Journal of Materials Chemistry A*, 1 (2013) 308-316.
 7. V. Aravindan, **N. Shubha**, W.C. Ling, S. Madhavi, Constructing high energy density non-aqueous Li-ion capacitors using monoclinic TiO₂-B nanorods, *Journal of Materials Chemistry A*, 1 (2013) , 6145-6151.
 8. V. Aravindan, J. Sundaramurthy, P.Suresh Kumar, **N. Shubha**, W. Chui Ling, S. Ramakrishna and S. Madhavi , A novel strategy to construct high performance lithium-ion cells using one dimensional electrospun nanofibers, electrodes and separators, *Nanoscale*, 5 (2013), 10636-1064.
 9. N. Arun, V. Aravindan, S.Jayaraman, **N.Shubha**, W.Chuiling, S.Ramakrishna and S.Madhavi, Exceptional performance of a high voltage spinel LiNi_{0.5}Mn_{1.5}O₄ cathode in all one dimensional architecture with an anatase TiO₂ anode by electrospinning, *Nanoscale*, 6 (2014), 8926-8934.

List of oral conference presentations

N. Shubha, W.C. Ling, H.H. Hng, M. Srinivasan, Preparation and Characterization of Non-Woven Glass Ceramic- Polymer Composite Electrolyte Based on P(VdF-*co*-HFP)/ Lithium Aluminium Germanium Phosphate for Lithium Ion Batteries, MRS Spring Meeting 2014.

List of awards/scholarships

Ian Ferguson Postgraduate Fellowship 2012