Short communication

Preparation and performances of porous polyacrylonitrile–methyl methacrylate membrane for lithium-ion batteries

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ABSTRACT

A copolymer, polyacrylonitrile–methyl methacrylate P(AN–MMA), was synthesized by suspension polymerization with acrylonitrile (AN) and methyl methacrylate (MMA) as monomers. With this copolymer, polymer membrane was prepared by phase inversion. The performances of the polymer were characterized by FTIR, SEM, DSC/TG, EIS and LSV. The copolymer contains CH_2, CN and CO bonds, and shows its thermal stability up to 300 °C. The polymer membrane has a porous structure with an average pore diameter of 0.5 μm. The conductivity of the polymer electrolyte is 1.25 mS cm^{-1} at room temperature, and it is electrochemically stable up to 5 V (vs. Li). Using the polymer electrolyte as the gel polymer electrolyte (GPE), the cell Li/GPE/LiCoO$_2$ shows its cyclic stability as good as the cell with liquid electrolyte.

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1. Introduction

In recent years, there has been increasing interest in research and development on rechargeable lithium-ion batteries employing solid polymer electrolytes [1], since solid polymer electrolytes are counted on to solve safe problem existing in conventional lithium-ion batteries using liquid electrolytes. However, the ionic conductivity of pure solid polymer electrolytes is too low to meet the requirement of high rate charge–discharge of lithium-ion batteries. Gel polymer electrolytes, which use polymer as matrix to convert liquid electrolyte into gel, are ideal alternatives to pure solid polymer electrolyte. Many polymers have been reported to be used as matrixes for gel polymer electrolytes, such as poly(vinylidenefluoride) (PVDF) [2–4], polyacrylonitrile (PAN) [5], poly(methyl methacrylate) (PMMA) [6] and poly(ethylene oxide) (PEO) [7–9]. However, these polymers are formed by same monomers, thus they are lack of enough mechanical strength or ionic conductivity for their application in commercial lithium-ion batteries.

These drawbacks can be made up to some extent by forming copolymers through cross-linking or copolymerization with two or more monomers that have different functions, such as strength, flexibility, ionic conductivity, and compatibility with electrolyte [10–18]. PAN-based polymer has good processibility and electrochemical stability, but it is brittle for the reason that the interaction of adjacent cyanogen groups which enhances the resistance of interior rotation of the main chain and decreases the flexibility of main chain. Considering the good flexibility of poly(methyl methacrylate) (PMMA) which is likely to reduce the brittleness and enhances the strength of PAN, we attempt to synthesize P(AN–MMA) copolymer by suspension polymerization of acrylonitrile (AN) with methyl methacrylate (MMA) as the matrix for gel polymer electrolyte.

2. Experimental

The monomers, AN and MMA as purchased, were distilled to remove the polymerization inhibitor, and then were mixed in the ratio of AN:MMA = 4:1 (in mass) with addition of the initiator, azobisisobutyronitrile (AIBN), and cross-linker, diallyl phthalate. The mixture was added into aqueous polyvinyl alcohol solution under stirring and nitrogen atmosphere and the reaction was kept under refluxing at 60 °C for 5 h. The polymer was isolated by filtration and was washed with the hot deionized water for the removal of any impurities such as residual monomers and initiator. The product was then dried in a vacuum oven at 80 °C for 12 h. The prepared P(AN–MMA) polymer was dissolved at a concentration of 10% (by weight) in dimethylformamide (DMF) at 80 °C for 30 min. After complete dissolution, the resulting viscous solution was cast with a doctor blade onto a glass plate, inducing phase inversion. After
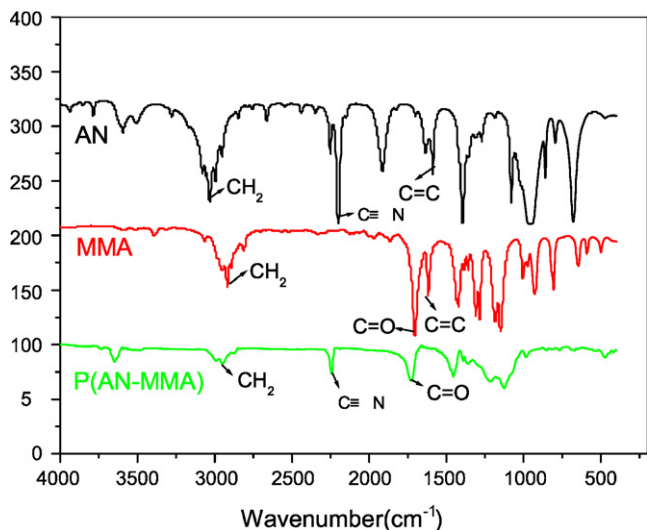
Fig. 1. FTIR spectra of monomers, AN and MMA, and their copolymer, P(AN–MMA).

the exchange of DMF and water by phase inversion, a substantial number of pores were formed in the films. The resulting membranes were washed, rinsed and dried at 60 °C under vacuum for 24 h, successively, before further processing.

The P(AN–MMA) polymer electrolytes were prepared by soaking the membranes in an electrolyte solution, 1 M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (1:1:1 in mass), for 30 min in an argon-filled glove box (Mikrouna).

The structure and properties of the polymer were characterized by Fourier transform infrared (FTIR) (PerkinElmer Spectrograph). The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) traces were obtained using a NETZSCH simultaneous TG-DTA/DSC analyser (model STA-449C). The morphology of the polymer membrane was characterized by scanning electron microscopy (SEM) (JEOL, JSM-6380LV, JAPAN, at an acceleration voltage of 15 kV). The electrochemical stability was carried out on the stainless steel electrode with lithium metal electrode as the reference and counter electrodes by the linear sweep voltammetry (LSV) at $2\,mV\,s^{-1}$ using Solartron 1260. The ionic conductivity of the polymer electrolyte was measured by the electrochemical impedance spectroscopy (EIS) using Solartron 1260 with ac amplitude of 10 mV from 100 kHz to 1 Hz. The polymer electrolyte was sandwiched between two parallel stainless steel (SS) discs.

To determine the battery performance, 2016 type cell $Li/GPE/LiCoO_2$ was assembled in the glove box. A positive electrode consisted of $LiCoO_2$ (84 wt.%), acetylene black (8 wt.%) and poly(vinylidenefluoride) (PVDF) (8 wt.%). LAND-CT2001A lithium-ion battery testing device (Wuhan Blue Electronic Industry Co., Ltd.) was used to test the cycle stability of the batteries. The batteries were charged and discharged with 0.1 C constant current between 3.0 and 4.2 V.

3. Results and discussion

Fig. 1 presents the FTIR spectra of monomers, AN and MMA, and their copolymer, P(AN–MMA). The monomer AN is characteristic of the adsorption peaks at 1597 and $2237\,cm^{-1}$, which correspond to the bonds C=C and C≡N, respectively. The monomer MMA is characteristic of the adsorption peaks at 1616 and $1725\,cm^{-1}$, which correspond to the bonds C=C and C=O, respectively. By comparing the FTIR spectrum of the copolymer with that of monomer, it can be found that the P(AN–MMA) keeps the absorptions at $1725\,cm^{-1}$ for C=O and $2237\,cm^{-1}$ for C≡N and loses the absorption
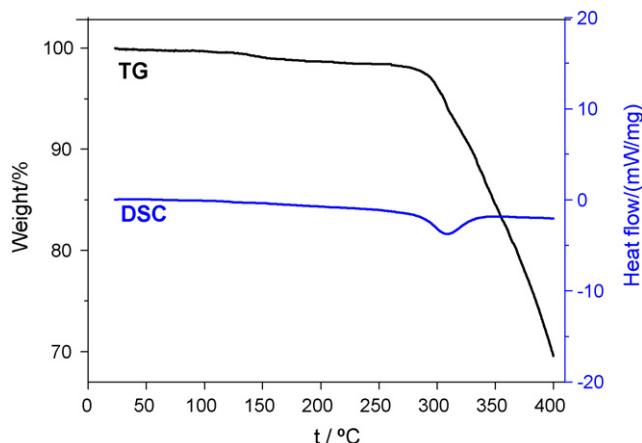

Fig. 2. DSC and TG curves of P(AN–MMA) copolymer.

at 1597 or $1616\,cm^{-1}$ for C=C, indicating that the copolymer maintains the main characteristics of the monomers and the monomers are copolymerized through the breaking of double bonds C=C in both monomers. It can be expected that the copolymer has good strength due to the cross-linking between two monomers and good conductivity due to the existence of strong polarity bonds CN and CO.

Fig. 2 presents the TGA and DSC curves of P(AN–MMA) copolymer. There is a large exothermic peak at 300 °C for the DSC curve, which is accompanied by the significant weight loss for TGA curve. These phenomena reflect the decomposition of the copolymer. Therefore, the copolymer is thermally stable at the temperature lower than 300 °C, which is better than PMMA and PAN [19]. Apparently, the cross-linking between MMA and AN can improve the thermal stability of the polymer with single monomer. It can be noted from Fig. 2 that there appears small weight loss at 100–150 °C, it may result from the volatilization of solvents remaining in the polymer.

Fig. 3 presents the SEM image of P(AN–MMA) membrane prepared by the phase inversion technique. In the phase inversion process, the porous membrane is formed by polymer precipitation. Usually, copolymer between different monomers forms more uniform pores than the polymer with single monomer. It can be found from Fig. 3 that the self-supporting membrane has a large number of micro-porous pores with an average size of 0.5 μm. It is expected
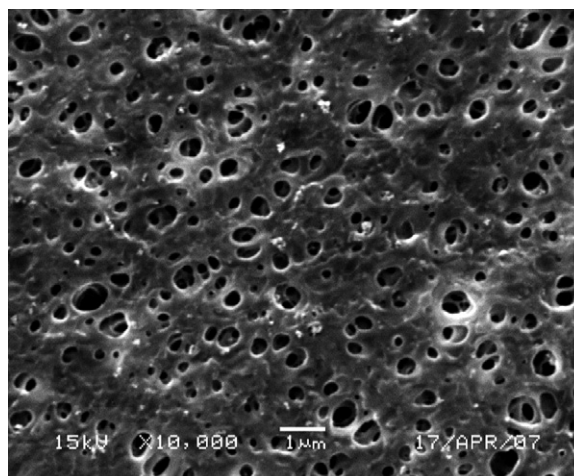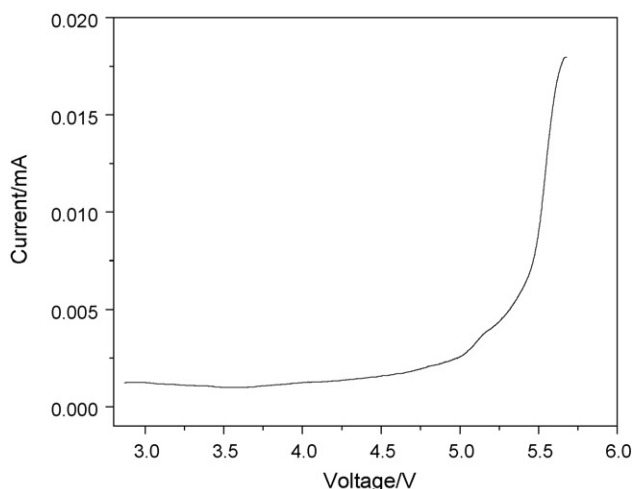

Fig. 3. SEM image of P(AN–MMA) membrane.

Fig. 4. Linear sweep voltammetry of the P(AN–MMA) electrolyte: scanning rate 2 mV s^{-1}.

Fig. 6. Comparison of cyclic stability between gel polymer and liquid electrolytes in LiCoO$_2$/Li 2016 type cell.

that the micro-porous pores are beneficial to the formation of gel electrolyte.

To understand the electrochemical stability of P(AN–MMA), gel electrolyte was prepared with P(AN–MMA) membrane and linear sweep voltammetry was carried out on 2016 type cell with stainless steel as working electrode and lithium as reference and counter electrodes. The obtained result is shown in Fig. 4. It can be seen from Fig. 4 that as the potential becomes higher, the current increases slightly at the potential lower than 5 V but increases significantly at the potential higher than 5 V. The slight increase in current might be ascribed to the change of the stainless steel surface, and the significant change in current should result from the decomposition of the gel electrolyte. Therefore, the copolymer is stable electrochemically at the potential lower than 5 V (vs. Li) and is better than PMMA, which is only 4.8 V (vs. Li) [20]. The electrochemical stability of a gel electrolyte reflects the stability of the solvent molecules in the electrolyte. The uniform pores of the membrane and the highly polarized groups, —CN and —CO [21], in the copolymer provide the membrane with stronger affinity with the solvent molecules, thus the solvent molecules are more stable than those in the polymer with single monomer. This stability of the copolymer is good for the lithium-ion batteries with high voltage cathode materials, such as LiCoO$_2$, LiNiO$_2$ and LiMn$_2$O$_4$.
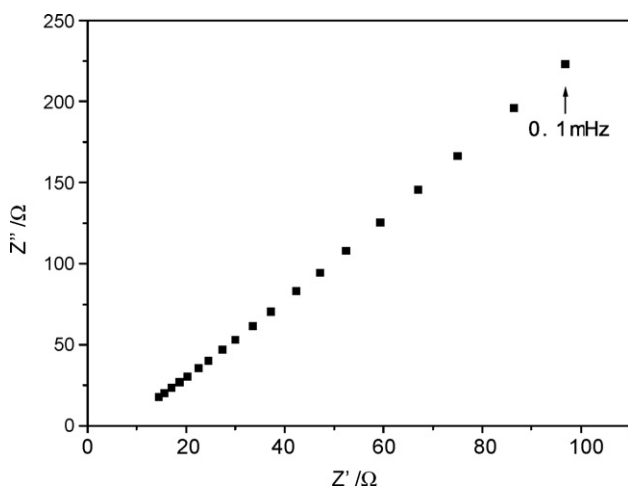

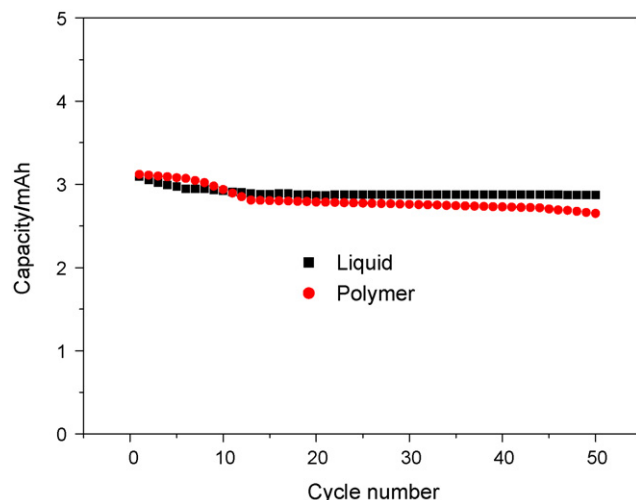**Fig. 5.** The electrochemical impedance spectroscopy of the cell SS/gel P(AN–MMA) electrolyte/SS.

To determine the ion conductivity of the gel electrolyte made from P(AN–MMA), electrochemical impedance experiment was carried out on the cell SS/gel electrolyte/SS. Fig. 5 presents the Nyquist plot of the electrochemical impedance. It can be seen from Fig. 5 that the imaginary part of the impedance is linearly related to its real part and the imaginary part increases more quickly than the real part as the frequency becomes lower. This is characteristic of an equivalent of a resistor and a capacitor in series, which corresponds to the resistance of the gel electrolyte and the double capacitance of the cell in this case. Therefore, the resistance of the gel electrolyte can be determined by the intersection of linear relation between the imaginary and real parts of the impedance with the real part axis. The ionic conductivity of the electrolyte obtained from the resistance of the gel electrolyte is 1.25 mS cm^{-1} at room temperature. This value is as good as that of PAN or PMMA [22,23]. Apparently, the cross-linking between AN and MMA does not reduce the ionic conductivity of the polymer with single monomer. The ionic conductivity of the copolymer is high enough for the application in lithium-ion batteries.

The high ionic conductivity of the gel P(AN–MMA) electrolyte can be ascribed to the existence of the strong polarity groups —CN and —CO. Moreover, a large number of pores in the porous membrane enlarge the contact areas between polymer and solvent so that the electrolyte solution is well retained in the membrane by polymer–solvent interactions.

Fig. 6 shows the cyclic stability of 2016 type cells with the gel P(AN–MMA) electrolyte and liquid electrolyte. The cells are subjected to a cycle test at a constant current of 0.3 mA (0.1 C) with cut-off voltages of 4.2 V at the upper limit and 3.0 V at the lower limit. It can be seen from Fig. 6 that the discharge capacity and the cyclic stability of the cell with the gel P(AN–MMA) electrolyte are as good as those of the cell with liquid electrolyte.

4. Conclusion

P(AN–MMA) copolymer has been synthesized by suspension polymerization and a porous membrane can be prepared by phase inversion from this copolymer. With this membrane, highly conductive and electrochemically stable polymer electrolyte can be obtained. The ionic conductivity of the polymer electrolyte is 1.25 mS cm^{-1} at room temperature and its electrochemical stability window is 5.0 V (vs. Li). With the polymer electrolyte as the gel

polymer electrolyte (GPE), the cell Li/GPE/LiCoO$_2$ shows its good cyclic stability as better as the cell with liquid electrolyte.

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