Structure and conductive properties of poly(ethylene oxide)/layered double hydroxide nanocomposite polymer electrolytes

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Abstract

The oligo(ethylene oxide) modified layered double hydroxide (LDH) prepared by template method was added as a nanoscale nucleating agent into poly(ethylene oxide) (PEO) to form PEO/OLDH nanocomposite electrolytes. The effects of OLDH addition on morphology and conductivities of nanocomposite electrolytes were studied using wide-angle X-ray diffractometer, polarized optical microscopy, differential scanning calorimetry and ionic conductivity measurement. The results show that the exfoliated morphology of nanocomposites is formed due to the surface modification of LDH layers with PEO matrix compatible oligo(ethylene oxide)s. The nanoscale dispersed OLDH layers inhibit the crystal growth of PEO crystallites and result in a plenty amount of intercrystalline grain boundary within PEO/OLDH nanocomposites. The ionic conductivities of nanocomposite electrolytes are enhanced by three orders of magnitude compared to the pure PEO polymer electrolytes at ambient temperature. It can be attributed to the ease transport of Li⁺ along intercrystalline amorphous phase. This novel nanocomposite electrolytes system with high conductivities will be benefited to fabricate the thin-film type of Li-polymer secondary battery.

Keywords: Poly(ethylene oxide); Layered double hydroxide; Nanocomposite; Polymer electrolyte; Ionic conductivity

1. Introduction

Polymer electrolytes play an important role in the development of lithium polymer rechargeable batteries because they can lead to flexible laminated structure with tailor-made geometries. Wright et al. [1] proposed that the poly(ethylene oxide)s (PEOs) doped with alkali salts as solid polymer electrolytes could serve as separators and ionic conductors in rechargeable batteries. Though the PEO based polymer electrolyte exhibits fast ionic conduction in its molten state, a poor conductivity results from the retardation of ionic transport imposed by the highly crystalline phase at ambient temperature. By adding liquid plasticizer or organic polar solvent into polymer electrolytes, the ionic conductivity is improved by enhanced segment motion and amorphous phase [2]. Nevertheless, the plasticized polymer electrolytes or gel electrolytes suffer the disadvantages of worsening mechanical properties, electrode interfacial instability and release of volatiles. An effective approach to achieve the balanced characteristics of conductivity, mechanical properties and interfacial stability of polymer electrolytes was reported by Scrosati et al. [3]. The all solid-state nanocomposite electrolyte was prepared by dispersing nanoparticles of TiO₂ or Al₂O₃ into the PEO-LiClO₄ polymer electrolytes. The recent research efforts in PEO electrolytes have been directed to the nanocomposite systems by use of miscellaneous nanoparticles such as TiO₂, Al₂O₃, SiO₂, ZnO and MgO [4–8].

There are majority of studies for polymer nanocomposites by use of cation-exchangeable layered silicate such as montmorillonite (MMT). The MMT was dispersed into various polymer matrixes with intercalating or exfoliating morphology [9]. The PEO/MMT nanocomposite polymer electrolyte, where the PEO was mixed with Li⁺-MMT by solution intercalation, exhibited high conductivity at temperature above 130 °C [10]. The single-ion conduction characteristic was attributed to the immobility of the
negative charges on the surface of silicates. The results of molecular dynamic simulations also illustrated that the Li$^+$ ions were basically pinned to oxygen atoms of silicate surface rather than being coordinated with PEO [11]. Alternatively, the melt-intercalated PEO/MMT nanocomposite electrolyte exhibited high conductivity with weak temperature dependence around ambient temperature [12]. It was probably attributed to the presence of excess PEO that was probably retained in the PEO/OMMT nanocomposites with an exfoliated dispersion of OMMT nanosheets favored a formation of PEO-rich phase. The formed amorphous phase thus enhanced the ionic conductivity. Another class of layered inorganic materials with positive charged surface such as LDHs has great opportunity to be used in the nanocomposites system. LDHs were formed with positive charged layers [M$^{x+}$-M$^{y+}$]$_{x+y}$[OH]$_{2}$ and interlayer exchangeable anions $[A^{m-}_n\cdot nH_2O]^{1+}$, where A was the anion, M$^x$ and M$^y$ were divalent and trivalent metal cations, respectively [17]. Recently, Zhang et al. [18] reported the intercalated LDH with polyoxyethylene sulfate as a candidate of anisotropic solid electrolytic materials. On the other hand, the poly(ethylene glycol)-n-alkyl-3-sulfopropyl diether and poly(ethylene glycol)dicarboxylic acid containing PEO chains of different ethylene oxide units were incorporated between the LDH layers of Cu$_2$Cr(OH)$_6$Cl-nH$_2$O using co precipitation method by Aranda and coworkers [19]. Though Wypych and coworkers [20] reported the preparation and characterization of nanocomposite composed with PEO and dodecyl sulfate intercalated LDH, there were no reported conductive properties.

In this work, we prepare the oligo(ethylene oxide) modified LDH to study the effect of OLDH addition on the morphology and conductivity of PEO/OLDH nanocomposite polymer electrolyte.

2. Experimental section

The anionic surfactant used to modified LDH was a mixture of equal molar ratio of mono- and bi-hydroxy oligo(ethylene oxide) phosphonate, which was synthesized by poly(ethylene glycol) methyl ether (Aldrich, Mn = 550) and P$_2$O$_5$ in benzene according to the literature procedures [21]. The OLDHs containing intercalated oligo(ethylene oxide) with a tentative formula of M$_{2}$Al(OH)$_{6}$Cl-n(PEO)–PO$_2$–OH were prepared by template method at pH of 10.0 [22], whereby the stoichiometric amount of Mg(NO$_3$)$_2$.6H$_2$O (0.18 M), Al(NO$_3$)$_3$.9H$_2$O (0.06 M) and NaOH (0.75 M) were mixed in N$_2$-purged deionized water and then were slowly added to the de-aerated anionic surfactants (0.135 M) aqueous solution while stirring. The obtained gels proceed with thermal aging (65 °C for 24 h), filtration, extraction and frozen drying. PEO/OLDH nanocomposite polymer electrolytes with various amounts of OLDH additives were formed by mixing of PEO (Mn = 6 × 10$^5$; Aldrich), OLDH and lithium percholate (LiClO$_4$; Aldrich) in anhydrous acetonitrile in a dry box, where PEO and LiClO$_4$ were dried previously in a vacuum oven at 60 °C for 3 days and OLDH dried at 200 °C for 30 min to remove the interlayer water. After continuous stirring at 70 °C for 24 h, the solution mixture was cast on the Teflon sheet maintained at 40 °C for 48 h under N$_2$ and a further drying in a vacuum oven at 60 °C for 24 h. The quantity of lithium salt added into the polymer electrolyte was calculated at a molar ratio of [ethylene oxide]/[Li$^+$] = 8 and termed as P(EO)$_n$LiClO$_4$ in this work.

X-ray diffraction data between 2θ and 40° 2θ were collected at 1°/min on a Shimadzu XRD6000 diffractometer equipped with nickel-filtered Cu Kα radiation operated at 40 kV and 30 mA. Thermal analysis was performed using a TA DSC 2910 differential scanning calorimeter. All specimens were heated to 100 °C and held for 10 min to remove the residual crystals and quenched with liquid nitrogen. The samples were then heated to 100 °C at a rate of 10 °C/min to measure the melting temperature and the crystallization enthalpy. Polarized optical microscopic analyses of the PEO crystal growth were performed by use of Axiolab polarized optical microscope equipped with a Mettler FP82 hot stage. Samples sandwiched between two glass slides were melted for 10 min at 100 °C then cooled to room temperature at a rate of 5 °C/min. The fractured surface of the PEO/OLDH nanocomposite was sputtered with gold and analyzed by scanning electron microscopy JEOl JSM-5600. Ionic conductivity was measured using the ac impedance techniques with a Solartron 1255B frequency response analyzer in the temperature range 10–90 °C, where nanocomposite electrolyte films were placed sandwiched between two polished stainless-steel blocking electrodes.

3. Results and discussion

X-ray diffraction data (XRD) for OLDH is shown in Fig. 1(a). There was only a weak broad diffraction pattern appeared at 2θ = 8.6° (d spacing = 10.3 Å), without any sharp and apparent diffraction peaks as compared to the (0 0 3) series of strong diffraction peaks of pristine LDH shown in Fig. 1(b). The absence of long-range order in c-direction of OLDH crystals as synthesized by template method is compared to the well ordered structure of oligo(ethylene oxide) sulfate or dicarboxylic acid intercalated LDHs by direct exchange reaction [19,20]. Subtracting the thickness of metal hydroxide (∼ 4.8 Å) [22], the intercalated oligo(ethylene oxide) accommodates the gallery region with a thickness of 5.5 Å. The hydrophilic chains of mono- or bi-hydroxy oligo(ethylene oxide) phosphonate interact strongly with metal hydroxide layers resulting into a
distorted conformation due to the steric hindrance of bulky PEO chains [19]. This renders the PEO oligomer chains adopting a disordered and liquid-like conformation confined between layered double hydroxides, which are similar with the results of PEO/MMT nanocomposites system [23]. Two strong diffraction peaks at 2\theta = 19.1^\circ and 23.2^\circ occurred for both pure PEO and PEO/OLDH nanocomposite in Fig. 1, are assigned as characteristic (1 2 0) and (1 1 2/0 0 4) reflections from the PEO crystallites. There are no apparent XRD peaks at 2\theta = 2\theta' = 10^\circ for PEO/OLDH nanocomposite as shown in Fig. 1(d), indicating that the d-spacing of intercalated layers is larger than 44 Å. According to the similar X-ray diffraction results of delaminated polyacrylate/LDH nanocomposites [24], an exfoliated morphology with almost complete dispersion of the LDH layers is purposed for the present PEO/OLDH nanocomposites system. Though the direct image evidence for LDH exfoliation by transmission electron micrograph is absent, the indirect evidence of much reduced size of crystallites due to the nucleating effect of exfoliated LDH layers is discussed as followed. The exfoliated morphology of PEO/OLDH nanocomposites can be attributed to the surface modification of LDH with oligo(ethylene oxide) phosphonate. The PEO oligomer modified LDH layers are compatible with PEO matrix that suppresses the strong attraction between metal hydroxides with high charge density.

To elucidate the effect of OLDH addition on thermal properties of PEO crystalline structure in nanocomposites, thermal analysis with DSC were performed. Fig. 2 shows the DSC heating scan of pure PEO and PEO/OLDH nanocomposites with various amounts of filler loading. The endothermic peak for pure PEO is located at 63.5 °C. The presence of OLDHs in nanocomposites increases the melting temperatures of PEO matrix by about 4 °C. It implies that the exfoliated dispersed OLDH sheets play a role as nucleate agent with strong heterogeneous nucleation effect on crystalline PEO.

In order to obtain more information relating to the PEO crystalline morphology in PEO/OLDH nanocomposites, polarized micrographs of the PEO crystallite formed from molten state are shown in Fig. 3. Microscopic imaging analysis reveals the degree of the OLDH dispersion or exfoliation in the PEO/OLDH nanocomposites. The positive Maltese cross pattern is evident in the spherulites of pure PEO as shown in Fig. 3(a). The average size of the crystalline domain appeared in the pure PEO is about 50 μm, meaning that the crystal growth of PEO proceeds without disturbance. The size of PEO spherulite decreases as the OLDH added into the PEO matrix by 1 wt.%. The Maltese cross pattern of PEO spherulite was disrupted, when the OLDH content increased to 3 wt.%. The displayed hedritic morphology of PEO crystallites shown in Fig. 3(c) indicates the structure of layered lamella. It grows from a central screw dislocation due to the restriction of spherulitic growth imposed by the exfoliation dispersed OLDH sheets [25]. For the content of OLDH in PEO matrix increasing above 5 wt.%, no apparent pattern of PEO crystallites is observed under polarized microscope. This can be attributed to the strong nucleating effect of nanoscale OLDH layers dispersion, which results in a too small spherulite to observe under our experimental condition. The average domain sizes are estimated about 25–50 nm for PEO/OLDH nanocomposites. The much smaller domain size existed in the PEO/OLDH nanocomposite is attributed to the confined size of crystallite imposed by oligomeric PEO phosphonate during synthesis. It is consistent with the result of polystyren sulfonate (PSS)/LDH system, where the LDH particle size is about 20–25 nm due to the nucleation promotion by PSS [22]. The SEM image of PEO/OLDH nanocomposite with 10 wt.% of filler loading is shown in Fig. 4. The platelet-like morphology resulted from lamellar arrangement of LDH sheets is clearly observed. It also indicates that the effective exfoliation of LDH layers exists in the PEO/OLDH nanocomposites.
As lithium salt added into the PEO matrix, crystalline polymer–salt complex structures and dissolved amorphous phase were eutectically formed. X-ray diffraction patterns of P(EO)\textsubscript{8}LiClO\textsubscript{4} and P(EO)\textsubscript{8}LiClO\textsubscript{4}/OLDH nanocomposites with various amount of filler loading are shown in Fig. 5. For polymer electrolyte P(EO)\textsubscript{8}LiClO\textsubscript{4}, two diffraction peaks at...
$2\theta = 15.2^\circ$ and $22.6^\circ$ are distinct from those of pure PEO. These two new diffraction peaks are attributed to the formation of crystalline PEO–salt complex with a composition of PEO$_8$LiClO$_4$ [26]. The dominant amount of amorphous PEO phase and a trace amount of crystalline PEO phase formed in the PEO$_8$LiClO$_4$ also can be seen in Fig. 5(a). However, the addition of OLDHs inhibit the formation of crystalline complex in the PEO$_8$LiClO$_4$/OLDH nanocomposites system. There are only amorphous halo pattern appeared near $2\theta = 20^\circ$ for PEO$_8$LiClO$_4$/OLDH nanocomposites as shown in Fig. 5(b–f). The different morphology of PEO$_8$LiClO$_4$/OLDH nanocomposites affecting the ionic conductivities of polymer electrolytes is elucidated as below.

Fig. 6 shows the temperature dependence of ionic conductivities of PEO$_8$LiClO$_4$ and PEO$_8$LiClO$_4$/OLDH nanocomposites electrolytes. The pure PEO$_8$LiClO$_4$ polymer electrolyte shows a conductivity of $1.0 \times 10^{-8}$ S/cm at 20 °C and exhibits an Arrhenius-type of temperature dependence below 50 °C. As the temperature reaching above $T_m$ ($\sim 60$ °C) of PEO, a discontinuity transition of conductivity by one-order of magnitude is observed. The observed conductivity transition around $T_m$ of PEO can be attributed to the precipitate crystalline phase by aging effect. Before the ionic conductivity measurement, the cast film of polymer electrolyte was placed in the dry box at room temperature for about one week. During this long time period, the flexible polyether chains of PEO with a $T_g$ of $-14$ °C tend to crystallize [13]. After heating scan, the temperature dependence of conductivity for PEO$_8$LiClO$_4$ under the immediately cooling cycle exhibits a conductivity enhancement. This conductivity hysteresis can be attributed to the non-equilibration of intracrystalline amorphous phase [27]. For PEO$_8$LiClO$_4$/OLDH nanocomposites electrolytes, the ionic conductivity at 20 °C increases as increasing OLDH content till 10 wt.% and level off to 20 wt.%. The maximum conductivity for PEO$_8$LiClO$_4$/OLDH nanocomposites system occurs in 10 wt.% of OLDH loading with a value of $1.6 \times 10^{-5}$ S/cm, which is larger than the one of pure PEO electrolyte by three orders of magnitude. The temperature dependence of conductivities under cooling scan for PEO$_8$LiClO$_4$/OLDH nanocomposites are the same for the heating cycles. No conductivity hysteresis appeared along with the Vogel–Tamman–Fulcher (VTF) type of conductivity dependence indicates that a completely amorphous phase is formed by the OLDH addition. This stable amorphous morphology is consistent with the size reduction of PEO crystallites in PEO/OLDH nanocomposite. The plenty amount of intercrystalline phase form an amorphous PEO-salt solution after the Li salt addition. For PEO$_8$LiClO$_4$/OLDH nanocomposite electrolytes, the higher conductivity and the VTF-type dependence of conductivity can be preserved even for one month. This long time stability of the ionic conductivity can be attributed to the stable amorphous morphology [28]. The PEO can not crystallize in nanocomposite electrolyte resulted from the nanoscale confinement effect of the exfoliated LDH layers dispersing in the PEO matrix.

Upon addition of OLDH into PEO matrix, the nanoscale exfoliated OLDH layers inhibit the crystal growth of PEO and result in the formation of tiny crystallites. The crystalline domain size existed in the PEO/OLDH nanocomposite was estimated as about 25–50 nm. As a result, there exists a plenty amount of intercrystalline grain boundary within PEO/OLDH nanocomposites. When LiClO$_4$ was added into PEO/OLDH nanocomposites to form polymer electrolytes, lithium salt was almost dissolved in the intercrystalline amorphous phase and reached to a thermodynamic equilibrium. The ease transport of Li$^+$ along this amorphous phase is attribute to the high conductivities at ambient temperature for PEO$_8$LiClO$_4$/OLDH nanocomposite electrolytes.

4. Conclusion

The layered inorganic materials with positive charged surface of LDHs are prepared by anionic oligo(ethylene oxide) template synthesis. It can serve as nanoscale fillers in PEO/OLDH nanocomposite electrolytes to avoid the trapping effect of anionic silicates used in PEO/MMT nanocomposite. An exfoliated morphology of PEO/OLDH nanocomposite occurs due to the compatible interaction between the modified surface of LDH layers and PEO matrix. The nanoscale dispersed OLDH sheets exhibit strong heterogeneous nucleation effect that inhibits the crystal growth of PEO crystallites and results in the formation of plenty amount of intercrystalline grain boundary within the PEO/OLDH nanocomposites. The enhanced conductivity along with a VTF-type dependence of conductivity for PEO/OLDH nanocomposite system is attributed to the ease transport of Li$^+$ along intercrystalline amorphous phase.
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References