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Delles sumar Preshan

(Dillip K. Pradhan)

## Preface

Human quest for energy from different sources, its conservation and better utilization are as parallely moving phenomena as the progress of mankind itself. It gradually becomes more significant to preserve energy because sources are limited and requirement has acquired a demonic structure. At the turn of the millennium, therefore, the consciousness of the need to use energy more efficiently spread, at least in the developed countries. The efficient use of energy also includes efficient storage of electricity, meaning that one needs to have high energy density batteries that have low energy losses during storage, electrical charging and discharging, and last but not the least, batteries with long life times and a minimum production and disposal cost. Ionically conducting solid polymer electrolyte display advantage over their liquid counterparts from the practical problems associated with the leakage of harmful liquids and gassing, to the likely hood of producing miniaturized structure using simple fabrication techniques or cells with exceptionally long lives and wide operating temperature range. So recently, much attention has been devoted towards "ionically conducting polymeric electrolytes" which are formed by complexation of a salt with a polar polymer host. The polymeric electrolytes have some specific properties such as fabrication of thin films of desirable sizes, flexibility, ability to form proper electrode-electrolyte contacts etc. that make them attractive for use as an electrolyte in a wide variety of energy storage/conversion devices such as batteries, fuel cells, supercapacitors and hybrid power sources etc.. Polymer electrolytes are generally semicrystalline materials and ion conduction occurs in their amorphous phase. The cooperative local segmental motion of host polymers with the cationic motion gives rise to ionic conduction in polymer electrolyte.

Most of the polymer electrolytes reported so far are having low ionic conductivity, poor mechanical, thermal and electrochemical stability, which restrict

their application in solid-state electrochemical devices. The primary quantity of interest is high conductivity at ambient temperature, which becomes crucial for the realization of technological application of these materials. Achievement of desired conductivity (~10<sup>-3</sup> Scm<sup>-1</sup>) at ambient temperature is an open problem. To improve the ionic conductivity of polymer electrolyte, several strategies such as plasticization, copolymerization, fabrication of composite/nanocomposite etc. have recently been tried in order to diminish polymer crystallinity favoring ion mobility as well as to increase the number of charge carriers and also to avoid ion pair formation. We have used a new approach to avoid ion pair formation by intercalating the polymer salt complex into the nanometric gallery of clay layer where anionic contribution for conduction expected to be absent. This class of materials is termed as polymer nanocomposite electrolytes (PNCEs). Addition of organically modified montmorillonite filler brings some changes in polymer electrolytes such as enhancement in electrical conductivity and improvement in thermal, mechanical, electrochemical/interfacial properties.

Most of the R & D activities in battery fabrication are centered around the development of lithium based polymer electrolyte batteries because of its unique properties. Another candidate having comparable physical properties in this area is sodium based polymer electrolyte. The electrochemical reduction potential of sodium is -2.71 V (close to lithium one -3.045V). Some added advantages of the sodium based polymer electrolyte are (i) reliable, low cost and abundance of sodium metal on earth crust, (ii) non-toxic nature of sodium which is safe and non-hazardous, due to which a higher cost-performance ratio may be expected.

The present work aims to develop sodium ion conducting polymer composite electrolytes for their application in solid-state batteries. We have fabricated five series of sodium ion conducting polymer nanocomposite electrolytes based on PEO (polyethylene oxide) complexed with NaClO<sub>4</sub> and NaI dispersed with montmorillonite (Na<sup>+</sup>-MMMT)/Dodecyl amine modified Montmorillonite (DMMT) clay (filler) The effect of fillers on structural, morphological, vibrational, thermal and electrical properties of these electrolytes have been studied using various experimental techniques. Further, the optimized PNCEs have been plasticised with polyethylene glycol (PEG<sub>200</sub>) to enhance the conductivity of the composite electrolytes.

The following series of electrolytes have been investigated in the present work

- (i)  $(PEO)_{25}$ -NaClO<sub>4</sub>+x wt.% Na<sup>+</sup> MMT (x = 0, 5, 10, 20, 30 and 50).
- (ii)  $(PEO)_{25}$ -NaClO<sub>4</sub>+x wt.% DMMT(x = 0, 2, 5, 10, 20, 30 and 50).
- (iii)(PEO)<sub>25</sub>-Nal+x wt.% DMMT (x = 0, 2, 5, 10, 20, 30 and 50).
- (iv)(PEO)<sub>25</sub>-NaClO<sub>4</sub>+5 wt.% DMMT + x wt.% PEG (x = 0, 5, 10, 20, 30, 40 and 50).

 $(v)^{-}(PEO)_{25}$ -NaI+5 wt.% DMMT + x wt.% PEG (x = 0, 5, 10, 20, 30, 40 and 50).

Polymer nanocomposite electrolyte (PNCE) films were prepared by a standard tape cast technique by using AR grade precursors with a self-designed tape caster of desirable thickness (resolution up to a micron thickness level). The x-ray diffraction (XRD) experiment was carried out in order to confirm the formation and to study structural properties of the PNCE films. For this, the XRD patterns of the PNCE films were recorded at room temperature using an x-ray powder diffractometer (Rigaku Miniflex) with CuK<sub>a</sub> radiation ( $\lambda$ =1.5405Å<sup>0</sup>) in a wide range of 20 (2<sup>0</sup> ≤ 20 ≤30<sup>0</sup>) at a scanning rate of 0.5<sup>0</sup> minute<sup>-1</sup>. XRD analysis shows that the polymer-salt complexes have been intercalated into the silicate layers of montmorillonite giving rise to polymer-clay nanocomposite.

The morphological features and surface properties of polymer nanocomposite electrolyte films were studied using a high-resolution scanning electron microscope, (SEM JOEL-JSM Model 5800). On addition of MMT/plasticizer, substantial changes in the morphological features (spherulite textures) have been observed, and the fillers appear to be homogeneously distributed through out the polymer matrix.

The vibrational spectroscopic studies were carried out using FTIR and Raman spectroscopy methods. The effect of MMT filler/plasticizer on polymer-ionclay interaction and ion-ion interaction was studies using FTIR and Raman spectroscopy in terms of ion association/dissociation effect and the changes in the chemical environment of the nanocomposite films. The effect of filler/plasticizer concentration on (i) D-LAM mode, (ii) metal-oxygen breathing mode and (iii) cation-anion interaction mode was also investigated using Raman spectroscopy. FTIR analysis reveals that there is a strong interaction between the polymer-salt complexes, clay layers and plasticizer. Crystalline polymer-salt complexes with a helical conformation is distorted between the nanometric channels of of PNCEs.

Thermogravimetric analysis (TGA) of the composites was performed using a SHIMADZU thermogravimetric analyzer. Samples were heated in a platinum pan from room temperature (25°C) to 600 °C at a heating rate of 10 °C/min under N<sub>2</sub> atmosphere. DSC (differential scanning calorimetry) data were recorded using Shimadzu DSC-50 with a low temperature measuring head and liquid nitrogen as coolant in a wide temperature range ( $-100^{\circ}$ C to  $150^{\circ}$ C) at the scan rate of  $10^{\circ}$ C/minute. TGA analysis reveals that the residual weight loss increases with increase in DMMT concentration, whereas the residual weight loss decreases with increase in PEG<sub>200</sub> (plasticizer) concentration. The glass transition temperature (T<sub>g</sub>) and melting temperature (T<sub>m</sub>) calculated form the DSC curves are found to shift initially towards the higher temperature side on increasing clay content of the composite and reaches their maximum value for 5% DMMT, but decreases as the clay content is further increased. On addition of plasticizer,  $T_g$  and  $T_m$  decrease with increase in plasticizer concentration.

Complex impedance spectroscopy technique was used to calculate the bulk resistance of the nanocomposite electrolytes. The complex impedance measurements were carried out using a computer-controlled impedance analyzer (HIOKI LCR Hi-Tester Model 3532, Japan) in a wide frequency range (100 Hz to 1MHz) on the cell SS | PNCEs | SS (SS stands for stainless steel as blocking electrode) at an a.c. signal level of 100 mV. The typical complex impedance spectrum of the samples comprising of a broadened semicircle in the high frequency region (due to the bulk properties of the materials) followed by a tail (spike) in the low frequency region indicates the double layer response at the electrode/sample interface. The fitting of the experimental data with the help of a software using a proposed equivalent circuit shows that there is good agreement between the experimental and theoretical values. The d. c. conductivity calculated from the bulk resistance of the materials is found increasing initially on addition of DMMT up to 5 wt.%, followed by a monotonous decrease on further increase in clay concentration. The conductivity increases on increase in plasticizer concentration. The temperature dependence of conductivity follows VTF pattern.

The frequency dependence of dielectric and conductivity properties have been studied to (a) understand the ion transport behavior and (b) obtain the information about ionic and molecular interaction in solid polymer electrolyte. The dielectric permittivity and electrical conductivity show frequency dispersion. The frequency dependence of dielectric permittivity suggest that, the decrease of relative dielectric constant ( $\varepsilon_r$ ) on increasing in frequency may be attributed to the electrical relaxation processes, but at the same time the material electrode

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polarization cannot be ignored, as the samples are ionic conductors. The conductivity spectra follow Jonscher's power law with a strong dispersion at low frequency due to electrode polarization effect. The electrical modulus formalism (used to describe the conductivity relaxation process), shows that the conductivity relaxation data can best be represented in terms of the stretched exponential correlation function,  $\Phi = \Phi_0 \exp[(-t/\tau)^{\beta}]$ . The conduction may be due to the long range drift of ions coupled with polymer segmental relaxation. A peak in the modulus spectra without a corresponding feature in dielectric spectra implies a strong coupling between the ionic motion and polymer segmental motion.