

Nanocomposite polymer electrolyte comprising PEO/LiClO₄ and solid super acid: effect of sulphated-zirconia on the crystallization kinetics of PEO

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Abstract

A novel PEO-based nanocomposite polymer electrolyte is prepared by using solid super acid sulphated-zirconia (SO₄²⁻ – ZrO₂, SZ) as the filler. Polarized optical microscopy (POM) and differential scanning calorimeter (DSC) results show that part of SZ particles may act as the nucleus of PEO spherulites and thus increase the amount of PEO spherulites. On the other hand, other SZ particles, which do not act as the nucleus, can restrain the recrystallization tendency of PEO chains through Lewis acid–base interaction and hence decrease the growth speed of PEO spherulites. As a result, the PEO component in PEO–LiClO₄–SZ can maintain a high amorphous state for a long time. The room temperature ionic conductivity of PEO–LiClO₄–SZ is relative high and stable compared with pristine PEO–LiClO₄, indicating that it is promising for all solid-state rechargeable lithium ion batteries.

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1. Introduction

PEO–LiX (X = ClO₄⁻, BF₄⁻, PF₆⁻ etc.) based solid polymer electrolytes (SPEs) have received extensive attentions [1–5], for their potential capability to replace traditional liquid electrolytes of rechargeable lithium ion batteries, since Wright et al. found that the complex of PEO and alkaline salts had the ability of ionic conductivity in 1973 [6]. Lithium polymer batteries (LPBs) may be one of the best choices for future electrochemical power source due to its high energy densities, good cyclability, reliability and safety [7,8].

General concepts of the transporting of Li⁺ in PEO-based polymer electrolytes are coupled with the local relaxation and segmental motion of PEO chains [1], of which the conditions can only be obtained when PEO is in its amorphous state. However, due to its particular structure, PEO often shows much higher crystalline ratios at sub-

ambient temperature region, and accordingly its ionic conductivity is lower than 10⁻⁷ S cm⁻¹ [1,2]. Development of PEO-based electrolytes capable of combining high ionic conductivity with superior interfacial stability towards the lithium metal anode, and good mechanical properties is the key issue for the R&D of all solid-state lithium polymer batteries [1,7]. When the third component, i.e. inorganic fillers, was introduced into the PEO-based electrolytes to form the composite polymer electrolytes (CPE), all the above performances could be improved [1,9–15].

In previous work [16], we have found that solid super acid sulphated-zirconia (SO₄²⁻ – ZrO₂, denoted as SZ), due to its strong acidity [17–20], can obviously enhance the ionic conductivity and other electrochemical properties of PEO–LiClO₄ based electrolyte. In order to elucidate the enhancement mechanisms of SZ, the crystallization kinetics of PEO in both pristine PEO–LiClO₄ and PEO–LiClO₄–SZ nanocomposite polymer electrolyte are studied by polarized optical microscopy (POM) together with differential scanning calorimeter (DSC) techniques, and the experiment results are discussed in this paper. In addition, the relation between the crystallinity of PEO and its ionic conductivity is also studied.

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2. Experimental

The zirconia support was prepared by hydrolysis of zirconium oxychloride with ammonia, as already described [16]. The white precipitate zirconium hydroxide was then dried at 383 K for 24 h. Sulphation of this hydrous zirconia was done by percolating 1 N H₂SO₄ solution through it. The sulphated zirconium hydroxide was then calcined in air at 923 K for 3 h to obtain the final SZ. SEM image shows that the particle of SZ has average diameter of about 60–70 nm [16].

The nanocomposite polymer electrolyte was prepared by dispersing SZ and LiClO₄ in anhydrous acetonitrile, followed by addition of the PEO and a thorough mixing of the obtained slurry. The slurry was then cast onto a Teflon plate to let the solvent evaporate slowly. Finally, the obtained films were dried under vacuum at 50 °C for 24 h to get rid of the residue solvent [16].

Polarized optical microscopy (POM) was performed using a LEICA-DMLP instrument equipped with a heating stage attached to a temperature controller. To study the recrystallization process of PEO, the sample was first annealed at 100 °C for 30 min and then quenched rapidly to a given temperature. The optical micrographs of recrystallized PEO spherulites were taken as a function of time after the initial appearance of spherulitic nucleus.

Differential scanning calorimeter (DSC) measurements were conducted on a Perkin–Elmer Pyris-1 analyzer. The measurements were carried out with a heating rate of 10 °C min^{−1} ranging 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.

Ionic conductivity of the nanocomposite polymer electrolyte films was determined by AC impedance spectroscopy. The electrolyte was sandwiched between two stainless steel (SS) blocking electrodes (with a diameter of 1 cm) 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 60 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

As has been found in previous work [16], SZ can obviously decrease the crystallinity of PEO, and hence improve the room temperature ionic conductivity of PEO–LiClO₄–SZ nanocomposite polymer electrolyte by more than two magnitudes. However, it is difficult to understand the effect of SZ on the crystallization kinetics of PEO only through the previous X-ray diffraction (XRD) and

differential scanning calorimeter (DSC) results. Polarized optical microscopy (POM) is one of the most effective techniques to study the crystallization of PEO and other polymers [21–23]. Fig. 1 displays typical room temperature POM images of pristine PEO₁₂–LiClO₄ and PEO₁₂–LiClO₄–7%SZ nanocomposite polymer electrolyte.

It is well known that pure PEO spherulites have a Maltese cross-extinction pattern and a very fine spherulitic texture [21,22]. For PEO₁₂–LiClO₄ case (Fig. 1(a)), PEO exhibit a typical compact spherulitic morphology and its cross-extinction pattern can be observed clearly. However, the boundaries of the spherulites are smooth after impingement with adjacent spherulites, in agreement with the result in other papers [21,22]. In addition, only few spherulites with an average radius of about 100–200 μm can be observed. It is interesting to note that, with the addition of SZ filler (Fig. 1(b)), the amount of PEO spherulites increase and the average radius of spherulites decrease to about 20–30 μm, which are both beneficial for decreasing the crystallinity of PEO, in other word, increasing the ratio of amorphous PEO, as shown in Fig. 2.

Thermal properties of PEO₁₂–LiClO₄ and PEO₁₂–LiClO₄–7%SZ obtained from DSC analysis are listed in Table 1. The relative percentage of crystalline PEO, X_c , can be calculated from the equation $X_c = \Delta H_m / \Delta H_m^*$, where ΔH_m^* is the melting enthalpy of a completely crystalline PEO sample [24]. It can be seen from Table 1 that both the melting temperature (T_m) and crystallinity (X_c) of PEO decrease obviously with the addition of SZ, which support the above model shown in Fig. 2. The glass transition temperature, T_g , of PEO also decreases with the addition of SZ. The decrease of T_g and X_c will increase the flexibility of the PEO chains and the ratio of amorphous PEO, respectively. Consequently, ionic conductivity should be enhanced at low temperature region [16]. In addition, compared with the continuous crystalline phase of PEO formed by the connections of adjacent large PEO spherulites in the case of PEO–LiClO₄ (Fig. 1(a) and left part of Fig. 2), there exist much more continuous amorphous phase of PEO in PEO–LiClO₄–SZ nanocomposite polymer electrolyte (Fig. 1(b) and right part of Fig. 2), which is very important for the transporting of Li⁺.

Table 1
Thermal properties of PEO₁₂–LiClO₄ and PEO₁₂–LiClO₄–7%SZ nanocomposite polymer electrolyte

Sample ^a	Glass point T_g (°C)	Melting point T_m (°C)	Melting enthalpy ΔH_m (J g ^{−1})	Crystallinity X_c^b (%)
PEO ₁₂ – LiClO ₄	−32.8	54.4	83.4	39.0
PEO ₁₂ – LiClO ₄ – 7%SZ	−45.7	48.5	40.4	18.9

^a All samples have the same thermal history like those samples used for room temperature POM analysis.

^b $X_c = (\Delta H_m / \Delta H_m^*) \times 100$, $\Delta H_m^* = 213.7$ (J g^{−1}).

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