

"Studies on composite polymer electrolytes"

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There has been a growing interest in the utilization of alternative resources for the substitution of petroleum based products due to the exhaustion of fossil fuel stocks by the late 21st century. The emphasis has been both on the conservation and judicious usage of current resources, and on finding alternative energy sources. Much attention has been focused on the latter of these two through the development of electric vehicles, fuel cells and portable power sources largely due to the mandate driven by the government initiatives. Lithium ion batteries constitute an important component in the techno-economic-growth and development of energy storage devices amongst many other possible electrochemical devices options, due to high energy power density, low weight and excellent performance. The addition of advanced polymer electrolytes in lithium ion batteries enhances the mechanical strength and favors gain in electrochemical properties that include manifestation of high ionic conductivity and low interfacial resistance

Initial work on polymer electrolytes was mainly based on the complexes of poly (ethylene oxide) (PEO) with various inorganic lithium salts. These systems fail to exhibit desirable ionic conductivity due to their high degree of crystallization. The melting of the crystalline phase of PEO around 60 °C restricts the application of electrolytes based on PEO in various electrochemical devices. Below this temperature the ionic conductivity of the polymer electrolyte is too low to warrant its practical application. To attain high ambient temperature conductivity a polymer that is amorphous in nature and has a flexible backbone is more preferred. The commonly used amorphous polymers include poly (acrylonitrile) [PAN] and poly (methylmethacrylate) [PMMA] and the high conductivity exhibited by them is due to "gel formation", the polymer network encaging the liquid electrolyte. PAN is reported to interact more with the liquid electrolyte taking active part in the conduction mechanism, while PMMA is regarded as more passive in nature.

Energy storage is equally important as energy consumption and production.

Electrochromic devices, though they do not produce energy, but are vital sources for energy conservation. In our efforts to develop transmissive electrochromic devices, it has been realized that PMMA based gel electrolytes are viable candidates as electrolytes in these devices due to their high transparency as well as good gelatinizing and solvent retention ability. The effect of different nanosized particles (SiO_2 , TiO_2 , Al_2O_3) in different proportions on PMMA based electrolytes on ionic conductivity of the resultant CPEs with different lithium salts using single or binary solvents are studied using electrochemical, rheological, spectral, calorimetric and morphological methods. Two new areas, as new generation electrolytes were also explored, which include electrolytes based on insitu prepared nanocomposite polymers and ionic liquids. These new generation electrolytes exhibit superior properties than their counterparts.

The thesis has been divided in eight chapters as follows:

This first chapter includes general introduction, literature review on different components of Li^+ based polymer electrolytes viz. salts, solvent, polymers and their applications. Types and kinds of different polymer electrolytes i.e. solid polymer electrolytes and gel polymer electrolytes and a detailed analysis of the latter due to their edge over the earlier. Finally from application point of view and of particular interest to us are, electrochromic devices, which have been discussed, followed by characterization techniques in second chapter.

The third chapter consists of composite polymer electrolytes (CPEs) and were prepared by adding hydrophilic nanosized fumed silica (SiO_2) in different proportions to gel polymeric electrolytes (GPE), comprising liquid electrolytes with different Li salts and immobilized with 15 wt % PMMA. The effect of fumed silica content in these CPEs on the electrochemical, rheological, calorimetric, spectroscopic and morphological properties has been studied. The observed ionic conductivity was one of the highest and in the order of \sim mS/cm at ambient temperature, which was studied as a function of concentration of fumed silica. It was further found that the fumed silica acted as passive filler and played a predominant role in controlling the rheological properties while ion transport properties were least affected. Fumed silica addition both to the liquid electrolyte as well as to GPE exhibits similar conductivity behaviour, which reveals the passive role of PMMA. At an optimum concentration of fumed silica (2wt.%) the observed maximum conductivity and morphology was attributed to the presence of a strong network structure, while at a higher concentration the elastic behavior was more pronounced which impeded ion transport. The differential calorimetry studies revealed a single glass transition temperature pointing towards homogeneous nature of the CPEs. The shear thinning behaviour indicative of easy processability, high thermal stability and low volatility make these CPEs potential candidates as solid like electrolytes for electrochemical devices.

The fourth chapter deals with a novel approach which has been adopted for synthesizing composite polymer electrolytes with a blend of atactic poly (methyl methacrylate) (a-PMMA) and isotactic PMMA (i-PMMA) owing to their ability to form stereocomplex

structures, especially double helix like structures. Nanocomposite polymeric electrolytes based on gel polymeric electrolyte (GPE) consisting of stereocomplex PMMA, propylene carbonate (PC) and LiClO_4 have been synthesized. For the stabilization of polymer electrolytes and for good processability, fumed silica nanoparticles have been added in different proportions up to 6 wt.% to GPE resulting in composite polymeric electrolytes (CPEs). Thermally stable, low volatile CPEs without the cost on electrochemical stability thus obtained, can be promising candidates as polymeric electrolytes in many electrochemical devices in general, and in particular in electrochromic windows.

Chapter fifth embodied of the electrochemical, X-ray diffraction, thermal, rheological and spectroscopic studies have been carried out to examine the effect of nanosized TiO_2 addition in different concentration to PMMA based gel polymer electrolytes (GPEs). This work demonstrates that with optimum concentration of TiO_2 loadings in GPE, the ionic conductivity enhances with negligible effect on other electrochemical properties. The obtained ionic conductivity value is $>10^{-3} \text{ Scm}^{-1}$. An increase in viscosity by an order of magnitude is obtained which also restricts the flow property of GPEs. The addition of TiO_2 retains the amorphicity of the GPEs while the T_g increases. Enhanced mechanical stability of these CPEs with solid like behavior is evident from their appearance. The activation energy has been calculated by fitting the conductivity profile in VTF equation, which decreases on the addition of fillers. FTIR characterization also confirms the interaction of the filler with $\text{C}=\text{O}$ of PMMA and ion pair bands of the salt. The capabilities and properties exhibited by these CPEs will be of immense interest for electrochemists to use them in solid-state devices.

Sixth chapter deals with the effect of $\gamma\text{-Al}_2\text{O}_3$ addition on PMMA based electrolytes. Inert inorganic particles, 11nm in size of $\gamma\text{-Al}_2\text{O}_3$ were dispersed in the gel polymer electrolytes in varying wt.% (0–10 wt.%). An enhancement in the conductivity for an optimum concentration using LiClO_4 as a salt could be obtained and is described in terms of free charge carrier concentration, while the other family of Lithium salts viz. LiTf , LiIm , LiBETI decreases the conductivity marginally. It has been realized that the mechanical integrity of these composites increases manifold, without affecting the conductivity significantly.

Hybrid materials, which consist of organic–inorganic materials, are of profound interest owing to their unexpected synergistically derived properties has been discussed in seventh chapter. These hybrid materials are replacing the pristine polymers due to their higher strength and stiffness in the recent years. The term "nanocomposite" is often used for polymers having dispersed fillers with particle size of less than 100nm. In the present work, studies concerning the preparation of poly (methylmethacrylate) [PMMA], PMMA/SiO_2 , and PMMA/TiO_2 nanocomposite are reported. These nanocomposite polymers were synthesized by means of free radical polymerization of methylmethacrylate using benzoyl peroxide as an initiator in a water medium. Further

"sol-gel" transformation based hydrolysis and condensation of corresponding alkoxide was used to prepare the inorganic phase during the polymerization process of MMA.

Electrolytes were synthesized based on these nanocomposite polymers and have shown superior properties as compared to conventional polymer electrolytes. The nanocomposites and the nanocomposite polymer electrolytes (NPEs) with different lithium salts were investigated by a series of characterization techniques including X-Ray diffraction, FTIR, and calorimetry along with microscopy and the electrochemical and rheological techniques.

Finally Ionic liquids based electrolytes has been discussed in eighth chapter and are regarded as environmentally friendly designer solvents. They can be divided into two categories, first is neoteric solvents as environmentally benign reaction media and the other is electrolyte solutions for electrochemical applications. Electrolytes play an important role in determining the performance of electrochromic devices (ECDs) and room temperature ILs are ideal candidates for such applications. Hydrophobic ionic liquids based on 1,3-dialkyl imidazolium cations and bis (trifluoromethene sulfonyl) imide were synthesized and investigated for different physical and chemical properties, their structures were confirmed by NMR analysis. These ILs also serve as excellent media to polymerize vinyl monomers. Insitu polymerization was performed on 1-ethyl, 3-methyl imidazolium bis (trifluoromethene sulfonyl) imide (EMITFSI) and 1-butyl, 3-methyl imidazolium bis (trifluoromethene sulfonyl) imide (BMITFSI) in the presence of initiator to result in a novel series of polymer electrolytes, which we termed as "ion gels". The solution mixture comprising ILs and methylmethacrylate and initiator were injected in a hermitically sealed electrochromic device through a port and set for thermal polymerization. The ECDs thus fabricated show superior properties than there conventional aprotic solvent based devices, which is discussed in detail in this chapter.