

Abstract

The concept of fast ion conduction in solids is a recent phenomenon in contemporary science that has led to the development of a new branch of science and technology referred as “Solid State Ionics”. It is devoted to conceptualization, understanding and optimization of physical properties (a proper balance between ionic conductivity and stability properties) of ionic conductors in solid state with the ultimate objective of applications in solid state ionic devices such as; high energy density lithium batteries, fuel cells, supercapacitors, gas sensors, electrochromic display etc.

This work aims to demonstrate a viable approach to overcome the inherent problems of polymeric ion conductors such as poor ambient conductivity and concentration polarization (ion pair formation) for application in energy storage/conversion devices. In order to address such crucial problems, a novel approach of intercalation, whereby an effective separation between anions and cations is maintained, has been adopted. An optimized ratio (~ 8) of electron rich site in the host polymer to cation (Li^+) has been maintained during sample preparation. Intercalation of cation coordinated polymer chains into dodecyl amine (DDA) modified montmorillonite clay galleries having channel width 12 \AA inhibits anion entry into the clay channels. In addition to the above, another idea explored in this work is related to the effect of anion size on ion transport and stability property. To achieve this goal, two different lithium salts having varying anion sizes; PF_6^- ($\sim 2.8 \text{ \AA}$) and CF_3SO_3^- ($\sim 3.1 \text{ \AA}$) has been investigated.

Two different series of polymer nanocomposite (PNC) films studied in this work indeed confirmed drastic improvements in the ambient temperature ionic conductivity ($\sim 10^{-3} \text{ S cm}^{-1}$) and stability (thermal ($\sim 220 \text{ }^\circ\text{C}$), voltage ($\sim 5.6 \text{ V}$) and mechanical ($\sim 58 \text{ MPa}$)) properties. An excellent correlation between their structure and microstructural property has been observed and explained. A role of clay concentration in the PNC films has been clearly noticed in terms of (i) relaxation (ii) ion dynamics (iii) ion pair separation/release of free mobile charge carriers, (iv) substantial enhancement in Li^+ transport ($t_{\text{Li}^+} \sim 67\%$) which is 11% higher than the literature report (v) enhanced conductivity at specific clay concentrations has been explained in terms of; $\sigma_{dc} = \sum_{i=1}^n q_i \mu_i n_i$ where, symbols have there usual meanings. To explain the clay concentration dependence of conductivity, an ion transport mechanism has also been proposed for the intercalated type PNC films. The central idea of the mechanism is based on the concept of an evidenced inherent polymer-ion-clay interaction in the PNC matrix. The optimized PNC film has been tested for its suitability as an electrolyte/separator in lithium polymer cells. It is concluded that ion conducting PNC films has the potential to act as separator component in futuristic energy storage devices.

Key words: Polymer Nanocomposites, Intercalation, Structure and Microstructure, Electrical Properties, Ion-Conduction mechanism, Energy Storage/Conversion devices.