

Investigations on the enhancement mechanism of inorganic filler on ionic conductivity of PEO-based composite polymer electrolyte: The case of molecular sieves

Jingyu Xi*, Xiaozhen Tang*

School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, Shanghai 200240, China

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Abstract

Polarized optical microscopy (POM) and differential scanning calorimeter (DSC) techniques are used to study the effect of ZSM-5 molecular sieves on the crystallization mechanism of poly(ethylene oxide) (PEO) in composite polymer electrolyte. POM results show that ZSM-5 has great influence on both the nucleation stage and the growth stage of PEO spherulites. ZSM-5 particles can act as the nucleus of PEO spherulites and thus increase the amount of PEO spherulites. POM and DSC results show that ZSM-5 can restrain the recrystallization tendency of PEO chains through Lewis acid–base interactions and hence decrease the growth speed of PEO spherulites. Room temperature ionic conductivity of PEO–LiClO₄-based polymer electrolyte can be enhanced by more than two magnitudes during long time storage with the addition of ZSM-5.

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1. Introduction

All solid-state lithium polymer batteries are one of the best choices for the future electrochemical power source, characterized by high energy densities, good cyclability, and safety [1,2]. Owing to its potential capability to replace the traditional liquid electrolytes of rechargeable lithium ion batteries, PEO–LiX (X = ClO₄[−], BF₄[−], PF₆[−], CF₃SO₃[−], etc.)-based solid polymer electrolytes (SPEs) have received extensive attentions [1–3], since Wright and co-workers found that the complex of PEO and alkaline salts had ionic conductivity in 1973 [4]. Although PEO-based polymer electrolytes have been studied for more than 30 years, there still exist two opposite opinions on the mechanism of the transporting of Li⁺ in PEO matrix.

Some researchers support the viewpoint that in PEO–LiX system, crystalline PEO is beneficial for the transporting of Li⁺. PEO can form double helix structure through the coordination

interactions between the ether O of PEO and Li⁺ and then Li⁺ can transport in this helix channel through the jump between adjacent coordinate sites [5]. Although Bruce and co-workers have proved that ionic conductivity of the single crystalline PEO₆:LiXF₆ (X = P, As, Sb) is much higher than those incomplete crystallization systems [5], this method is inconvenient for the large-scale manufacture and process of PEO-based polymer electrolytes. General concepts of the transporting of Li⁺ in PEO-based polymer electrolytes are coupled with the local relaxation and segmental motion of PEO chains, of which condition can only be obtained when PEO is in its amorphous state [6–8]. Unfortunately, due to the particular structure, PEO often shows much higher crystalline ratios at room temperature, resulting in a very low room temperature ionic conductivity ($\sim 10^{-7}$ S cm^{−1}) of PEO-based polymer electrolytes, which is a drawback for its applications in the consumer electronic market such as cell phone and notebook PC [6]. When the third component, i.e., inorganic fillers, was doped into PEO-based polymer electrolytes to form the composite polymer electrolytes (CPEs), ionic conductivity could be improved obviously [6–11]. Inorganic fillers help to increase the conductivity of CPEs by lowering the reorganize tendency of PEO through Lewis acid–base

* Corresponding authors. Tel.: +86 21 54747142; fax: +86 21 54743264.

E-mail addresses: xijingyu@gmail.com (J. Xi), xtang@sjtu.edu.cn (X. Tang).

interactions between ether O of PEO (Lewis base) and Lewis acid sites on the surface of inorganic fillers [6]. XRD, DSC, and FT-IR methods have been widely used to study the crystallization of PEO [6–11], however, it is hard to obtain the information about how inorganic fillers affect the crystallization of PEO only through these techniques.

ZSM-5 molecular sieves have been used successfully in a great deal of catalysis fields, due to its high surface area and strong Lewis acidity [12,13]. In previous work [14–16], we have found that ZSM-5 can obviously enhance ionic conductivity, Li transference number (t_{Li^+}), and other electrochemical properties of PEO-based polymer electrolyte. In order to elucidate the enhancement mechanisms of ZSM-5, the effect of ZSM-5 on the crystallization behavior of PEO are studied by polarized optical microscopy (POM) and differential scanning calorimeter (DSC) techniques and the experiment results are discussed in this communication.

2. Experimental

2.1. Preparation of composite polymer electrolytes

Poly(ethylene oxide) (PEO), $M_w = 1,000,000$ (Shanghai Liansheng Chem. Tech.) and $LiClO_4$, A.R. (Shanghai Second Regent Company) were vacuum dried for 24 h at 50 and 120 °C, respectively, before use. Acetonitrile, A.R. (Shanghai Chemical Regent Company), dehydrate by 4 Å molecular sieves before use. Li-ZSM-5 was obtained by ion exchange method from H-ZSM-5 (Si/Al = 25, obtained from Nankai University Catalyst Company) and denoted as ZSM-5. The preparation of composite polymer electrolytes involved first the dispersion of PEO and $LiClO_4$ in anhydrous acetonitrile, followed by the addition of filler. The resulting slurry was cast on to a Teflon plate, and then the plate was placed into a self-designed equipment, under the sweep of dry air with a flow rate of $10 L min^{-1}$, to let the solvent slowly evaporate. Finally, the result films were dried under vacuum at 50 °C for 24 h to get rid of the residue solvent. These procedures yielded translucent homogeneous self-supporting films of thickness ranging from 100 to 200 μm .

2.2. DSC analysis

Differential scanning calorimeter was carried out on Perkin-Elmer Pyris-1 analyzer at a heating rate of $10 ^\circ C min^{-1}$ from –60 to 100 °C in the heating scan. A flow of nitrogen gas was maintained over the perforated pan to avoid any contact with atmospheric moisture.

2.3. Polarized optical microscopy study

Polarized optical microscopy was performed using a LEICA-DMLP instrument equipped with a heating stage (Linkam Scientific Instruments Ltd. TMS 94). To study the isothermal crystallization of PEO, all samples were first annealed at 100 °C for 30 min and then quenched rapidly ($50 ^\circ C min^{-1}$) to the given temperature.

2.4. Ionic conductivity

Ionic conductivity of the composite polymer electrolytes was determined by electrochemical impedance spectroscopy (EIS). The electrolyte was sandwiched between two stainless steel (SS) blocking electrodes to form a symmetrical SS/electrolyte/SS cell. The cell was placed into a self-designed oven coupled with a temperature controller. For each temperature, at least 30 min were waited before the impedance response was recorded. The impedance tests were carried out in the 1 MHz–1 Hz frequency range using a Solartron 1260 Impedance/Gain-Phase Analyzer coupled with a Solartron 1287 Electrochemical Interface.

3. Results and discussion

Fig. 1 displays the typical room temperature POM images of different samples. For pristine $PEO_{10}-LiClO_4$ (Fig. 1a), only few spherulites with the size of 80–100 μm can be observed. PEO spherulites exhibit a typical compact spherulitic morphology and the cross-extinction pattern can be observed clearly. It is interesting to note that, with the addition of ZSM-5, the amount of PEO spherulites increases and the average radius of spherulites decreases to only about 20 μm (Fig. 1b).

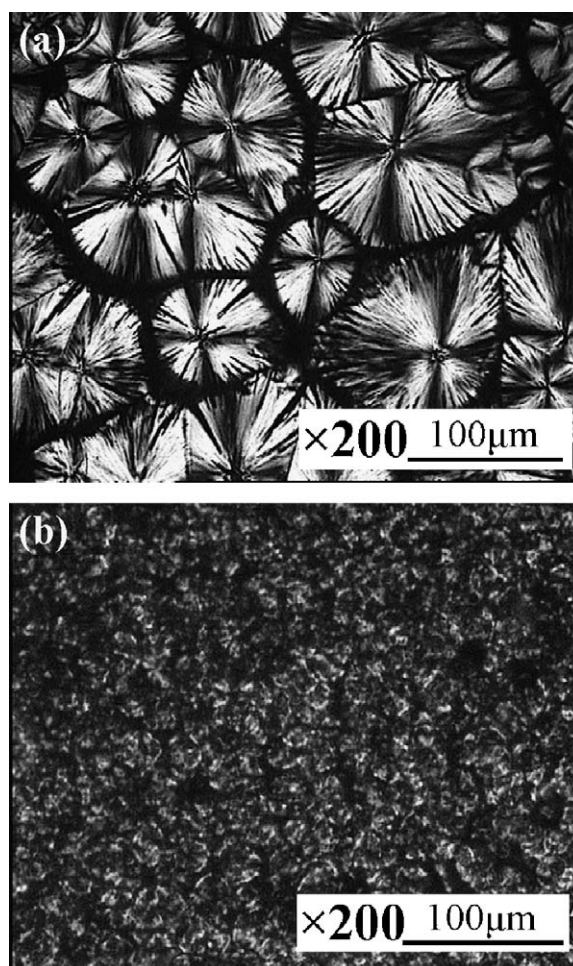


Fig. 1. Polarized optical microscopy (POM) images at 25 °C for: (a) $PEO_{10}-LiClO_4$ and (b) $PEO_{10}-LiClO_4/10\% ZSM-5$.

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