Solid Polymer Electrolytes based on Nanocomposites of Polyethylene oxide/Sodium thiocyanate/Montmorillonite

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ABSTRACT

The rapid development of portable electronic devices and electric/hybrid vehicles has increased the demand for compact, lightweight, high capacity betteries. Considerable efforts have been devoted to the development of solid polymer electrolytes (SPE) with high ionic conductivity (~10^{-4} S/cm) and dimensional stability. Poly(ethylene oxide)/alkali metal salt-based solid electrolytes is the most interesting base material because of its high chemical and thermal stability. PEO is a semicrystalline polymer, possessing both an amorphous and a crystalline phase at room temperature. It can also solvate a wide variety of salts, even at very high salt concentrations. The solvation of salts occurs through the association of the metallic cations with the oxygen atoms in the backbone. The multi-phase nature of PEO is most often regarded as a major problem in real working systems, since the ionic conduction has been shown to take place mainly in the amorphous phase. Many investigations have been done to reduce the crystalline content, via various approaches such as using blends, copolymers, comb-branch polymers and cross-linked polymer networks. Our interest is to overcome these problems by the incorporation of mineral clay which is an inorganic filler with intercalation property. Intercalating polymer in layered clay host can produce huge interfacial area to sustain the mechanical property of polymer electrolyte system and imparts salt-solvating power to dissolve the lithium salts. In this work, we present polymer electrolyte nanocomposites consisting of $(PEO)_8NaSCN/MMT$ at various clay (Montmorillonite, MMT) content. Structures, interaction, thermal behavior and ionic conductivity of $(PEO)_8NaSCN/MMT$ were studied to clarify the role of clay fillers on properties of these materials.

Sample Preparation: PEO (MW 1 x 10^5 g mol^{-1}, Aldrich) and Montmorillonite (MMT) (SWy-2, Clay Mineral Depository) were used as received. The salts, sodium thiosulfate (NaSCN, Fluka), were dried in the vacuum oven at ~140 °C for 48 hours. Stoichiometric amount of PEO, salt and clay were dissolved in methanol and stirred continuously for 24 hours at room temperature. The gelatinous polymer solution was cast on the glass plate and then dried in vacuum oven at 50 °C for 24 hours to remove solvent.

X-Ray Diffraction (XRD): The intercalation of the polymer chains usually increases the interlayer spacing of clay, leading to a shift of the diffraction peak towards lower angle values (angle and layer spacing values being related through the Bragg's relation: $\lambda=2d\sin\vartheta$). Upon intercalation, the basal spacing expanded from 1.24 to 2.07 nm indicating the incorporation of large PEO molecules. The magnitude of a shift is not constant but varied with the clay content. The diffractograms of the 8:1 PEO/NaSCN with 0-20 wt% MMT display characteristic crystalline peaks centered around 15°, 19° and 23° which is ascribed to crystalline PEO. Addition MMT to the sample also gives peaks at the same positions but with lower intensities. It should be emphasized that 8:1 PEO/NaSCN at different % weight of MMT crystalline phase still existed but at a lower crystalline content than 8:1 PEO/NaSCN.

Fourier Transform Infrared Spectroscopy (FTIR): Upon mixing NaSCN with PEO and PEO/MMT system, the new bands appear at 2000-2100 cm^{-1} regions (stretching modes of SCN^{-} in PEO/NaSCN), indicating that the formation of crystalline complex P(EO)$_8$NaSCN (the band at 2060 cm^{-1} is ascribed to the contact ion-pairs and solvent-separated dimers). With addition of MMT to SPE, the relative intensity of 2060 cm^{-1} band increases at the expense 2031 cm^{-1} band, indicating that the disintegration of crystalline PEO phase results in the decrease of crystalline P(EO)$_8$NaSCN complex. The 1000-800 cm^{-1} band is the characteristics of C-O stretching and CH$_2$ rocking modes. Spectral changes in this region reflect changes occurring in the local structure of the polymer backbone. With adding more salt, the bands split at 860, 834 cm^{-1} which particularly sensitive to the local conformation of the O-C-C-O torsional angle. The appearance of one mode at a higher frequency and the second mode at a lower frequency than observed in pure PEO, originates from the interaction of sodium ion with ether oxygens. For the IR spectra in the 1400-1300 cm^{-1} region, the peaks at 1360 and 1345 cm^{-1} are CH$_2$ wagging modes which are the characteristic of crystalline PEO. When NaSCN was mixed in, the intensity of two peaks decreased drastically and replaced by sharp band at 1350 cm^{-1}, indicated an amorphous content for P(EO)$_8$NaSCN. The character of 1280 cm^{-1} peak (CH$_2$ twisting mode in pure PEO) are also changed, while this peak shifts if clay was added. Therefore there is an interaction between cation with ether group of PEO in P(EO)$_8$NaSCN compound and it is not only salt but also clay that can reduce the crystalline phase of pure PEO.

Differential Scanning Calorimeter (DSC): The effect of adding MMT on the changes of T_m and ΔH_m of PEO and PEO-NaSCN were investigated using DSC technique. The melting temperature of PEO changed from 69.0 °C to 66.8 °C which imply that there is more amorphous domain in the complex due to the miscibility of MMT with PEO. ΔH_m and the percentages crystallinity of PEO+MMT are lower than that of PEO. It reveals that MMT is compatible with PEO and MMT can reduce the crystallinity of PEO in agreement with XRD results.

Impedance Analyzer: The ionic conductivity was increased by 5 time the undoped P(EO)$_8$NaSCN system. The ionic conductivity increases with an increase of the clay content and approaches a maximum (5 x 10^{-5} S/c) when the clay concentration is around 15 wt%. Subsequently, the conductivity decreases drastically with further increase in the clay content. Since the ionic conductivity depends on the amount of charge carriers (n_i) in the system and the mobility (μ_i) of the various species. Addition of MMT can increase the fraction of 'free' anions (increase n_i), meanwhile, the ionic mobility may be reduced (decrease μ_i) owing to the higher viscosity of MMT concentration. These two adverse and competitive effects occur in this system, one is favorable and other is unfavorable for ionic conductivity. It can be concluded that the addition of optimum clay content to the complex provides the most suitable environment for the ionic transportation and achieves the highest conductivity.