CHAPTER II

REVIEW OF POLYMER ELECTROLYTES

To date, several types of polymer electrolytes have been developed and characterized. PEO, PVC, PAN, PMMA, PVdF, PVA, PVAc and PEMA are some polymers that have been investigated as hosts for polymer electrolytes and a collection of reviews is presented in this chapter.

2.1. PEO Based Polymer Electrolytes

Xi et. al. [1] reported that a novel microporous polymer electrolyte based on poly(vinylidene fluoride) and poly(ethylene oxide) (PVdF–PEO) blends was prepared by a simple phase inversion technique. The addition of PEO obviously improved the pore configuration, such as pore size, porosity, and pores connectivity of PVdF-based microporous membranes, and hence, the room temperature ionic conductivity was greatly enhanced. They have obtained the highest porosity of about 84% and ionic conductivity of about 2 mS cm$^{-1}$ when the weight ratio of PEO to PVdF was 50%.

Cha et. al. [2] synthesized a novel polymer electrolytes with poly(N,N-dimethylamino-ethyl-methacrylate) (PDMAEMA), polyethylene oxide (PEO), LiTFSI as a salt, tetraethylene glycol dimethyl ether (tetraglyme), EC/PC and DEP as plasticizers. The ionic conductivity of various compositions of polymer electrolytes was investigated as a function of temperature, various concentrations of LiTFSI, plasticizers and various ratio of PDMAEMA/PEO. They have
estimated the ionic conductivity of PDMAEMA/PEO/LiTFSI (1.5 mol kg\(^{-1}\)) as 1.5 \(\times 10^{-4}\) S/cm with DEP as a plasticizer.

Poly (ethylene oxide)-based composite polymer electrolyte (CPE) using absorptive glass mat (AGM) as filler was prepared by Tang et al. [3] and characterized by SEM, FTIR, DSC and ac impedance technique. The results of Fourier-transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD) and differential scanning calorimetry (DSC) indicated that the inclusion of LiClO\(_4\) salt and the addition of AGM filler could reduce the crystallinity of PEO. It was concluded that the addition of AGM plays two roles in PEO-based CPEs, namely, interruption of PEO recrystallization and reinforcement of CPEs, accordingly enhancing room temperature ionic conductivity of CPEs and improving its mechanical strength and electrochemical stability at high temperatures.

2.2. PVC Based Polymer Electrolytes

A microporous composite polymer membrane composed of poly(vinyl alcohol) (PVA) and poly(vinyl chloride) (PVC), was prepared by Yang et al [4]. The characteristic properties of microporous PVA/PVC composite polymer membranes containing 2.5–10 wt.% PVC polymers as fillers were characterized by thermogravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM), capillary flow porometry (CFP), micro-Raman spectroscopy, dynamic mechanical analyzer (DMA) and ac impedance method. The electrochemical properties of a secondary Zn electrode with PVA/PVC composite
polymer membrane were studied using the galvanostatic charge/discharge method. PVA/PVC composite polymer membrane showed good thermal, mechanical and electrochemical properties. As a result, the PVA/PVC composite polymer membrane appears to be a good candidate for use in the electrochemical devices.

Composites of polyaniline with poly(vinyl chloride) and polystyrene have been prepared by Gupta et al. [5] and concluded that the IR, TGA and XRD spectra of the composites were superimposed on their parent materials, indicating that the composites were just the physical mixture of their constituents. These composites were semiconducting in nature with electrical conductivities in the range of $10^{-2}$ to $10^{-13}$ S/cm.

Tian et al [6] prepared Poly(acrylonitrile-co-butyl acrylate) (P(AN-co-BuA))/poly(vinyl chloride) (PVC) blend-based gel polymer electrolyte (BGPE) for lithium-ion batteries. They showed that the mechanical strength of this new blend electrolyte was found to be much higher, with a fracture stress as high as 29 MPa in dry membrane and 21 MPa in gel state and the blended gel polymer electrolyte exhibited ionic conductivity higher than $1.5 \times 10^{-3}$ S cm$^{-1}$ and electrochemical stability up to 4.8 V.

2.3. PMMA Based Polymer Blend Electrolytes

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 was reported by Deepa et al. [7] and declared that the ionic conductivity occurs at salt concentrations ≥ 1.25 M.

Shanmukaraj et al. [8] investigated the role of fillers namely TiO2, Al2O3 and SrBi4Ti4O15 on the ionic conductivity and electrochemical properties of polymer blend 15 wt%. PMMA+PEO8: LiClO4+2 wt% EC/PC electrolytes. The lithium-ion transport number and the electrochemical stability of the composite polymer electrolytes at ambient temperature were also analyzed.

Ali et al. [9] reported the electrical properties of polymer electrolytes comprising PMMA, PC or EC as plasticizer and different lithium salts like LiCF3SO3 and LiN(CF3SO2)2. The polymer electrolytes investigated exhibited high ionic conductivity at room temperature in the range of 10−6 to 10−4 S/cm. The temperature dependence studies showed that the samples were ionic conductors and seemed to obey the VTF rule. FTIR spectroscopy studies confirmed the polymer-salt interaction.

2.4. PAN Based Polymer Blend Electrolytes

Subramania et. al. [10], reported a micro-porous PAN based polymer blend electrolytes by phase-inversion technique. The ionic conductivity values of the micro-porous polymer blend electrolyte films were studied by varying the PAN
content in the (PVdF-\textit{co}-HFP) matrix. Charge–discharge studies were carried out in an assembled cell using carbon as anode and LiSr_{0.25}Mn_{1.75}O_{4} as cathode.

PAN-PVA based copolymer was synthesized by Fabio et. al \cite{11}. These new electrolytes were characterized by electrochemical techniques such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) in order to determine their stability window and conductivity. The charge/discharge performance of the PAN–PVA-based gel electrolytes was studied for two different systems: Li/gel/LiMn_{2}O_{4} and Li/gel/PANIi (PANI = Polyaniline). FT-IR analysis showed that PAN–PVA was not a passive polymer host but an active component in the gel, where Li^{+} ions were located close to C=O groups of the plasticizers and C=\equivN groups of PAN. The ionic conductivity was found to be higher than 10^{-3} S cm^{-1}.

Sun et. al. \cite{12}, reported that the PAN based electrolytes were prepared by encapsulating Li salt solutions obtained by dissolving LiN(CF_{3}SO_{2})_{2}, LiAsF_{6}, LiCF_{3}SO_{3}, LiPF_{6} and LiClO_{4} in DMF with EC and PC as plasticizers. It was found that the lithium ions strongly interacted with the C=N groups of PAN and it enhanced the maximum conductivity to the order of 10^{-3} S/cm at room temperature.

\textbf{2.5. PVA Based Polymer Electrolytes}

A novel composite polymer electrolyte membrane composed of PVA polymer host and montmorillonite (MMT) ceramic fillers (2–20 wt.%), was
synthesized by Yang et. al, [13]. The composite electrolyte was characterised by TGA, DSC, DMA, SEM, micro-Raman spectroscopy and AC impedance spectroscopy. The highest ionic conductivity of the PVA-MMT (10 wt%) composite polymer membrane was 0.0368 S cm\(^{-1}\) at 30 °C. The PVA/MMT composite polymer membrane appears to be a good candidate for DMFC and battery applications.

Rajendran et. al. [14], prepared the solid polymer electrolyte films containing PVA/PMMA-LiBF\(_4\) with different plasticizers such as EC, PC, DEC and GBL by solvent casting technique. They have reported that EC based complex showed maximum ionic conductivity of the order of 10\(^{-3}\) S cm\(^{-1}\) because of the higher dielectric constant of EC compared to other plasticizers.

PVA films doped with KSCN were prepared and their current-voltage characteristics were studied by Nagaraj et al [15]. The CV plot showed a linear behaviour with an appreciable deviation from linearity at lower voltages, which might be due to accumulation of space charges at the electrodes.

2.6. PVdF Based Polymer Electrolytes

Wang et. al.[16], prepared the nanocomposite polymer electrolytes comprising of poly (vinylidene fluoride) (PVdF), lithium perchlorate (LiClO\(_4\)) and by solution-cast method. The films were characterised by XRD, DSC and SEM.
The conductivity value was found to be of the order of $10^{-3}$ S/cm for the sample with 10% TiO$_2$.

An attempt was made to investigate the effect of PVdF in the plasticized PVC-LiClO$_4$ systems by Vickraman et al. [17]. DSC confirmed the miscibility of the polymer electrolytes. The crystallinity and surface morphology of the polymer electrolytes were studied by XRD and SEM respectively.

PVdF based gel electrolytes with ternary solvent mixture consisting of EC, PC, DMAc (Dimethyl acetamide) as solvents and different (ortho-, meta- and para-) hydroxyl-substituted carboxylic acids were studied by Sekhon et al. [18]. The conductivity was reported to be of the order of $10^{-4}$ S/cm at 20º C for higher concentrations of the acid based system.

Nicotera et al. [19], measured the ionic conductivity and the lithium salt diffusion coefficient of PMMA/PVdF blend based electrolytes with EC/PC as plasticizers and lithium perchlorate as salt by the PFG-NMR method, which revealed a maximum lithium mobility for the composition PMMA 60%-PVdF 40%. Raman spectroscopic study revealed the change of the interaction between the lithium cations and the plasticizer molecules for different PMMA/PVdF ratios.
2.7. PVdF-co-HFP Based Polymer Electrolytes

PVdF-co-HFP polymer electrolytes with EC and DEC as plasticizers and LiN(CF$_3$SO$_2$)$_2$ as salt were prepared by Capiglia et al. [20]. The ionic conductivity was estimated in the range of $10^{-2}$–$10^{-8}$ S/cm by varying the salt concentration.

Saika and Kumar [21] have made systematic studies on the ionic conductivity and transport properties of polymer electrolytes comprising of the co-polymer PVdF-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.

Stephan et. al. [22], reported that the ionic conductivity, thermal stability and compatibility of PVdF-co-HFP gel electrolytes with EC/PC as plasticizers and LiX (X=CF$_3$SO$_3$, BF$_4$ and ClO$_4$) as salts. Among these electrolytes, LiBF$_4$ based system exhibited maximum ionic conductivity because of its low lattice energy. It was also found that LiBF$_4$ based complex exhibited poor compatibility with lithium metal anode due to the formation of LiF in the layer.

Kim et al. [23], reported the electrochemical and cycling behaviour of PVdF-co-HFP (25%) –EC/PC (65%)-LiN(CF$_3$SO$_2$)$_2$ (10%) system. The cells comprising LiCoO$_2$/gel polymer electrolyte/ MCMB were found to deliver higher capacity and columbic efficiency compared to LiCoO$_2$/ GPE/ Li cells.
2.8. PVAc Based Polymer Electrolytes

Baskaran et al. [24], reported the ionic conductivity and transference number of PVAc/ PVdF blend based polymer electrolytes with constant lithium salt. The a.c. impedance and dielectric spectroscopy studies were carried out. The temperature dependence of ionic conductivity followed VTF behaviour. The highest ionic conductivity $6.4 \times 10^{-4}$ S/cm at 343K was obtained for 75:25 (PVAc/PVdF) based polymer electrolyte system. The ionic transference number of mobile ions was also estimated by Wagner's polarization method.

Animitsa et al. [25] studied the ionic conductivity of P(EO)$_{10}$ LiClO$_4$ system using amorphous poly(vinyl acetate) (PVAc) as an additive. It was found that the ionic conductivity increased with the increase of PVAc content.

Rajendran et al. [26] reported PVAc/PMMA based polymer blend electrolytes with constant weight ratio of lithium salt. XRD and FTIR revealed the amorphous nature and the complexation of the polymer electrolytes. The highest ionic conductivity ($10^{-4}$ S/cm) was observed for polymer electrolyte having the blend ratio 25:75 (PVAc/PMMA).

2.9. PEMA Based Polymer Electrolytes

Aravindan et al. [27], studied the ionic conductivity and coherence length of PEMA/PVdF-HFP based polymer blend electrolytes with DEC/EC as plasticizers, sodium trifluoromethanesulfonate (NaCF$_3$SO$_3$) as salt and nanosized
Sb$_2$O$_3$ as filler. The highest ionic conductivity 0.569 mS/cm was obtained for 10 wt% of Sb$_2$O$_3$.

Han et al. [28] reported the characteristics of polymer electrolyte based on PVC/PEMA blend. They inferred that the mechanical strength of PVC/PEMA polymer electrolyte was found to be higher than that of PVC/PMMA based system.

Sivakumar et al. [29] reported the compositional effect of PEMA with PVdF. The maximum ionic conductivity was obtained in the range $10^{-4}$ S/cm at room temperature.

2.10. Scope of the Work

Besides the research efforts to synthesise new monomers, there are continuous interest to modify and transform known polymers in order to diversify their usage as well as to create materials with superior properties for specific properties will always complement the advances in technology. Therefore the objective has been to identify solid polymer electrolytes with sufficiently high ionic conductivity to allow the operation of the solid state lithium batteries at ambient temperature. The electrochemical properties of these material systems can be modulated by mixing the polymeric material with alkali salts.

With this requirement, an attempt is made to enhance the ionic conductivity of PEMA based system blending with compatible polymer like PVC. Poly (ethyl methacrylate) (PEMA) has good superior mechanical properties and considering
the miscibility and the chemical and mechanical compatibility of PEMA with PVC, it has been chosen as the guest polymer for our studies. Proof of the blend concept was demonstrated with a PVC/PEMA gel electrolyte by Han et al [28].

PVC is a commonly used polymer in the gel polymer electrolytes for lithium battery applications. In electrolyte, PVC acts as a mechanical stiffener.

The work embodied in this thesis is thus aimed at understanding PVC/PEMA blend electrolyte phases so as to (i) develop polymer electrolyte phases for possible device applications and (ii) view the ionic conductivity of the polymer electrolytes from their structural aspects.

Thus this work relates to

(i) the preparation of PVC/PEMA polymer blend electrolytes using the solvent casting technique.

(ii) structural and morphological characterization of the cast membranes.

(iii) an investigation of the variation of ionic conductivity as a function of temperature

(iv) a study of the thermal characteristics of the films with a view to establishing the thermal stability region of the polymer electrolyte.
References


