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Effect of nanoscopic confinement on improvement in ion conduction and stability properties of an intercalated polymer nanocomposite electrolyte for energy storage applications

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ABSTRACT

Nanoscopic confinement of a cation coordinated polymer in the channels of organo-modified montmorillonite clay results in substantial improvement in conductivity, cation transport and stability properties required for energy storage/conversion devices. X-ray diffraction analysis confirms composite formation as evidenced by: (i) intercalation of PEO_8–$LiClO_4$ into the clay channels for clay loading $\geq$7.5 wt.% and (ii) partial intercalation/exfoliation for a lower clay loading ($\leq$5 wt.%). Transmission electron microscopy analysis corroborates these findings as indicated by an enhancement in clay gallery width from 6 to 9 Å for 20 wt.% clay providing evidence for intercalation at higher clay loadings. Energy dispersive X-ray dot-mapping images confirm the homogeneous distribution of clay in nanocomposites. Thermal analysis indicates a strong dependence of thermodynamic parameters, e.g., glass transition (T_g), crystalline melting (T_m), melting enthalpy, glass transition width (ΔT_g), and thermal relaxation strength (ΔC_p), on clay concentration. These observations agree well with changes in electrical properties on nanocomposite formation. Substantial enhancement in ambient conductivity (~208 times) occurs in a nanocomposite film (2 wt.% clay) relative to a clay-free film. The temperature dependence of conductivity obeys Arrhenius behaviour below T_m and the VTF (Vogel–Tamman–Fulcher) relationship above T_m. The ionic transport number (~99.9%) confirms ionic charge transport with a cation contribution (t_{Li^+}) ~ 0.5 for 2 wt.% clay. It represents an increase by ~65% in comparison with PEO_8–$LiClO_4$. Improvement in voltage and thermal stability is also observed with the nanocomposites.

1. Introduction

Ion-conducting polymers have drawn considerable attention for more than a decade in view of their potential application in ionic devices such as high specific energy solid-state batteries, supercapacitors, and proton-exchange membrane fuel cells. An ion-conducting solid polymer film has the ability to function both as the separator and an electrolyte in storage devices unlike the case of present-generation Li-ion cells. Due to this, the development and scaling-up of the properties of ionically conducting solid polymer membranes, conventionally known as solid polymer electrolytes (SPEs), is considered attractive and challenging. It has always been an important and highly competitive research and development activity due to the stringent requirements of the material parameters driven by the application criteria and the high-end commercial value of the SPEs for electrochemical power sources. As a consequence, there has been a pressing demand for the development of a suitable ion-conducting polymer based separator along with the parallel development of electrode materials for application in energy-conversion/storage devices.

Inherent deficiencies of stability and ambient conductivity have been identified as the major drawback of SPEs. The primary factors that imposed severe restraint on the applicability of ion-conducting polymer films in devices are: (i) low ambient ionic conduction; (ii) concentration polarization; (iii) poor stability properties (thermal, electrochemical, mechanical interfacial, etc.). One of the major reasons for poor ionic conductivity and concentration polarization has been attributed to possibility of an ion-association (ion-pairing) effect [1]. It arises due to columbic interaction between cations and anions in the solid polymer matrix. This is because the mobile charges in the polymer-based ion-conducting films originate due to dissociation of cations (M^+) and anions (X^-) of the salt (MX) in the host polymer, having weak permittivity (~3–5), swollen into a volatile polar organic solvent. Thus there is a high probability of ions remaining both as free charges (cation/anion) and ion-pairs [2–4]. Ion-pair formation can cause concentration polarization and immobilization of conducting species whenever an excess number of ion-pairs are present in the host polymer matrix in comparison

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with the available number (fraction) of free-charge carriers (i.e., the anions and hence the cations). The overall effect is a lowering in electrical conductivity that imposes serious limitations on the suitability of SPEs for devices. This has therefore prompted the search for new alternative materials with superior properties.

A number of approaches have been proposed to solve the state-of-the-art problems of ion-conducting polymers [5,6]. Nanocomposite formation is the latest suggestion. Polymer nanocomposite (PNCE) films formed via the intercalation of cation-coordinated polymers in the nanometric channels of inorganic clay (e.g., montmorillonite, zeolite etc.) have drawn considerable attention in recent years. They are known as "intercalation nanocomposites". The intercalation of an ion-conducting polymer–salt (PS) complex in the nanometric channels of an organo-modified clay such as montmorillonite, which is endowed with an organophilic property on modification, is considered effective in minimizing the ion-pairing effect. The central idea is based on the concept that organic modification of the clay causes an accumulation of negative charge on its surface and thereby restricts the entry of bulky anions into the nanometric channels (galleries). On the other hand, clay galleries develop a capability for accommodating cation-coordinated polymer chains favoured by Coulombic interaction. In view of this, the intercalation approach of nanocomposite formation appears to be a novel procedure [7,8] to overcome existing challenges with polymer-based ionic conductors. In addition, this approach seems to be attractive with definite scope to minimize concentration polarization (i.e., to reduce ion-pairing) due to an effective separation between the cations and anions on nanoscopic confinement of the ion-coordinated polymer chains into the clay channels.

Aranda and Hitzky [9] first attempted nanocomposite formation by direct intercalation of an insulating polymer, polyethylene oxide (PEO), into montmorillonite (MMT) clay. They succeeded in intercalation without any significant achievement of the desirable properties (e.g., conductivity) of the nanocomposite for applications in devices under ambient conditions. Subsequently, Giannelis and co-workers [7,8,10–12] explored the possibility of intercalation on the basis of thermodynamical free energy considerations and simulation studies to investigate the conformational and structural arrangement of polymer chains between successive clay layers. They observed that the intercalation of a cation-coordinated polymer chain via an ion-exchange reaction is easier than intercalating pure PEO. Following these reports in the literature, a large number of smectic clays such as montmorillonite [5–9], hectorite [13,14], and laponite [15] have been used for composite formation in combination with different polymers. Of these, montmorillonite is still a favoured choice in view of its special features of high aspect ratio (~1000), high cation-exchange capacity (CEC ~ 80 meq/100 g), large specific surface area (~31.82 $m^2 g^{-1}$), appropriate interlayer charge (~0.55) and length scale (clay channel width ≡ 16 Å). Nevertheless organo-modification of the clay is an essential prerequisite to make it organophilic [2] in order to achieve the desirable features in the material system to be fabricated.

Recently, Kim et al. [16] reported composite formation of a plasticized polymer electrolyte ($PEO_{16}LiClO_4$ + 50 wt.% EC) with tallow modified Na-MMT. They observed an optimum value of room temperature conductivity of $\sim 10^{-5}$ S cm^{-1} for the plasticized electrolyte and $\sim 10^{-4}$ S cm^{-1} for the composite (10 wt.% modified MMT). Fan et al. [17] studied composite formation with combination of organo-modified Li-MMT/Na-MMT and $PEO_{16}LiClO_4$. They reported an enhancement in conductivity at room temperature by 30 times for the composite polymer film ($\sim 3.5 \times 10^{-6}$ S cm^{-1}) in comparison with that of pure $PEO_{16}LiClO_4$ ($\sim 1.2 \times 10^{-7}$ S cm^{-1}). These reports could not, however, cover a number of scientifically and technologically important aspects such as the stability (thermal, voltage), ion transport properties and confirmation of the phase structure (i.e., intercalation) of the composite polymer film. In addition, the ambient conductivity is still far below the desirable value for device application. Further, use of a plasticizer is normally expected to degrade the stability of solid polymer films. The problem of relatively lower ambient conductivity in the above studies may be related to the selection of the polymer–salt stoichiometric ratio. Literature reveals that an optimized ratio of Ö/Li ≡ 8:1 represents a eutectic composition in the case of a PEO:$LiClO_4$ complex that shows maximum conductivity and a lower crystalline melting point (T_m) [18,19].

Based on these reports, the present experimental investigation has been conducted with emphasis on analyzing the properties of polymer nanocomposite films to judge their suitability for application in energy storage/conversion devices. The work aims to demonstrate a practical approach to overcome the inherent problems of ion conducting solid polymer films by means of nanoscopic confinement of an optimized combination of a Li^+ cation coordinated polymer matrix into dodecyl amine (DDA) modified montmorillonite clay (DMMT) galleries having a channel width of ~16 Å. Structural, microstructural, stability (thermal, voltage), electrical conductivity (before and after polymer phase transition) and ion transport properties are analyzed.

2. Materials and methods

2.1. Sample preparation

Free-standing polymer clay nanocomposite (PNCE) films were prepared using high purity (AR grade) poly(ethylene oxide) (PEO) from Aldrich (USA), salt ($LiClO_4$) from (M/s Acros Organics) and Na-montmorillonite (MMT) (SWy-2) supplied by the Clay Minerals Society (USA). The MMT is organically modified using dodecylamine as a surfactant by an ion-exchange reaction. In the process, Na^+ ions, the natural occupants of clay channels, are replaced by dodecyl ammonium ion and hence the MMT becomes organophilic. As a result, the ambiguity of the presence of the two alkali cations (Li^+ and Na^+) of the PNCE films in the clay channel is resolved. The process for organo-modification of clay was followed from literature [20]. PCNE films were prepared by a solution-casting technique with different weight ratios of modified montmorillonite clay. The precursors were vacuum dried and the host polymer (PEO) and salt ($LiClO_4$) were dissolved in acetonitrile at a constant ratio of ether oxygen to lithium ion (O/Li) ~8:1. The polymer–salt solution was stirred for 8 h followed by the addition of modified montmorillonite (MMT) clay. Subsequently, this viscous composite fluid was cast into a polypropylene dish and the solvent was allowed to evaporate slowly. The resulting free-standing clay based polymer nanocomposite (PNCE) films have the general formula: ($(PEO)_8LiClO_4 + x$wt.% DMMT) where x varies from 0 (pure polymer–salt complex, PS) to 20 wt.% with respect to the host polymer (w/w).

2.2. Sample analysis

X-ray powder diffraction (XRD) patterns of the PNCEs were taken using Rigaku Miniflex X-ray diffractometer with Cu Kα radiation (λ = 1.5405 Å). Sample microstructure was studied by transmission electron microscopy (TEM) analysis using C M 12 PHILIPS TEM equipment. Samples for TEM analysis were prepared by a drop casting-technique on a carbon coated copper grid. The samples were dried for 24 h in vacuum prior to scanning under the transmission electron microscope. The distribution of clay particulates in the PS matrix was examined by an energy dispersive X-ray (EDAX) dot mapping technique available in the scanning electron microscope (SEM JOEL-JSM Model 5800). Thermal analysis techniques of differential scanning calorimetry (DSC) and thermo-gravimetric analysis (TGA) were carried out using PerkinElmer (Model: Sapphire DSC)