

# Effect of molecular sieves ZSM-5 on the crystallization behavior of PEO-based composite polymer electrolyte

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## Abstract

Polarized optical microscopy (POM) results show that ZSM-5 has great influence on both the nucleation stage and the growth stage of PEO spherulites. Part of ZSM-5 particles can act as the nucleus of PEO spherulites and thus increase the amount of PEO spherulites. On the other hand, ZSM-5 can restrain the recrystallization tendency of PEO chains through Lewis acid–base interaction and hence decrease the growth speed of PEO spherulites. The increasing amount of PEO spherulites, decreasing size of PEO spherulites and the incomplete crystallization are all beneficial for creating more continuous amorphous phases of PEO, which is very important for the transporting of  $\text{Li}^+$  ions. An adequate amount of ZSM-5 can enhance the room temperature ionic conductivity of PEO- $\text{LiClO}_4$  based polymer electrolyte for more than two magnitudes.

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**Keywords:** Composite polymer electrolyte; PEO; ZSM-5; Spherulites; Ionic conductivity

## 1. Introduction

All solid-state lithium polymer batteries may be one of the best choices for the future electrochemical power source, characterized by high energy densities, good cyclability, reliability and safety [1,2]. Owing to its potential capability to replace the traditional liquid electrolytes of rechargeable lithium ion batteries, PEO- $\text{LiX}$  ( $X = \text{ClO}_4^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{CF}_3\text{SO}_3^-$ ,  $\text{N}(\text{CF}_3\text{SO}_2)_2^-$ , etc.) based polymer electrolytes has received extensive attentions [3–5], since Wright et al. found that the complex of PEO and alkaline salts had ionic conductivity in 1973 [6].

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  $\text{Li}^+$  in PEO matrix. Some researchers support the viewpoint that in PEO- $\text{LiX}$  system, crystalline PEO is beneficial for the transporting of  $\text{Li}^+$ . PEO can form double helix structure through the coordination interactions between the ether O of PEO and  $\text{Li}^+$  and then  $\text{Li}^+$  can transport in this helix channel through the jump between adjacent coordinate sites [7–9]. Although Bruce et al. have proved that ionic con-

ductivity of the single crystalline  $\text{PEO}_6:\text{LiXF}_6$  ( $X = \text{P}, \text{As}, \text{Sb}$ ) is much higher than those incomplete crystallization systems [7,8], this method is inconvenient for the large-scale manufacture and process of PEO-based polymer electrolytes. General concepts of the transporting of  $\text{Li}^+$  in PEO-based polymer electrolytes are coupled with the local relaxation and segmental motion of PEO chains, of which the conditions can only be obtained when PEO is in its amorphous state [10–14]. 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 ( $\sim 10^{-7} \text{ S cm}^{-1}$ ) of PEO-based polymer electrolytes, which is a drawback for its applications in the consumer electronic market such as cell phone and notebook PC [10].

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 [15–17]. Inorganic fillers help to increase the conductivity of CPEs by lowering the reorganize tendency of PEO through Lewis acid–base interactions between ether O of PEO (Lewis base) and Lewis acid sites on the surface of inorganic fillers [10]. XRD, DSC and FT-IR techniques have been widely used to study the crystallization of PEO [10–17]; however, it is hard to obtain the information about how inor-

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ganic fillers affect the crystallization of PEO only through these techniques.

ZSM-5 molecular sieves have been used in a great deal of catalysis fields, due to its high surface area, special channel structures and strong Lewis acidity [18–20]. In previous work [21–23], we have found that ZSM-5 can obviously enhance ionic conductivity, lithium ion transference numbers 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 of PEO are studied by polarized optical microscopy (POM) technique and the experiment results are discussed in this paper.

## 2. Experimental

### 2.1. Materials

Poly(ethylene oxide), PEO,  $M_w = 1,000,000$  (Shanghai Lian-sheng Chem. Tech.) and  $\text{LiClO}_4$ , 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 4A molecular sieves before use.  $\text{Al}_2\text{O}_3$  (60 nm, Zhoushan Nano Co. Ltd., China) was vacuum-dried for 24 h at 200 °C prior to 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 [22].

### 2.2. Preparation of composite polymer electrolytes

The preparation of composite polymer electrolytes involved first the dispersion of PEO and  $\text{LiClO}_4$  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  $10 \text{ L min}^{-1}$ , 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  $\mu\text{m}$ . The composite polymer electrolytes used in this study were denoted as  $\text{PEO}_{10}\text{-LiClO}_4/x\%$  filler, in which the EO/Li ratio was fixed at 10 and the content of filler,  $x$ , ranged from 0 to 30 wt.% of the PEO weight.

### 2.3. XRD measurement

X-ray diffraction (XRD) patterns were recorded by using a Bruker D8 Advance instrument equipped with  $\text{Cu K}\alpha$  radiation performed at 40 kV and 40 mA. A scan rate of  $4.0^\circ \text{ min}^{-1}$  over the range of  $10\text{--}60^\circ$  ( $2\theta$ ) were used for detecting the characteristic diffraction peak of crystalline PEO.

### 2.4. DSC analysis

Differential scanning calorimeter (DSC) was carried out on Perkin-Elmer Pyris-1 analyzer at a heating rate of  $10^\circ \text{ C min}^{-1}$  from  $-60$  to  $100^\circ \text{ C}$  in the heating scan. A flow of nitrogen gas

was maintained over the perforated pan to avoid any contact with atmospheric moisture.

### 2.5. Polarized optical microscopy study

Polarized optical microscopy (POM) was performed using a LEICA-DMLP instrument equipped with a heating stage (Linkam Scientific Instruments Ltd. TMS 94). To test the melting temperature range of PEO spherulites, the sample was heated from room temperature at  $5^\circ \text{ C min}^{-1}$ . To study the isothermal crystallization of PEO, all samples were first annealed at  $100^\circ \text{ C}$  for 30 min and then quenched rapidly ( $50^\circ \text{ C min}^{-1}$ ) to the given temperature.

### 2.6. 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 to 1 Hz frequency range using a Solartron 1260 Impedance/Gain-Phase Analyzer coupled with a Solartron 1287 Electrochemical Interface.

## 3. Results and discussion

Polarized optical microscopy (POM) is one of the most effective techniques to study the crystallization of PEO and other polymers [24–26]. Fig. 1 displays room temperature POM images of different samples. For pure PEO (Fig. 1(a)), only few spherulites with the size of  $100\text{--}200 \mu\text{m}$  can be observed. PEO spherulites exhibit a typical compact spherulitic morphology and the cross-extinction pattern can be observed clearly. The boundaries of these spherulites are smooth after impingement with adjacent spherulites. After the addition of  $\text{LiClO}_4$ , the amount of spherulites increases and the size of spherulites decreases to about  $40\text{--}50 \mu\text{m}$  (Fig. 1(b)). Although the cross-extinction pattern can be observed clearly in  $\text{PEO}_{10}\text{-LiClO}_4$  complex, some dark area can also be observed simultaneously, which corresponds to the amorphous PEO. It is interesting to note that, with the addition of  $\text{Al}_2\text{O}_3$  and ZSM-5, the amount of PEO spherulites increases further and the average radius of spherulites decreases to only about  $20 \mu\text{m}$ , as shown in Fig. 1(c) and (d), respectively. The cross-extinction pattern of PEO spherulites cannot be observed clearly in  $\text{PEO}_{10}\text{-LiClO}_4/10\%\text{Al}_2\text{O}_3$  and  $\text{PEO}_{10}\text{-LiClO}_4/10\%\text{ZSM-5}$  because PEO chains are hard to form full spherulites due to the existence of inorganic fillers. The dark area in  $\text{PEO}_{10}\text{-LiClO}_4/10\%\text{Al}_2\text{O}_3$  and  $\text{PEO}_{10}\text{-LiClO}_4/10\%\text{ZSM-5}$  are larger than that in  $\text{PEO}_{10}\text{-LiClO}_4$ , suggesting that the ratio of amorphous PEO in composite polymer electrolytes is higher than that in  $\text{PEO}_{10}\text{-LiClO}_4$ .

Fig. 2(a) shows wide angle X-ray diffraction patterns of PEO,  $\text{PEO}_{10}\text{-LiClO}_4$ ,  $\text{PEO}_{10}\text{-LiClO}_4/10\%\text{Al}_2\text{O}_3$ , and  $\text{PEO}_{10}\text{-LiClO}_4/10\%\text{ZSM-5}$ . It is obviously that the characteristic

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