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1. Introduction

A battery generally consists of three important parts namely, anode, cathode and electrolyte. The batteries further classified into primary and secondary batteries. Among the different kinds of batteries, Li-ion batteries are plays a very important role in the development of modern technologies especially in the portable electronic device industries and in heavy electrical vehicles because of its advantages such as high theoretical capacity, improved safety, lower material costs, ease of fabrication into flexible geometries, and the absence of electrolyte leakage. In the battery system different kinds of electrolytes were used for promoting the ions from anode to cathode (during charge) and cathode to anode (during discharge). For this purpose, liquid electrolyte is identified as suitable electrolytes which facilitate higher ionic conductivity ($10^{-2}$ Scm$^{-1}$) than other electrolyte systems. However, it has several disadvantages namely gas formation during the operation, leakage, difficult to utilise for portable applications and etc. To overcome these difficulties, many attempts were made on solid polymer electrolyte systems. The main objective of the researchers is to improve the ambient temperature ionic conductivity, mechanical stability, thermal and interfacial stability of the electrolytes. However, it is difficult task for the researchers, inorder to improve these basic requirements of the electrolytes simultaneously because the ionic conductivity and mechanical strength of a polymer electrolyte are disparate to each other, i.e., mechanical strength of the electrolyte decreases as conductivity increases.

In recent years, Polymer electrolytes have been attracted scientific and technological importance because of their potential applications in many areas such as Li-ion polymer batteries, super capacitor, electro chromic devices and etc. The idea of preparation of
polymer electrolytes was first proposed by Wright and Fenton et al. in 1973 [wright et al., 1973] but their technological significances are fulfilled and appreciated by Armand et al. few years later [Armand et al., 1998]. Poly (ethylene oxide) was the first solvating polymer to be proposed and studied in solid polymer electrolyte (SPE) Li-rechargeable batteries. Most of the solid polymer electrolytes (SPEs) are prepared by dissolving lithium salts in a solvating polymer using common solvent or by diffusion in the solid (or) molten state. An effort is also made to fix or immobilize the anion on the polymer matrix by covalent bonding (or) another chemical or physical process.

In general, Polymer electrolytes are plastic materials that can be modified and processed by conventional techniques. If the polymer chains are helped for a charge transport of the ionic type, often called “polymer electrolyte”. Solid polymer electrolytes (SPEs) afford two important roles in Li-ion battery. 1) It is used as a separator in the battery system because of its rigid structure, at the same time to avoid the electrical contact between the anode and the cathode; 2) it is the medium in which the ions are transported between the anode and cathode during the cell operations. As a result, the polymer electrolyte should act as good electrical insulator but at the same time it should have high ionic conductivity.

1.1 Classification of polymer electrolyte systems
The polymer electrolyte systems could be classified into three categories, namely, i) Polyelectrolyte, ii) Solvent swollen polymer electrolyte and iii) solvent free polymer electrolytes.

1.2.1 Polyelectrolyte’s
Polyelectrolytes are polymers which have their own ion-generating groups chemically bound to the macromolecular chain and the presence of a counter-ion maintains the electroneutrality of the salt. This class of materials either positively or negatively charged ions covalently attached to the polymer backbone and therefore only the unattached counter ion has long range mobility. The conductivity of these polymers is very low (10^{-10} to 10^{-15} Scm^{-1}) in dry conditions but hydrated polyelectrolytes achieve high conductivity in the presence of high dielectric constant solvent (e.g. Water). In hydrated polyelectrolytes, ionic transport takes place through the aqueous medium in which the polymer is dispersed. Slade et al. [Slade et al., 1983] reported high ambient temperature conductivity of 10^{-2} Scm^{-1} in hydrated Nafion.

1.2.2 Solvent swollen polymer electrolytes
In solvent swollen polymers, solvents (aqueous/non-aqueous) swell the basic polymer host [like poly(vinyl alcohol) or poly(vinyl pyrrolidone)]. The dopant ionic solutes like H_3PO_4 are accommodated in the swollen lattice which permits the ionic motion in solvent rich swollen region of the polymer host. These materials are, in general, unstable and their conductivity depends on the concentration of the solvent in the swollen region. The properties of such polymers depend on the pre-treatment, structure of the sample, temperature, relative humidity, etc.

Examples: Nafian, complexes of poly(vinyl alcohol) (PVA) with H_3PO_4 [Polak et al., 1986] poly (silamine) with H_3PO_4 [Rekukawa et al., 1996], PEI with H_3SO_4 [Daniel et al., 1988].
1.2.3 Solvent free polymer electrolytes

The polymer –salt complexes are formed by complexes between salts of alkali metals and polymer containing solvating heteroatoms such as O, N, S, etc. The most common examples are complexation between poly (ethylene oxide) (PEO) and alkali metal salts. The polymer salt complexes are further classified into: i) Solid polymer electrolytes ii) Blend polymer electrolytes iii) Gel polymer electrolytes iv) Composite polymer electrolytes. Among the various polymer electrolytes which are used in Li-ion batteries, solvent free polymer electrolytes are the most favourable for device fabrications. The solvent free polymer salt complexes are further classified into: i) Solid polymer electrolytes ii) Gel polymer electrolytes iii) Composite polymer electrolytes.

a) Solid polymer electrolytes

Solid polymer electrolytes (SPEs) have an ionic conductivity when modified by dissolving alkali salts in suitable polymer matrix. SPEs are typically thin films, which have a wide range of electrochemical applications such as batteries and electrochromic devices. They have several advantages when used in a battery and can be formed into thin films of large surface area giving high power levels. The flexibility of the films allows space-efficient batteries to be constructed [Quartarone et al., 1998].

b) Gel polymer electrolytes

Plasticizers incorporated polymer- salt complex is called gel polymer electrolytes. The addition of plasticizers into the polymer matrix softens the polymers and they increase free volumes which are used for ion migration. Addition of plasticizer also increases the chain flexibility, reduces crystallinity, decreases the glass transition temperature and hence increases the ionic conductivity. The conductivity of PEO: LiBF₄ is of the order of \(10^{-6}\) Scm⁻¹ which has been increased to the order of \(10^{-4}\) Scm⁻¹ when the complex is plasticized at 25°C [Chiodelli et al., 1988] this is mainly due to the specific nature of the plasticizers and the prepared gels has both the cohesive properties of solids and the diffusive property of liquids. Even though the gel polymer electrolyte exhibits high ionic conductivity, its thermal and mechanical stability are poor and it has higher reactivity towards the electrode. Gel electrolytes may undergo solvent exudation upon long storage, especially under open atmosphere conditions. This phenomenon is known as ‘Syneresis effect’, and has been encountered in many systems such as PAN: EC: PC: LiClO₄, PAN: EC: PC: LiAsF₆ [Groce et al., 1994 and Slane & Salomon et al., 1995].

c) Composite polymer electrolytes

This is another approach in which both the ionic conductivity and the mechanical stability of the electrolytes were considerably enhanced simultaneously. Composite polymer electrolytes are prepared by the addition of high surface inorganic fillers such as Al₂O₃, SiO₂, MgO, LiAlO₂, TiO₂, BaTiO₃ and Zeolite powders. The mechanical strength and stiffness of the complex systems were improved appreciably when the fillers are incorporated into the polymer matrix. However the main advantages of the composite electrolyte is the enhancement of room temperature ionic conductivity and an improved stability at the electrode electrolyte interface. The inert fillers due to its large surface area prevent the local chain reorganization with the result of locking in at ambient temperature, a high degree of disorder characteristic of the amorphous phase, which is more favour for the high ionic conductivity.
The nano sized BaTiO$_3$ incorporated PEO composite electrolytes exhibits ionic conductivity of the order of x10^{-3} Scm$^{-1}$ and good electrochemical stability (4.0V).

### 1.3 Blend polymer electrolytes

Blend is a mixture of two or more polymers. Mixing of two polymers is a well established strategy for the purpose of obtaining materials with combined superior properties or avoiding the need to synthesize novel structures constitutes an attractive research area. As many emerging applications are of limited volume and require specific property profiles not suitable for broad application utility, polymer blend technology is often the only viable method to deliver the desired material. These polymer blends have some unique properties that are different from the basic polymers from which these have been produced. To improve the processing behaviour for end use, one polymer blending with another polymer is a common practice. The exploitation of certain unique set of properties of individual polymer for the benefit of the overall properties of a multi component system forms the basis of polymer blending. Hence blending of polymers has resulted in the development of polymeric materials with desirable combination of properties. Polymer blend electrolytes are developed in such a way that they remain structurally stable during manufacturing, cell assembling, storage and usages as well as to prevent leakage from the cell container or without the cell.

### 1.4 Some commonly available polymer electrolytes for lithium ion batteries

#### 1.4.1 PEO based electrolytes

PEO is a crystalline polymer. The oxygen in PEO acts as a donor for the cation and the anion generally of large dimension stabilizes the PEO alkali salt complex.

The polymer electrolytes composed of a blend of poly (ethylene oxide) (PEO) and poly (vinylidenefluoride-hexa fluoropropylene) as a host polymer, mixture of EC and PC as plasticizer and LiClO$_4$ as a salt were prepared by Fan et al. [Fan et al., 2002]. The ionic conductivity of various compositions of blend polymers was found to be in the order of x10^{-4} Scm$^{-1}$ at 30ºC. On increasing the PEO content in the matrix, the conductivity decreased due to its high crystalline nature. The mechanical strength of the polymer electrolytes was measured from stress-strain tests. The electrolytes were also characterized by SEM, XRD and thermal analysis techniques. Xi et al. [Xi., 2006] aimed to improve ionic conductivity with a novel approach using PEO and PVdF as host polymers by phase inversion technique. The room temperature conductivity was measured as a function of PEO content. As the weight ratio of PEO was increased from 40 to 50%, the ionic conductivity increased more than one magnitude from 0.15 to 1.96 x10^{-4}Scm$^{-1}$ which is mainly due to the increasing of pore connectivity. This is very important for the transport of charge carriers in microporous polymer membrane. The plasticizer effect on PEO-salt complex was studied by Fan et al [Fan et al., 2008] using succinitrile (SN) as a plasticizer, LiClO$_4$, LiPF$_6$ and LiCF$_3$SO$_3$ as lithium salts. They found that the addition of plasticizer was responsible for high ionic conductivity which could be attributed to the high polarity and diffusivity of succinitrile. This, in turn, decreased the crystallinity of PEO polymer. Activation energy of the electrolytes was also estimated from Arrhenius plot. Itoh et al. [Itoh et al., 2003] prepared
the composite polymer electrolytes using poly(ethylene oxide)/ poly(triethylene glycol) benzoate, BaTiO$_3$ and lithium imides. They estimated the ionic conductivity value as $1.6 \times 10^{-3}$ Scm$^{-1}$ at 80°C and the electrochemical stability window as 4.0V. The membrane was also characterized by TG/DTA and it is thermally stable up to 307°C. Novel effect of organic acids such as malonic, maleic and carboxylic acids on PEO/LiClO$_4$/Al$_2$O$_3$ complexes was studied by Park et al. [Park et al., 2006]. It was noted that the ionic conductivity of the film consisting of PEO/LiClO$_4$: Citric acid (99.95:0.05 wt%) was $3.25 \times 10^{-6}$ Scm$^{-1}$ at 30°C and it was further improved to $3.1 \times 10^{-3}$ Scm$^{-1}$ at 20°C by adding 20wt% of Al$_2$O$_3$ filler. The prepared membranes were also characterized by Brewster Angle Microscopy (BAM), thermal analysis and cyclic voltammetry.

1.4.2 PVC based electrolytes

PVdF/PVC blend composite polymer electrolyte was prepared by Aravindhan et al. [Aravindhan et al., 2007] incorporating lithium bis(oxalate) borate and ZrO$_2$. All the prepared membranes were subjected to SEM, XRD and ac impedance studies. The maximum ionic conductivity ($1.53 \times 10^{-3}$ Scm$^{-1}$) was obtained for 2.5wt% of ZrO$_2$ at 343K. The ionic conductivity and FTIR studies on plasticized polymer electrolyte based on PVC and PMMA as host polymer were studied by Manuel Stephan et al. It was found that LiBF$_4$ based PVC/PMMA/EC/PC complexes exhibited higher ionic conductivity compared to that with LiClO$_4$. The thermal stability of the films was also ascertained using TG/DTA analysis.

1.4.3 PAN based polymer electrolytes

Kim et.al [Kim,D.W. Sun,Y.K. 2001] prepared highly porous polymer electrolyte employing P(VdF-co-HFP) and PAN with a view to attain high ionic conductivity and good mechanical strength. Lithium-ion polymer battery using these gel polymer electrolytes was assembled, and its charge-discharge characteristics were also reported. Panero et al. [Panero et al., 2002] studied the characteristics and the properties of a polymer electrolyte formed by trapping LiPF$_6$-PC solution in a poly(acrylonitrile) matrix with the addition of Al$_2$O$_3$. They reported the ionic conductivity value as $0.8 \times 10^{-3}$ Scm$^{-1}$ at 25°C. The performances of the electrolyte were found to be promising in terms of cycle life and basic energy density content. Very recently, Moreno et.al [Moreno et al., 2010] reported a series of composite electrolytes basically constituted by poly(acrylonitrile), Clay and montmorillonite as filler. The structural and complex formations of the CPEs were also studied. However, the composite based on PAN system showed poor ionic conductivity of the order of $10^{-6}$ Scm$^{-1}$.

Tsutsumi and Kitagawa [Tsutsumi and Kitagawa et al., 2010] synthesized a new type polymer electrolyte films based on poly(acrylonitrile), and Cyanogenylated poly(vinyl alcohol) (CN-PVA) and its conductivity behaviour was also investigated. They found the ionic conductivity value as $14.6 \times 10^{-5}$Scm$^{-1}$ at 30°C for PAN (10)-CN-PVA (10)-LiClO$_4$ (8)-PC (4) complex system. The interactions of Li$^+$-ion and nitrile groups of PAN in the matrix were confirmed by FTIR analysis. The ionic conductivity and FTIR studies were carried out on PAN based gel electrolytes with EC: PC and EC: DMC mixtures as plasticizers, LiClO$_4$ or LiBF$_4$ as the salt by Amaral et al [Amaral et al., 2007]. The high ionic conductivity ($1.47 \times 10^{-3}$ Scm$^{-1}$) was estimated for 20:28:45:7 molar ratio of PAN-PVA: EC: DMC: LiBF$_4$ system.
Charge/discharge performance of the maximum ionic conductivity complex was also studied. The practical performance and thermal stability of Li-ion polymer batteries with LiNi_{0.8}Co_{0.2}O_{2}, mesocarbon microbead-based graphite, and poly (acrylonitrile) (PAN) based gel electrolytes were reported by Akashi et al. [Akashi et al., 2002].

1.4.4 PVdF based polymer electrolytes

PVdF is a semicrystalline polymer and the electrolytes based on PVdF are expected to have high anodic stabilities due to strong electron withdrawing functional groups (-C-F). It also has high permittivity, relatively low dissipation factor and high dielectric constant ($\varepsilon = 8.4$) which assist in high ionization of lithium salts, providing a high concentration of charge carriers. Choe et al. [Cheo et al., 1995] reported that the PVdF based electrolytes plasticized with a solution of LiN(SO$_2$CF$_3$)$_2$ in PC had a conductivity of 1.74x10$^{-3}$ Scm$^{-1}$ at 30°C and has a oxidatively stable potential limits between 3.9 and 4.3V vs Li$^+$/Li. Nicotera et al. [Nicotera et al., 2006] measured the ionic conductivity and the lithium salt diffusion coefficient of PMMA/PVdF based blend electrolytes with EC/PC as plasticizers and lithium perchlorate as salt by the PFG-NMR method, which revealed maximum lithium mobility for the composition PMMA 60%-PVdF 40%. Raman spectroscopic study confirmed the change of interaction between the lithium cations and the plasticizer molecules for different PMMA/PVdF ratios. Wang et al. [Wang et al., 2007] prepared the nanocomposite polymer electrolytes comprising of poly (vinylidene fluoride) (PVdF) as a host polymer, lithium perchlorate (LiClO$_4$) as salt and TiO$_2$ used as a filler by solvent-casting technique. The prepared films were characterized by XRD, DSC and SEM. The conductivity value was found to be of the order of 10$^{-3}$ Scm$^{-1}$ for the sample with 10% TiO$_2$.

1.4.5 PMMA based electrolytes

Ali et al. [Ali et al., 2007] reported the electrical properties of polymer electrolytes comprising PMMA, PC, EC as plasticizer and different lithium salts LiCF$_3$SO$_3$ and LiN(CF$_3$SO$_2$)$_2$. The polymer electrolytes exhibited high ionic conductivity at room temperature in the range of 10$^{-6}$ to 10$^{-4}$ Scm$^{-1}$. The temperature dependence studies confirmed that the conduction in electrolyte is only by ions and seemed to obey the VTF rule. FTIR spectroscopy studies confirmed the polymer-salt interactions. FTIR spectroscopic investigations coupled with ionic conductivity and viscosity measurements on lithium imide LiN(CF$_3$SO$_2$)$_2$-propylene carbonate (PC)-poly(methyl methacrylate) (PMMA) based liquid and gel electrolytes over a wide range of salt (0.025–3 M) and polymer (5–25 wt.%) concentration were reported by Deepa et al. [Deepa et al., 2004] and found that the high ionic conductivity occurs at salt concentrations $\geq$1.25 M.

1.4.6 PVdF-co-HFP based polymer electrolytes

In recent years, the studies on PVdF-co-HFP based systems are electrochemically stable and indispensable for the electrode properties. The PVdF-co-HFP based electrolyte system shows high electrochemical stability in the range 4V. Fan et al. [Fan et al., 2002] studied the thermal, electrical and mechanical properties of EC/PC/LiClO$_4$ based PEO/P(VdF-co-HFP) blends. They concluded that the polymers have good compatibility and PVdF-HFP hinders the crystallinity of PEO. Saika and Kumar [Saika and Kumar, 2004] made systematic studies on the ionic conductivity and transport properties of polymer electrolytes comprising of co-
polymer PVdF-co-HFP/ PC/ DEC/ LiClO$_4$ and PVdF/ PC/ DEC/ LiClO$_4$ separately. The co-polymer complex showed higher ionic conductivity and transport number compared to PVdF system. The higher conductivity of the polymer electrolyte based on copolymer was attributed to its higher amorphosity. Wang et al. [Wang et al, 2004] reported that the polymer electrolyte composed of poly(methyl methacrylate-co-acrylonitrile-co-lithium methacrylate) (PMAML) and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-co-HFP) exhibited high ionic conductivity and good electrochemical stability. The ionic conductivity was about $2.6 \times 10^{-3}$ Scm$^{-1}$ at ambient temperature and the electrochemical window of the polymer electrolyte was about 4.6V. Charge –discharge test results revealed that lithium ion batteries with these gel polymer electrolytes have good electrochemical performance.

Manuel Stephan et.al [Manuel Stephan et al., 2006] prepared the composite polymer electrolyte membranes, comprising Poly(vinylidene fluoride-hexafluoropropylene), Aluminum Oxhydroxide of two different sizes 7nm/14 nm and LiN(C$_2$F$_5$SO$_2$)$_2$ as lithium salt and they found that the incorporation of the inert filler not only reduces the crystallinity of the polymer host but also acts as ‘solid plasticizer’ capable of enhancing the transport properties and also provides a better interfacial property towards lithium metal anode. Nam-Soon Choi et.al [Choi et al., 2001] reported that the interfacial stability between the polymer electrolyte and the lithium electrode was enhanced by blending PVAc with P(VdF-co-HFP)(Kynar 2801). The ionic conductivity of the polymer electrolyte based on the Kynar 2801: PVAc (7:3, w:w) blend was $2.3 \times 10^{-3}$ S cm$^{-1}$ at 25°C. Kim et.al [Kim et al., 2005] prepared and characterized gel polymer electrolytes consisting 25wt% PVdF-co-HFP/65 (EC+PC)/10 wt% LiN(CF$_3$SO$_2$)$_2$. They reported the ionic conductivity value as $1.2 \times 10^{-3}$ Scm$^{-1}$. The electrochemical stability window of the membrane was obtained at around 4.8V Vs Li/Li$^+$ using linear sweep voltametry technique. The Charge – discharge behaviour of the membrane was also studied and they estimated the specific discharge capacity as 140 mAhg$^{-1}$ for up to 20 cycles at different current densities.

### 1.4.7 PVAc based polymer electrolytes

Though variety of polymer electrolytes were characterized for the fast four decades, a limited number of studies were made on PVAc based polymer electrolytes. PVAc polymer has a large dipole moment and high relaxation time. Baskaran et al [Baskaran et al., 2006] prepared the polymer electrolyte comprising of PVAc-PMMA and reported the conductivity value as $1.76 \times 10^{-3}$ Scm$^{-1}$ at 303K. The DSC thermograms of the blend electrolytes showed two Tg’s and they decreased with an increase of LiClO$_4$ concentration. The structural and complex formations of the electrolytes were confirmed by X-ray diffraction analysis. They established that the optimized blend ratio of PVAc: PMMA: LiClO$_4$ is suitable for lithium battery applications. Structural, thermal and transport properties of PVAc-LiClO$_4$ base complexes were studied by Baskaran et al [Baskaran et al., 2007]. The bulk conductivity of PVAc: LiClO$_4$ system was found to vary between $7.6 \times 10^{-5}$Scm$^{-1}$ and $6.2 \times 10^{-3}$ S cm$^{-1}$ at 303K with an increase in the salt concentration. The amorphous nature of the polymer complexes was confirmed by XRD and SEM analysis.

Surface morphology and ionic conductivity of the membrane based on P(EO)/PVAc /LiClO$_4$ were studied by Animitsa et al [Animitsa et al., 1998]. They reported the conductivity value as $10^{-5}$ Scm$^{-1}$ for lower concentration of PVAc at 25°C. Baskaran et al.
[Baskaran et al., 2006] studied the ac impedance and dielectric properties of PVdF/PVAc blend electrolytes. They reported that the blend ratio (75:25) of PVAc/PVdF exhibited a maximum ionic conductivity value of the order of $6.4 \times 10^{-4}$ S cm$^{-1}$ at 343K. The ionic transference number of mobile ions was also estimated by Wagner's polarization method. The complex formation and thermal behaviour of the electrolytes were also studied by FTIR and DSC analysis respectively.

2. Basic requirements of polymers and the salt for polymer electrolytes

Atoms or groups of atoms with sufficient electron donor power to form coordinate bonds with cations.

- Low barriers to bond rotation so that segmental motion of the polymer chain can take place readily.
- A suitable distance between coordinating centres for the formation of multiple intrapolymers ion bonds appears to be important.
- Low glass transition temperature to increase the segmental motion.
- The polymer should have amorphous phase which lowers the barrier for ionic movement and yields high ionic conductivity.
- The lattice energy of the salt should be low.
- High electrochemical reduction potential.

Electron pair donicity (DN)

DN measures the ability of the solvent to donate electrons to solvate the cations considered as a Lewis acid. So the polymer host should have high DN number.

Acceptor number (AN)

The acceptor number quantifies the possibility of anion salvation. It should be less for an inorganic salt so that cationic salvation is high compared to anionic salvation.

Entropy term

The entropy term depends on the optimal spatial disposition of the solvating units which should be high for the polymer host.

2.1 Importance of Li$^+$ cation

Last four decades, many alkali salts consisting Li$^+$, Na$^+$, K$^+$, Ag$^+$, Mg$^+$, NH$_4^+$ cations were mixed with the polymers (PEO), (PPO) etc in the preparation of polymer electrolytes. Among the various cations in the periodic table, Li$^+$ is the most electropositive. Lithium easily gives up electrons to form a positive Li$^+$ which has small ionic radii (0.6Å). Lithium is promising candidate for high energy density batteries because of its high specific capacity of 3860 Ah/Kg, its light weight and high electrochemical reduction potential [Scrosati et al., 1994; Abraham et al., 1993; Dell, 2000].

2.2 Preparation of polymer blend electrolytes

Polymer blend electrolytes have been prepared using various approaches namely, Phase inversion method, Hot pressed method, Solvent casting method and etc. Each method has
own advantages and disadvantages. Among the various method of preparation solvent costing is the cost effective one and easier to control the moistures during the preparation of electrolytes as well as in the cell assembling. However, when assembling the cells, these membranes show poor cyclic behaviour. As a result many research groups have been mainly focused on phase inversion method for preparing the suitable electrolytes. Preparation of polymer electrolyte system is explained using the following flow chart (Fig.1).

**Preparation of Polymer Salt Complex**

In the present study, all the electrolytes were prepared using solvent casting technique. The polymers PVAc, PVdF-co-HFP, and the salt LiClO$_4$ were dissolved in a common solvent (tetrahydrofuran) separately. All three solutions were mixed together and starrier continuously using magnetic stirrer until got a homogeneous mixture. The low molecular weight plasticizer and the inorganic fillers were added into the matrix inorder to get the gel and composite polymer electrolytes systems. In the present study, ethylene carbonate(EC) and barium titanate (BaTiO$_3$) were used a plasticizer and fillers respectively. Thus the obtained homogenous slurry was degassed to remove air bubbles for about five minutes and the slurry was poured on a well cleaned glass plate. The casted slurry was allowed to evaporate the solution at room temperature about 5h followed by the electrolyte membranes were heated using hot air oven at a temperature of 60 °C for 6h in order to removing the
residual solvent present in the electrolyte films. Finally, the harvested electrolyte films were stored in highly evacuated desiccators to avoid the moistures absorption.

3. Characterization of polymer blend electrolytes

Ac impedance analysis was carried out with the help of stainless steel blocking electrodes by using a computer controlled micro auto lab type III Potentiostat/Galvanostat of frequency range 1 Hz–300 KHz in the temperature range 303–373 K. The XRD equipment used in this study was X’pert PRO PANlytical X-ray diffractometer. FTIR spectroscopy studies were carried out using SPECTRA RXI, Perkin Elmer spectro-photometer in the range 400–4000 cm$^{-1}$. FTIR spectroscopy studies were carried out for confirming the complex formation using SPECTRA RXI, Perkin-Elmer spectro-photometer in the range 400–4000 cm$^{-1}$. TG/DTA thermal analysis of the film having maximum ionic conductivity was studied using PYRIS DIAMOND under air atmosphere with the scan rate of 10 $^{\circ}$C min$^{-1}$. The electrolyte film having maximum ionic conductivity was subjected to atomic force microscopy [model Veeco-diCP-II]. The pore size and the root mean square (rms) roughness of the film were measured from the topography image. Secondary electron images of the sample were examined by using JEOL, JSM-840A scanning electron microscope

3.1 FTIR analysis

Infrared spectral (IR) analysis is a powerful tool for identifying the nature of bonding and different functional groups present in a sample by monitoring the vibrational energy levels of the molecules, which are essentially the fingerprint of different molecules [Nagatomo et al., 1987]. Fig.2. depicts the FTIR transmittance spectra in the range 400-4000 cm$^{-1}$ for polymers, the LiClO$_4$ salt, the blend electrolyte with the incorporation of plasticizer ethylene carbonate and the filler BaTiO$_3$.

The vibrational bands observed at 2933 cm$^{-1}$ and 2465 cm$^{-1}$ are ascribed to –CH$_3$ asymmetric and symmetric stretching vibrations of PVAc respectively. The strong absorbance at 1734 cm$^{-1}$ represents the C=O stretching vibration mode of PVAc polymer. The existence of C-O band has been confirmed by the strong absorbance band at around 1033 cm$^{-1}$. The strong band at 1373 cm$^{-1}$ is ascribed to C-H symmetric bending vibration mode of pure PVAc. The band at 1243 cm$^{-1}$ is assigned to C-O-C symmetric stretching mode of vibration. The peak at 947 cm$^{-1}$ is ascribed to CH bending vibration and the peak at 609 cm$^{-1}$ is assumed to be linked with CH$_3$ (C-O) group. The C-H wagging mode of vibration has been confirmed by the presence of a band at 799 cm$^{-1}$ [Baskaran et al., 2004]. The vibrational peaks at 502 and 416 cm$^{-1}$ are assigned to bending and wagging vibrations of –CF$_2$ of PVdF-co-HFP polymer respectively. Crystalline phase of the PVdF-co-HFP polymer is identified by the vibrational bands at 985, 763, and 608 cm$^{-1}$ and the amorphous phase of the co-polymer is confirmed by the presence of vibrational band at 872 cm$^{-1}$ [Rajendran et al., 2002].

The strong absorption peak appeared at 1173 cm$^{-1}$ is assigned to the symmetrical stretching of –CF$_2$ group. The peak appeared at 1390 cm$^{-1}$ is assigned to the CH$_2$ groups [Rajendran et al., 2002; Singh Missan et al., 2006]. Table.1. shows the comparison of band spectra of pure polymers and their blends with different blend ratios. From the table, it is clear that the band assignments of FTIR spectra of blend samples are shifted from their pure spectra. For
all the blends, some peaks are found above 3000 cm$^{-1}$, which correspond to the C-H stretching vibration modes of blend electrolytes.

In addition, some new peaks are present and some of them are absent in the blend electrolytes. Thus the spectral analysis confirms the complexation of these two polymers and lithium salt.

![Fig. 2. FTIR analysis of LiClO$_4$, PVAc, PVdF-co-HFP and their complexes](image)

**3.2 X-ray diffraction analysis**

XRD patterns of LiClO$_4$, PVdF-co-HFP, PVAc and their complexes A, B, C are shown in Fig. 3. The presence of characteristic peaks corresponding to the lithium salt reveals the high crystalline nature of the salt. Three peaks found at $2\theta = 17.3, 18.59$ and $38.78^\circ$ for PVdF-co-
HFP confirms the partial crystallization of PVdF units present in the copolymer, to give an overall semi-crystalline morphology for PVdF-co-HFP [Saika, Kumar, 2004]. Presence of broad humps in the XRD pattern of PVAc confirms the complete amorphous nature of the polymer. It is observed that the characteristic peaks corresponding to the lithium salt in their respective electrolyte systems (A, B and C) were absent and it confirms the complete dissolution of the lithium salts in the complex matrix which implies that the salt do not have any separate phase in the electrolytes. The addition of plasticizer in the blend complex enhances the amorphous region thus permitting the free flow of ions from one site to another site; hence the overall ionic conductivity of the electrolyte has been significantly improved. According to Hodge et al. [Hodge et al., 1996] the ionic conduction in the polymer electrolytes occurs mostly in the amorphous region and it has been achieved by the addition of low molecular weight plasticizer. Further addition of inorganic filler into the polymer salt matrix would increase the dissolution of the charge carriers in the matrix; hence, the ionic conductivity was improved. The XRD pattern of the sample contains the filler BaTiO₃ shows a broad hump confirms the further enhancement of the amorphous region in the polymer electrolyte complex systems.

![Fig. 3. X-ray diffraction analysis of LiClO₄, PVdF-co-HFP, PVAc and their complexes.](image)

### 3.3 DC impedance analysis

Ac studies are similar to the DC techniques in that the ratio of voltage to current is measured. For DC, this ratio provides the value of the resistance, $R$, measured in ohms.
For AC the ratio gives an analogous quantity, the impedance, $Z$, also measured in ohms. The impedance contains four main contributions; these are from resistance, capacitance, constant phase elements, and inductance. The induction is not an important factor for the polymer electrolytes although it can play a role in other electrochemical applications of polymers.

Measurement of the impedance as a function of frequency is called impedance spectroscopy. In general, impedance is complex quantity, in which the real and the imaginary parts are labelled $Z'$ and $Z''$ respectively. In the complex impedance plot, the real quantity $Z'$ (X-axis) is plotted against $Z''$ (Y-axis) which displayed the polymer electrolytes characteristics as an arc followed by the linear spike is straight line inclined to the real axis. From the plotted graph, we can easily read the bulk resistance of the electrolyte system.

The complex impedance plot of the PVAc/PVdF-co-HFP/LiClO$_4$ electrolyte is shown in Fig.4a. Figure shows the semicircular portion which is mainly due to the parallel combination of the geometrical capacitance, $C_g$ and the bulk resistance, $R$. When adding the plasticizer and the filler (Fig.4b.) into the electrolyte matrix, the impedance spectra shows only a linear spike which corresponds to the lower frequency region. It confirms the idea that the current carriers are ions and the majority of the conduction only by the ions not by the electrons. And the disappearance of the semicircular portion is may be due to the fact the corresponding characteristic frequency is higher than the frequency 300kHz and it is mainly depends on the instrument limit. From the obtained bulk resistance value, we can estimate the ionic conductivity value of the electrolyte system using the relation $\sigma = \frac{1}{R_b A}$, where, $R_b$ is the bulk resistance of the electrolyte film, $A$ is the area of the electrode surface and is the thickness of the electrolyte medium and $\sigma$ is the ionic conductivity.

It is noted from the spectra that the addition of plasticizer (ethylene carbonate) in to the polymer salt matrix greatly being reduced the bulk resistance of the system; this is because of the high dielectric nature of the low molecular weight plasticizer. The addition of plasticizer would considerably enhance the amorphous phase of the polymer electrolyte which will improve the ionic conductivity of the system. However, the gain in conductivity is adversely associated with a loss of the mechanical properties and by a loss of the compatibility with the lithium electrode, both effects resulting in serious problems since they affect the battery cycle life and increase the safety hazard. So it is necessary to identify the solid additives which would not affect the mechanical stability and interfacial stability of the electrolyte, at the same time will enhances the ionic conductivity. The addition of solid additives should improve the amorphicity of the electrolyte at room temperature. The addition of solid additives in the present study, such as nano filler BaTiO$_3$ highly being enhanced the amorphpicity of the electrolyte medium, hence the room temperature ionic conductivity and the interfacial stability of the electrode-electrolyte interface is increased. The ceramic dispersed electrolyte shows good thermal stability. The BaTiO$_3$ incorporated sample is thermally stable up to 320 °C. The temperature dependence of the conductivity is given by the Vogel–Tamman–Fulcher (VTF) equation $\sigma = \sigma_0 \exp (-B/T-T_0)$, where $\sigma_0$ is the pre-exponential factor, $B$ should not be confused with an activation energy in the Arrhenius expression and $T_0$ is related to the so called thermodynamic Tg. Plots of logs vs 1/T are curved because of the reduced temperature (T-T0).
Fig. 4a. Room temperature complex ac impedance spectrum of PVAc/PVdF-co-HFP/LiClO$_4$ electrolyte

Fig. 4b. Room temperature complex ac impedance spectra of PVAc/PVdF-co-HFP/LiClO$_4$/EC and PVAc/PVdF-co-HFP/LiClO$_4$/EC+PC/BaTiO$_3$ electrolyte
3.4 TG/DTA analysis

Thermo gravimetric analysis /differential thermal analysis have been used widely to study all physical processes involving the weight changes. It is also used to investigate the thermal degradation, phase transitions and crystallization of polymers. Fig.5(a-c) shows the TG/DTA curves of PVAc/PVdF-co-HFP/LiClO$_4$, PVAc/PVdF-co-HFP/LiClO$_4$/EC and PVAc/PVdF-co-HFP/LiClO$_4$/EC+PC/BaTiO$_3$ polymer electrolytes. From the thermogram, it is observed that the sample A is thermally stable up to 238°C. The sample starts to decompose at 238°C, beyond which, there is a gradual weight loss of 20% in the temperature range 240-280°C. DTA curve of the sample shows an exothermic peak at 265°C, which is well correlated with the weight loss of the sample observed in TG curve. It is also observed that the complete decomposition of the sample takes place between 490-510°C with the corresponding weight loss of about 80-90%. After 520°C, there is no appreciable weight loss (Fig.5a). The remaining residue around 15% may be due to the formation of impure crystalline metal oxide and lithium fluoride. It is also observed from DTA curves that the exothermic peaks at 90, 225, and 445 ºC are concurrent with the weight losses observed in the TG trace. The sample (Fig.5b) exhibit gradual weight loss of about 10-15%, which is due to the removal of the residual solvent and the moisture from the electrolyte sample in the temperature range 90-115 ºC. From the TG curve of the sample PVAc/PVdF-co-HFP/LiClO$_4$/EC, it is observed that the decomposition occurred at 229ºC with the weight loss of about 20%. After the second decomposition, there is sudden weight loss of 40-45% in the temperature range 446-460 ºC for the electrolyte. The thermogram of the sample having BaTiO$_3$ inert filler is shown Fig.5c. From the themogram, it is observed that the sample is thermally stable up to 320°C. The sample exhibits gradual weight loss of about 8% in the temperature range 100-110 ºC, which is due to the removal of the residual solvent and the moisture. DTA curve of the sample shows an exothermic peak at 320°C, which is well correlated with the weight loss of the sample observed in the TG curve. The remaining residue around 30% may be due to the presence of BaTiO$_3$. It is noted from the above analysis that the additions of plasticizer into the polymer blend-salt matrix slightly influence the thermal stability of the electrolyte medium; however it has enhanced the ionic conductivity of the electrolyte. But, the addition of nano composite in to the matrix greatly being increased the thermal stability and the room temperature conductivity simultaneously. It is concluded that the incorporation/dispersion of inorganic filler in the electrolyte significantly increased the thermal stability of the electrolyte membrane.

3.5 SEM analysis

The scanning electron microscope (SEM) is one of the most versatile instruments available for the examination and analysis of the microstructure morphology of the conducting surfaces. Scanning electron microscope (SEM) image of PVAc-LiClO$_4$, PVdF-co-HFP-LiClO$_4$, PVAc/PVdF-co-HFP/LiClO$_4$, PVAc/PVdF-co-HFP/LiClO$_4$/EC, and PVAc/PVdF-co-HFP/LiClO$_4$/EC+PC/BaTiO$_3$ electrolyte films are shown in Fig.6(a-e). Fig.6a. clearly shows smooth and uniform surface morphology of the PVAc- LiClO$_4$. This smooth morphology confirms the complete amorphous nature of PVAc polymer and complete dissolution of the lithium salt, which also coincides with the XRD result. Fig.6b shows the photograph of PVdF-co-HFP-LiClO$_4$ salt complex with maximum number of pores giving rise to high ionic conductivity. Presence of the spherical grains in the microstructure image
Fig. 5. TG/DTA Thermal analysis of a) PVAc/PVdF-co-HFP/LiClO$_4$; b) PVAc/PVdF-co-HFP/LiClO$_4$/EC; c) PVAc/PVdF-co-HFP/LiClO$_4$/EC+PC/BaTiO$_3$

of the samples A and B (Fig.6b and d) are belongs to the co-polymer and it means that the copolymer do not dissolve completely in the matrix which results, the membrane gets brittle nature. The appearance of number of uniform tracks of few micrometer sizes is responsible for the appreciable ionic conductivity of the electrolyte (Fig.6c). The maximum ionic conductivity of the polymer blend electrolyte also depends on the segmental motion of the PVAc and PVdF-co-HFP. The better miscibility of these two polymers can be depicted from the microstructural photograph. Fig.6d shows the scanning electron micrographs of PVAc/PVdF-co-HFP/LiClO$_4$/EC-based electrolyte system. The micrograph shows the spherical grains, and they are uniformly distributed in the electrolyte system. It is observed that the numerous pores (dark region) with the size of 1–10μm are responsible for the high conductivity of the sample, i.e., the membrane shows highly porous structure. This
increased number of porosity leads to entrapment of large volumes of the liquid in the pores accounting for the increased conductivity. The interconnected micropores in the membrane helped in absorbing liquid electrolytes and hence the ionic conductivity of the membrane is enhanced. The presence of pores in the microstructure is mainly due to the solvent removal and increased amorphous region and solvent retention ability in the electrolyte system. Surface images of the samples BaTiO$_3$ is shown in Fig.6e. The pores in the complexes are responsible for entrapping the large volume of the solution (plasticizer +salt) in the cavities accounting for the enhanced ionic conductivity. It is observed from image that the membrane has numerous number of randomly distributed spherical grains and shows maximum number of pores with very small size of the order of 50-100nm. The smooth surface of the sample reveals that the polymers and salt used in this study have a good compatible nature and the light gray region indicates the presence of plasticizer rich medium which assists for ionic motion. It is also studied that the content BaTiO$_3$ increases beyond certain percentage the film surface becomes rough above the optimum level the grain size increases, with a reduction in the number of grain aggregates, that tend to restrict the ionic movement. Finally, the SEM photograph of the polymer electrolyte indicates good compatibility of these two polymers and the other constituents which are used in the electrolyte preparation. The enhancement of the amorphous region in the matrix has also been confirmed from the images. The miscibility of these two polymers has also been confirmed from FTIR analysis.

3.6 AFM analysis

An AFM is a mechanical imaging instrument, which is used to obtain the three dimensional topography images of the samples. In the present study, the scanning probe spectroscopic method was used to measure the pore size of the prepared sample as well as the roughness factor of the sample. The two dimensional and three dimensional topography images of PVAc/PVdF-co-HFP/LiClO$_4$ complex are shown in Fig.7a. This image clearly shows the presence of pores within the scanned area of 3x3µm and the measured pore size of the sample is approximately 600nm. The size of the chain segment is also obtained and it is in the order of 688 nm. The root mean square (rms) roughness of the topography image over the scanned area is found to be 122 nm. The topography image of the sample PVAc/PVdF-co-HFP/LiClO$_4$/EC is shown in Fig.7b. The two dimensional image shows smooth surface. The modified surface image of the sample is mainly due to the addition of plasticizer which increases the amorphous phase of the matrix and hence the ionic conductivity. In addition, small pores are also observed in the surface entrapping the liquid solution, which are responsible for easy ionic movement. From the topography image we have determined the pore size of the order of 100nm which is in close agreement with the value obtained from SEM photograph. In addition, the rms roughness of the sample over the scanned area 1.4x1.4µm has been estimated and it is of the order of 53nm, it is quiet low when compare with sample without plasticizers. The micropores, amorphous phase and the chain segments of the plasticized polymer electrolytes are responsible for the enhancement of ionic conductivity. Two and three dimensional topographic images of the sample having BaTiO$_3$ are shown in Fig.7c. The image shows the dispersion of the fillers and it also contains small pore with a size of 100nm entrapping the ionic liquid which assists for fast ionic motion. In addition, the rms roughness of the sample over the scanned area 1x1µm has been obtained and it is of the order of 4nm. It is noted that the sample contains BaTiO$_3$ showed lower roughness value than the other two
samples which means that the incorporation of the fillers and the plasticizers are significantly improved the amorphous phase in the matrix is helpful for the ionic movement.

Fig. 6. SEM images of a) PVAc/LiClO$_4$ b) PVdF-co-HFP-LiClO$_4$; c) PVAc/PVdF-co-HFP/LiClO$_4$; d) PVAc/PVdF-co-HFP/LiClO$_4$/EC; e) PVAc/PVdF-co-HFP/LiClO$_4$/EC+PC.
Fig. 7. AFM images of a) PVAc/LiClO$_4$; b) PVdF-co-HFP-LiClO$_4$; c) PVAc/PVdF-co-HFP/LiClO$_4$; d) PVAc/PVdF-co-HFP/LiClO$_4$/EC; e) PVAc/PVdF-co-HFP/LiClO$_4$/EC+PC
4. Conclusion

All the polymer electrolytes were prepared using solvent costing technique. The specific interactions of the constituents were confirmed using FTIR analysis. The enhanced amorphous region of the polymer electrolyte has been identified from X-ray diffraction analysis. The porous natures of the samples were identified using scanning electron microscope. The Atomic force microscope study was used to estimate the roughness factors of the scanned area. The thermal stability of the electrolyte samples were estimated using TG/DTA analysis. It is concluded that the addition of plasticizer (Ethylene Carbonate) and the dispersion of inorganic filler into the PVAc/PVdF-co-HFP/LiClO\(_4\) electrolyte system significantly improve the amorpahicity of the medium, which will helped for easy ionic motion. These enhanced regions have been confirmed from the impedance and the surface image studies. The change in bulk resistance of the electrolytes mainly due to the interactions of the basic constituents which cause produce more amorphous phase in the matrix. It is no doubt about that the addition of plasticizers and the fillers are greatly enhanced the amorphous phase of the electrolyte, hence the ionic conductivity is improved. To conclude, polymer electrolyte for possible applications as in high energy density batteries has been identified in terms of parameters such as conductivity, thermal stability.

5. References


Akashi, H. Shibuya, M. Orui, K. Shibamoto, G. Sekai, K. Practical performances of LiNi\(_{0.8}\)Co\(_{0.2}\)O\(_2\), MCMB, and PAN-based gel electrolyte, J.Power Sources, Vol.112, No.2, (November 2002), pp.577-582, ISSN 0378-7753


Armand, M.B, Chabango, J.M, Duclot, M (1998), Second International Meeting on Solid Electrolytes, Standee’s, Scotland, Extended Absts.

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Slane, S. Salomon, M. Composite gel electrolyte for rechargeable lithium batteries, *J. Power Sources Vol.55*, No.1, (May 1995), pp.7-10, ISSN 0378-7753


Today, an individual would be hard-pressed to find any science field that does not employ methods and instruments based on the use of fine focused electron and ion beams. Well instrumented and supplemented with advanced methods and techniques, SEMs provide possibilities not only of surface imaging but quantitative measurement of object topologies, local electrophysical characteristics of semiconductor structures and performing elemental analysis. Moreover, a fine focused e-beam is widely used for the creation of micro and nanostructures. The book’s approach covers both theoretical and practical issues related to scanning electron microscopy. The book has 41 chapters, divided into six sections: Instrumentation, Methodology, Biology, Medicine, Material Science, Nanostructured Materials for Electronic Industry, Thin Films, Membranes, Ceramic, Geoscience, and Mineralogy. Each chapter, written by different authors, is a complete work which presupposes that readers have some background knowledge on the subject.

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