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Nanoparticle-dispersed PEO polymer electrolytes for Li batteries

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Abstract

Nanoparticle-dispersed polymer electrolytes have been prepared by stirring or high-energy ball milling of polyethylene oxide (PEO), lithium salt ($LiCF_3SO_3$, $LiClO_4$ and $LiPF_6$), and nanometer-size ceramic powder (TiO_2, SiO_2 and Al_2O_3). The smaller the size of ceramic particles, the better they influence the crystallization kinetics of the PEO polymer chains. High-energy ball milling lowers the glass transition temperature of the composite polymers, and thus increases the ionic conductivity greater than the order of the magnitude compared with the un-milled samples. The highest ionic conductivity was reported when using $LiPF_6$ as added lithium salt and Al_2O_3 as dispersed particle. Cyclic voltametric measurements showed that the PEO-system is electrochemically stable in the range of 2–5 V.
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Keywords: PEO-based polymer electrolyte; Ionic conductivity; Nanoparticles; High-energy ball milling; Amorphous phases

1. Introduction

The development of novel solid-state lithium-ion conducting materials are strongly needed for many kinds of electrochemical applications such as separators in high-energy density lithium batteries, because of their high safety and reliability [1]. Among the polymeric materials reported, polyethylene oxide (PEO)-based polymer electrolytes are the most commonly studied [2–5]. However, the ionic conductivity of PEO–lithium salt (LiX) electrolytes only reaches practically useful values at high temperatures. The ionic conductivity decay at low temperatures is closely related to the transition from its amorphous state to its crystalline phases of PEO–LiX electrolytes. Consistent research efforts have been devoted to increase the conductivity and to lower the operation temperatures of the PEO–LiX polymer electrolytes to near ambient temperature. The addition of liquid solvents is one of the approaches. However, this promotes deterioration of the mechanical properties of the electrolyte and increases its reactivity toward the lithium metal anode. It is difficult to combine good conductivity and mechanical properties over a wide temperature range. Recently, it has been reported that the addition of ceramic nanoparticles such as TiO_2, $LiAlO_2$ or SiO_2 to PEO–LiX or PEO-like polymers induces consistent improvement in the transport properties as well as the mechanical strength

[6–11]. Nanoparticles are believed to kinetically inhibit crystallization from the amorphous state. However, the ceramic-dispersed PEO–LiX composite electrolytes exhibit still an insufficient ionic conductivity at room temperature with implications for the general requirement of practical electrochemical devices.

In the present work, we have examined several parameters influencing the electrochemical properties of the nanophase-dispersed PEO–LiX polymer electrolytes: the nature and content of lithium salt ($LiCF_3SO_3$, $LiClO_4$ and $LiPF_6$), the nature of nanoparticles (TiO_2, SiO_2 and Al_2O_3), the size of nanoparticle, etc. In particular, we have examined the effect of high-energy ball milling on the retention of the amorphous state in the nanophase-dispersed PEO–LiX composite electrolytes. Recently, high-energy ball milling (or mechanical alloying) method has been effectively used for non-equilibrium processing, similar to rapid quenching, in metallic or ceramic materials. In this processing, high mechanical energy input by ball milling can induce various metastable phases such as amorphous phases, reducing crystallinity of materials, even at room temperature.

2. Experimental procedures

The starting materials were high molecular weight (mol wt. = 400,000) PEO, ceramic powders with its particle sizes <20 nm, lithium salts ($LiCF_3SO_3$, $LiClO_4$ and $LiPF_6$) and anhydrous acetonitrile (ACN) of <50 ppm of moisture.

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Ultra dry lithium salts were obtained from Merck company and used in the as-received condition. Each bottle of these anhydrous salts was opened in a glove box under an argon atmosphere just before using. The lithium metal was in the form of a ribbon of 0.5 mm thickness, and was scraped to a metallic luster in the glove box just before sample preparation. The ceramic fillers, molecular sieves and PEO were dried over phosphorous pentoxide (P_2O_5) in vacuum for 48 h at 150, 200 and 50 °C, respectively. Thin films (~150 μm) of polymer electrolyte were prepared as follows. The mixture containing 20–25 g of acetonitrile, 1–2 g PEO and appropriate weighted quantities of lithium salts and ceramic nanopowders, were introduced into a beaker and stirred for 24 h using rotating magnetic bars. The ratio between the PEO and $LiPF_6$ varied from 5 to 20%. The homogeneous slurry was then transferred into a sealed container and was ultrasonically agitated for 5 min at 20,000 Hz. This procedure was to avoid both agglomeration of TiO_2 particles and to remove gas bubbles present in the solution, which could significantly affect the casting process. The slurry was also high-energy ball-milled using a Fritsch planetary mill. A ball to powder weight was 100:1. Both the milling ball and the vial are made of hardened stainless steel (SS). The high-energy milling was carried out in an Ar atmosphere. The mixed or the ball-milled slurry was immediately cast onto fine polished stainless steel sheets, and introduced into a vacuum container. Then, the acetonitrile was slowly evaporated under vacuum. All electrolytes obtained in this manner were stored in a glove box for 24 h before using.

Electrochemical experiments were carried out by utilizing an EG&G Model 6310 Electrochemical Impedance Analyzer. Model 398 Electrochemical Impedance software was used to control the computer for conductivity and stability measurements. The ac impedance was measured with a 10 mV ac signal over a frequency range of 100–0.1 Hz. Disc samples of electrolytes were sandwiched between two equivalent metallic lithium (Li) or stainless steel electrodes. The universal 'three-electrode' cell design was used in cyclic voltametry measurements, which allows the introduction of a lithium reference electrode on the electrolyte film. All samples for the electrochemical measurements were prepared and tested under an argon atmosphere.

3. Results and discussion

Fig. 1 shows the relationship between ion conductivity and Li salt concentrations for PEO–$LiPF_6$–TiO_2 electrolytes. The electrolytes with 8–20% TiO_2 showed a conductivity of the order of 10^{-5} S cm^{-1} at room temperature, while the PEO-system without TiO_2 showed a conductivity of below 10^{-6} S cm^{-1}. Conductivity of TiO_2-free sample increases as a function of salt concentration very slowly at first, and exhibits a sharp increase at about 12 wt.% $LiPF_6$, followed by a sharp decline, while conductivity for electrolytes with 10 wt.% TiO_2 shows a steady increase and
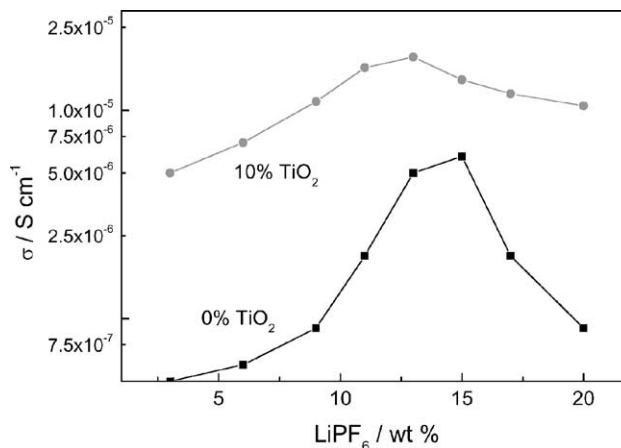

Fig. 1. Ionic conductivity of PEO–$LiPF_6$–TiO_2 electrolytes as a function of lithium salt content (at 25 °C).

decrease. The possible reason may be because TiO_2 particles enables plasticising liquid to be loaded into the polymer electrolyte film by absorption. Both samples showed maximum conductivity in the range of 10–15 wt.% $LiPF_6$. The maximum conductivity at specific ratios of PEO–LiX can be explained by the alteration of the carrier density and segmental motion [12]. The ionic conductivity increases with increasing lithium salt concentration due to the increase in the carrier density. However, the formation of ion-pairs becomes more serious in the case of high salt concentration than in the case of low concentration, leading to a drop in the ionic conductivity.

The content and particle size of ceramic dispersoids also played an important role in conductivity. Fig. 2 shows the ionic conductivities of PEO–$LiClO_4$–Al_2O_3 electrolytes. The PEO electrolyte with Al_2O_3 exhibits a maximum conductivity at ~10 wt.% Al_2O_3. Beyond the maximum, an addition of the Al_2O_3 powder decreases the ionic conductivity, probably due to the restriction of the ionic motion. It is also obvious that Al_2O_3 with a nanometer-size particles

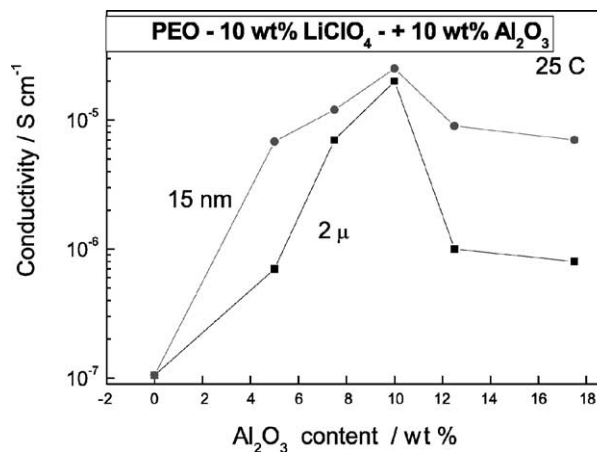Fig. 2. Ionic conductivities of PEO–$LiClO_4$ (10 wt.%)–Al_2O_3 (10 wt.%) electrolytes as a function of Al_2O_3 content.
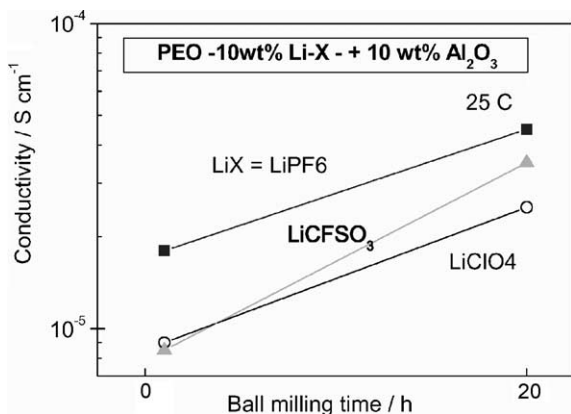
Fig. 3. The effect of high-energy ball milling on room temperature ionic conductivity for various PEO–LiX (10 wt.%)–ceramic nanocomposite electrolytes.

(∼15 nm) exhibited a higher conductivity than that with micrometer particles. The particle size may influence the re-crystallization kinetics of the PEO polymer chains, promoting localized amorphous regions and thus enhancement of Li^+ ion transport. Recent X-ray and Raman spectroscopy results [13] have shown the effect of fine ceramic particles in influencing ion aggregation in amorphous polyether electrolytes by promoting ceramic–salt interactions.

Fig. 3 shows the effect of high-energy ball milling on room temperature ionic conductivity for various PEO–LiX–ceramic nanocomposite electrolytes. It is obvious for all examined PEO–LiX–ceramic nanocomposite electrolytes that ionic conductivity increased markedly by high-energy ball milling. Fig. 4 compares, the time evolution of conductivity at room temperature for PEO–LiPF6-based polymer electrolytes with and without ceramic filler. As shown in Fig. 1, the presence of ceramic nanoparticles induces an

enhancement of the conductivity of greater than one order of magnitude, and this enhancement remains almost unchanged for the entire duration of the test (Fig. 4). For electrolytes based on the PEO–LiPF6 complex, the conductivity quickly decays with time, and the initial value is one order of magnitude lower than that of the ceramic-added polymer electrolyte sample, which stabilizes at a high value after a long period. Besides influencing the re-crystallization kinetics of PEO polymer chains, Scrosati et al. [14] suggested the occurrence of specific interactions between the added ceramic and the polymeric electrolyte, such as to induce structure modification of the polymer chains in the proximity of the filler's surface. We have also examined the optimum combination of lithium salt ($LiCF_3SO_3$, $LiClO_4$ and $LiPF_6$) and ceramic dispersoid (TiO_2, SiO_2 and Al_2O_3) for room temperature conductivity in PEO-based composite electrolytes. The best results were obtained for the PEO–$LiPF_6$–Al_2O_3 system. However, no prominent difference was observed.

The enhanced conductivity is evidently related to the loss of crystallinity induced by high-energy ball milling. Fig. 5 shows the result of X-ray diffraction of various PEO-based composite electrolyte film. The crystalline peaks of the composite electrolytes broaden and their intensity becomes weaker as the time of the ball milling increases. This indicates that the ball-milled electrolyte films contain a partly amorphous phase even at room temperature. Scanning microscopy morphology of PEO–$LiCF_3SO_3$–Al_2O_3 electrolytes shows that the size of crystalline spherulitic texture is reduced by ball milling (Fig. 6). Also, the straight texture boundaries inside individual spherulitics are much less distinct for the ball-milled electrolyte than for un-milled sample. This indicates that the chains of the polymers were broken by mechanical milling, inducing more favorable formation of amorphous phases. Also, for all PEO–LiX–
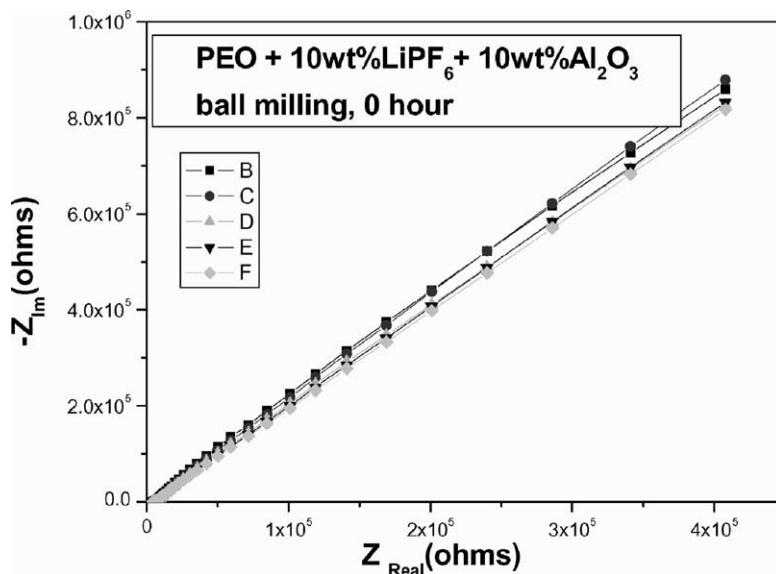

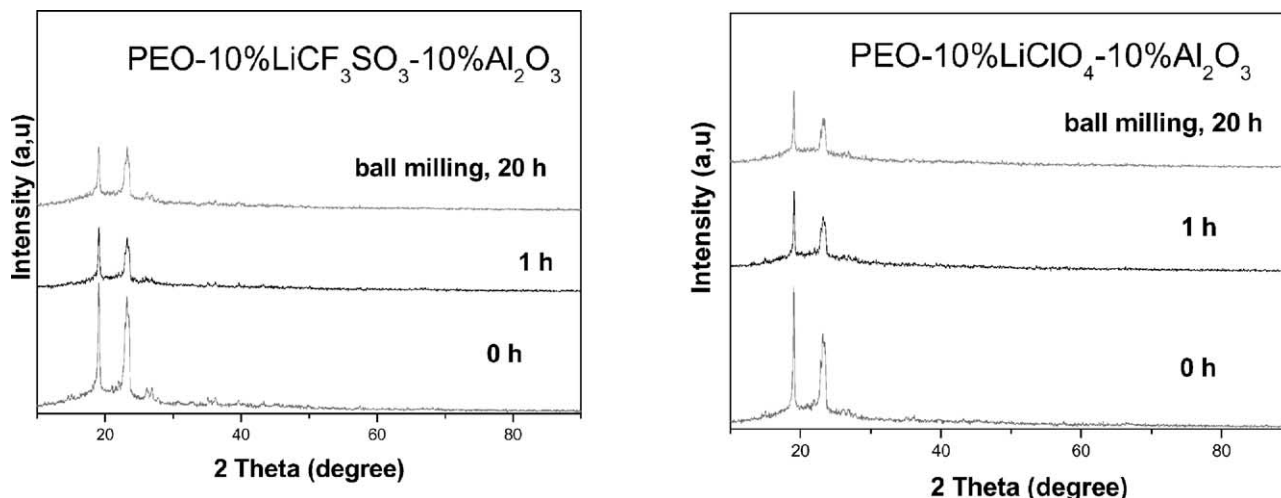Fig. 4. Time evolution of room temperature conductivity for PEO–LiPF6 (10 wt.%)-based polymer electrolytes.

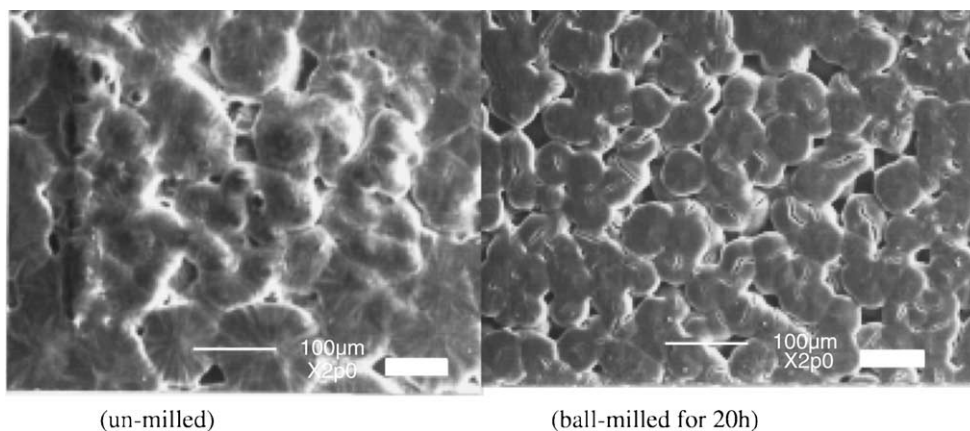Fig. 5. X-ray diffraction of various PEO-based composite electrolyte films.

(un-milled)   (ball-milled for 20h)

Fig. 6. SEM morphology of various PEO–LiCF$_3$SO$_3$ (10 wt.%)–Al$_2$O$_3$ (10 wt.%) composite electrolyte films: (a) before and (b) after ball milling.

ceramic composite electrolyte samples, the glass transition temperature (T_g) was decreased by ball milling (Fig. 7). The sample weight for the thermal analysis was the same for all samples.

Cyclic voltammograms for a Li/electrolyte/SS cell at a scan rate of 10 mV s^{-1} at room temperature showed that the electrolyte appears stable in the potential regime between 2 and 5 V versus Li, with little or no leakage current. However,
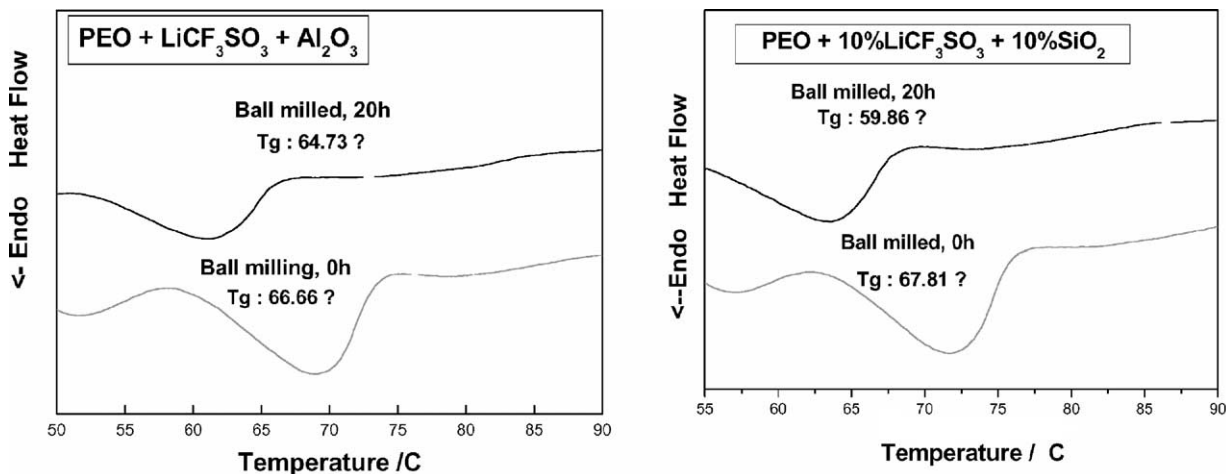

Fig. 7. DSC curves of PEO–LiX (10 wt.%)–nanoceramic (10 wt.%)-based composite electrolyte films.

a cathodic peak is observed at about −0.575 V, which correspond to the plating of lithium on to the SS electrode. On the reverse scan, stripping of lithium is observed at about 0.7 V. The voltammograms ascribed to lithium deposition/dissolution are highly reversible, because the peak currents remain fairly constant with repeated cycling. On sweeping the electrode to 5 V, there are no additional peaks related to the decomposition of the electrolyte, which means that the PEO-system is electrochemically stable up to 5 V versus Li.

4. Conclusions

PEO–LiX (X = CF_3SO_3, ClO_4 and PF_6)-nanodispersed (TiO_2, SiO_2 and Al_2O_3) composite polymer electrolytes have been synthesized and examined. The smaller the size of ceramic particles, the higher ionic conductivity was obtained, influencing crystallization kinetics of the PEO polymers. High-energy ball milling also increase ionic conductivity greater than the order of magnitude compared with un-milled samples by lowering the glass transition temperature of the composite polymers. The highest ionic conductivity was reported when using $LiPF_6$ as added lithium salt and Al_2O_3 as dispersed particles. Cyclic volta-metric measurements shows that the PEO-system is electro-chemically stable in the range of 2–5 V.

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