

Preparation and Ionic Conductivity of Solid Polymer Electrolyte Based on Polyacrylonitrile-Polyethylene Oxide

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ABSTRACT: The transparent and flexible solid polymer electrolytes (SPEs) were fabricated from polyacrylonitrile-polyethylene oxide (PAN-PEO) copolymer which was synthesized by methacrylate-headed PEO macromonomer and acrylonitrile. The formation of copolymer is confirmed by Fourier-transform infrared spectroscopy (FTIR) measurements. The ionic conductivity was measured by alternating current (AC) impedance spectroscopy. Ionic conductivity of PAN-PEO-LiClO₄ complexes was investigated with various

salt concentration, temperatures and molecular weight of PEO (*M_n*). And the maximum ionic conductivity at room temperature was measured to be 3.54×10^{-4} S/cm with an [Li⁺]/[EO] mole ratio of about 0.1. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 461–464, 2006

Key words: solid polymer electrolyte; PEO; acrylonitrile; copolymer; ionic conductivity

INTRODUCTION

Increasing interest has been focused on solid polymer electrolytes (SPEs) of rechargeable lithium batteries, because of their high-energy density, safety, wide electrochemical stability windows, and the flexibility in both their shapes and production processes. Typical examples of polymers used as matrices for polymer electrolyte are polyethylene oxide (PEO),^{1,2} poly(methyl methacrylate) (PMMA),³ polyvinylidene fluoride (PVDF),⁴ and polyacrylonitrile (PAN).⁵ Among the first and most studied host for SPEs is poly(ethylene oxide) (PEO), because of its high-solvating power and complexing ability to a wide variety of salts. Recognizing that the ionic conductivity of PEO-based electrolytes is facilitated in the amorphous phase of PEO, many approaches have been adopted to reduce the crystallinity of PEO-based electrolytes and increase segmental mobility of the host polymer through copolymerizing^{6–8} and crosslinking.^{9–12} In addition, PAN-based polymer electrolytes provide good pro-

cessability, mechanical strength, and electrochemical stability. To prepare SPEs for practical applications, the high conductivity and the good physical properties, such as chemical stability and mechanical strength, have to be considered in the meantime regarding its structure. In this study, we synthesized a series of polyacrylonitrile-polyethylene oxide (PAN-PEO) copolymer containing PEO of different molecular weight, and investigated the influence of salt concentration, temperature, and molecular weight of PEO on the crystalline and electrochemical properties of SPE membranes.

EXPERIMENTAL

Toluene and dimethylformamide (DMF) were distilled over calcium hydride and P₂O₅ before use. Polyethylene oxide (PEO, *M_n* = 2000, 4000, 6000, and 10,000) was purchased from Shanghai Chemical Factory, and dehydrated in vacuum at 50°C for 24 h before use. Acrylonitrile (AN) was distilled in vacuum before use. 2,2-Azobisisobutironitrile (AIBN) was recrystallized by methanol. And, lithium perchlorate (LiClO₄) was used after drying at 120°C for 24 h under high vacuum.

IR measurement was carried out by BrukerV-Fourier in the range of 400–4000cm⁻¹. Film X-ray diffraction (XRD) measurement was carried out by Rigaku D/max-3B.

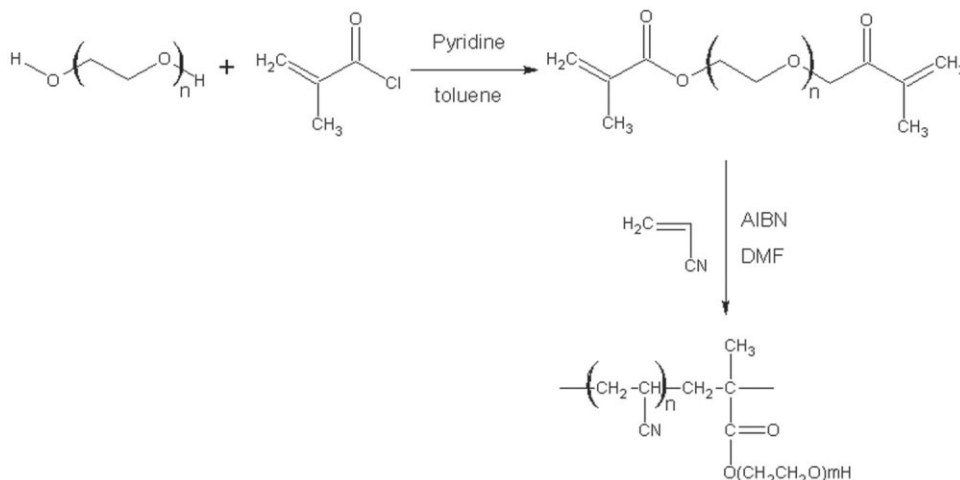
The ionic conductivity of the solid polymer electrolyte films was determined by ac impedance spectroscopy (Electrochemistry analyzer CHI660). Sample

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Scheme 1 Synthesis route of PAN-PEO copolymer.

films were sandwiched between two parallel stainless steel (SS) discs ($\Phi = 1.6$ cm). The frequency ranged from 100 kHz to 100 Hz at a perturbation voltage of 5 mV. The ionic conductivity was calculated from the bulk electrolyte resistance value (R_b) found in the complex impedance diagram according to eq. (1).

$$\sigma = \frac{l}{R_b S} \quad (1)$$

where l is the thickness of the polymer electrolyte film, and S is the surface area of the polymer electrolyte film.

Methacrylate-headed PEO macromonomer (MAPEO) was prepared by reaction of PEO with methacryloyl chloride in toluene solution containing pyridine.¹³ After filtration of pyridine salt, the macromonomer was precipitated out from petroleum ether, filtrated, and dried in vacuum oven at 30°C to give the MAPEO. A solution of MAPEO, AN, and AIBN in DMF was placed in a reactor equipped with a reflux condenser under N_2 flow.¹⁴ The initiator concentration was varied between 0.3 and 1.5 mol % of monomers. In all cases, the resulting solution was poured into a large excess of deionized water to yield the yellow precipitate, which was subsequently filtered, washed with ethanol, and dried in vacuum at 60°C to constant weight. The copolymers were then purified by extracting with deionized water as eluent for 72 h to remove thoroughly MAPEO and AN unreacted. The synthesis route is shown in Scheme 1.

Lithium salts were dissolved in the copolymers with various $[Li^+]/[EO]$ mole ratios of 0.67, 0.5, 0.1, 0.067, and 0.025, using DMF as a solvent. The electrolyte solutions were cast on the Teflon plate and dried in vacuum at 60°C for 48 h to form polymer electrolyte complex films.

RESULTS AND DISCUSSION

Preparation of PAN-PEO copolymer

Figure 1 shows the FTIR spectra of the PEO ($M_n = 10,000$)(A), MAPEO(B), and PAN-PEO(C). Compared with the FTIR spectrum of PEO, there are new absorption bands at 1729, 1640 cm^{-1} in the spectrum of MAPEO, which were ascribed to the stretching vibrations of the C=O and C=C groups, respectively. Comparing the FTIR spectrum of MAPEO with that of PAN-PEO, it is found that the spectrum of PAN-PEO shows sharp band at 2244 cm^{-1} , which was the stretching vibrations of the CN group. All the results suggest that the copolymer of PAN-PEO is indeed obtained.

Crystallization properties of SPE

Ionic mobility is attributed by chain flexibility in polymer matrix, and the increase of chain flexibility may

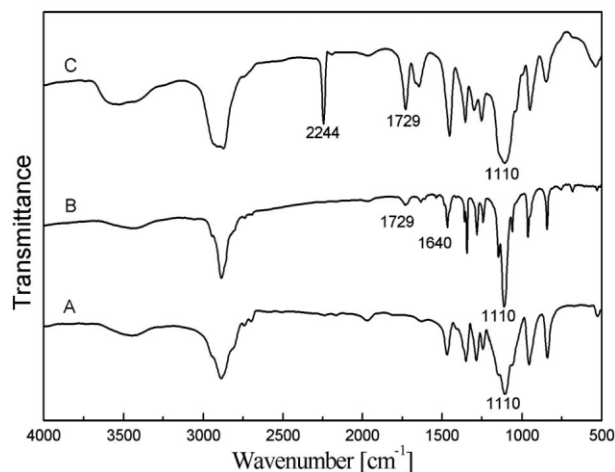


Figure 1 Infrared spectra of polymers: (A, PEO; B, MAPEO; C, PAN-PEO).

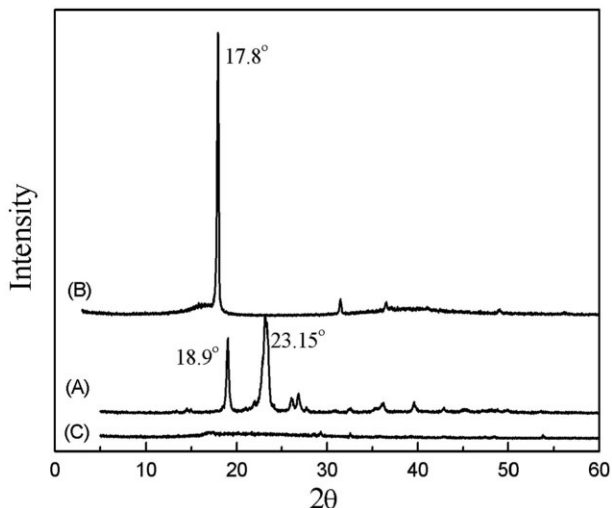


Figure 2 X-ray diffraction patterns for (A, PEO; B, PAN-PEO; C, PAN-PEO-LiClO₄).

assist ion transport to raise the ionic conductivity of polymer-salt complex. Generally, ionic conduction in polymer electrolytes is dominated by the amorphous elastomeric phase, so reducing the crystallinity of polymer electrolytes always takes a great role in recent researches. XRD patterns of PEO ($M_n = 10,000$), PAN-PEO, and PAN-PEO-LiClO₄ at room temperature are shown in Figure 2. We can find that the diffraction peak at $2\theta = 23.15^\circ$ disappears and another peak moves from $2\theta = 18.9^\circ$ to 17.8° after copolymerization, which indicates the decrease of the crystallization of PEO owing to AN introduction. After the complex PAN-PEO-LiClO₄ is formed, the diffraction peak at $2\theta = 17.8^\circ$ disappears; this is because the complex of lithium salt and copolymer destroys the crystallization of PEO, which results in the amorphous characterization of SPE. The increase of amorphous area will make ionic mobility in matrix easier, and then improve the ionic conductivity at room temperature.

Ionic conductivity of SPE

Figure 3 represents the temperature dependence of ionic conductivity for SPE prepared from PEO with different molecular weight, where the mole ratio of AN/MAPEO and $[Li^+]/[EO]$ is 120 and 0.1, respectively. As shown in Figure 3, ionic conductivity of SPE increases with the increase of temperature. At high temperature, the segments of polymer wriggle intensely, which is favorable for the couple of lithium salt and polymer segment, and ionic conductivity is high comparatively. In contrast, at low temperature, ionic conductivity decreases due to the restricted segmental motion of polymer and the motion of lithium ion. For amorphous polymer electrolyte, the temperature dependence of ionic conductivity often described

by empirical Vogel-Tamman-Fulcher (VTF) equation [eq. (2)],

$$\sigma = AT^{\frac{1}{2}} \exp\left[\frac{-B}{T - T_0}\right] \tag{2}$$

where constant A is corresponding to the number of charge carriers in the electrolyte system, constant B is related to the activation energy of ion transport associated with the configurational entropy of the polymer chains, and T_0 is a reference temperature related to T_g . The VTF equation was regressed onto the conductivity data and found to provide a good fit.

In addition, it is observed that ionic conductivity of SPE increases with the increase of the molecular weight of PEO. That the improved conductivity together with the higher molecular weight of PEO may be explained by the increased chain length, more ether oxygens and greater probability of the interaction of Li^+ and ether oxygens. This result accords with conduction mechanism, dynamic disordered hopping (DDH) model for ion transport in polymer electrolyte.^{15,16}

Figure 4 shows the effect of lithium salt concentration on ionic conductivity of SPE prepared from PEO ($M_n = 10,000$) at various temperature. As shown in Figure 4, as the salt concentration increases, ionic conductivity increases gradually to the maximum, and then decreases for higher salt concentration. The highest ionic conductivity was shown at salt concentration of 0.1 in the overall range of temperatures studied. It indicates a balance between these two opposing forces: increasing the number of charge carrier and decreasing ionic mobility. As the salt concentration increases, the number of charge carriers and T_g of SPE

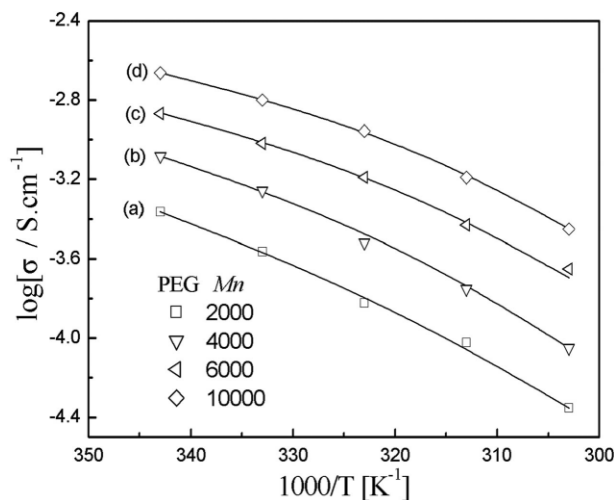


Figure 3 Arrhenius plots of the ionic conductivity for SPE prepared from different PEO (M_n), (a, 2000; b, 4000; c, 6000; d, 10,000). The solid lines are the results of regressing the VTF equation onto the data.

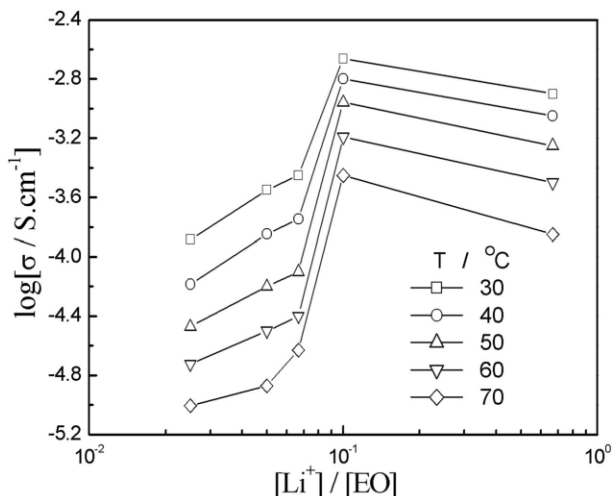


Figure 4 The ionic conductivity plotted against lithium salt concentration for the SPE film at different temperature.

increase.^{17,18} And, the increase in T_g owing to the interaction of Li^+ with ether oxygens inhibits ionic mobility. At low-salt concentration, the increase in the number of charge carriers dominates, and the decrease in ionic mobility is compensated by the larger increase in the number of charge carriers. Hence, the conductivity is found to increase with salt concentration up to 0.1. With further increase in the salt concentration, the decrease in ionic mobility becomes more pronounced. Therefore, conductivity decreases with the increase in salt concentration at higher salt concentration. Additionally, at higher salt concentration considerable formation of ion pairs or aggregates¹⁹ decreases the number density of charge carriers present and also lowers the mobility of charge carriers throughout the polymer host. Both of them result in a reduction in ionic conductivity.

CONCLUSIONS

The PAN-PEO copolymers are synthesized with solvent polymerization, complexing with lithium salt in

different mole ratio, and then the PAN-PEO-based SPE films were fabricated by solution casting. It is found that ionic conductivity of SPE increases with the increase of the molecular weight of PEO and temperature and that there is a maximum conductivity with the increase of salt concentration. When the molecular weight of PEO is 10,000, $[\text{Li}^+]/[\text{EO}]$ mole ratio is 0.1, the maximum conductivity reaches to $3.54 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature.

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