



Short communication

Performance improvement of poly(acrylonitrile-vinyl acetate) by activation of poly(methyl methacrylate)

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ABSTRACT

Poly(acrylonitrile-vinyl acetate) (P(AN-VAc)) was synthesized by emulsion polymerization with different mole ratios of acrylonitrile (AN) to vinyl acetate (VAc). P(AN-VAc) membrane was prepared with phase inversion method and was activated by poly(methyl methacrylate) (PMMA) to prepare a new type of gel polymer electrolyte matrix, P(AN-VAc)/PMMA. The performances of the synthesized copolymer and prepared polymer matrixes were characterized with FTIR, TGA, SEM, electrochemical and mechanical test. Compared with P(AN-VAc), P(AN-VAc)/PMMA is better as the matrix for gel polymer electrolyte for lithium ion battery use. P(AN-VAc)/PMMA has higher mechanical strength than P(AN-VAc) and the gel polymer electrolyte based on P(AN-VAc)/PMMA has higher electrochemical and chemical stability and ionic conductivity.

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1. Introduction

Polymer lithium ion batteries have been extensively studied in recent years for applications in various electrochemical devices, due to their excellent thermal and mechanical stability, flexibility and safety. However, the ionic conductivity of pure solid polymer electrolytes is insufficient for practical application at room temperature. In order to provide good ionic conductivity and mechanical strength simultaneously, most of the recent studies have been focused on the gel polymer electrolytes in which the liquid electrolyte are immobilized by polymer matrixes [1–7]. Among the polymer matrixes for gel polymer electrolytes, polyacrylonitrile (PAN)-based porous polymer has been most extensively studied [8–12], because there is the interaction between cyanogen groups in PAN and lithium ions, which contributes to high conductivity of the gel polymer electrolyte [13–18]. However, the porous PAN membrane is brittle because the interaction between the adjacent cyanogen groups enhances the resistance for the interior rotation of the main chain and thus reduces the flexibility of main chain.

To reduce the brittleness and enhance the strength of PAN, poly(acrylonitrile-vinyl acetate) (P(AN-VAc)) was synthesized [19].

However, the ionic conductivity of the gel polymer electrolyte using P(AN-VAc) as matrix is only 1.46 S cm^{-1} at room temperature and needs to be improved. In this paper, P(AN-VAc) was synthesized by emulsion polymerization and P(AN-VAc) membrane was prepared via phase inversion method. Considering the compatibility of poly(methyl methacrylate) (PMMA) with electrolyte and electrodes of lithium ion battery [20,21], PMMA was used to activate P(AN-VAc) to develop a new polymer matrix, P(AN-VAc)/PMMA, for the preparation of gel polymer electrolyte.

2. Experimental

P(AN-VAc) was prepared with AN and VAc as monomers, potassium persulfate (KPS) as an initiator, sodium dodecyl sulfate (SDS) as an emulsifier and diallyl phthalate (DAP) as cross-linking agent. Commercial AN (>99.5%) and VAc (>99.5%) were distilled to remove the aggregation preventer. The required amount of AN and VAc were dissolved in deionized water with SDS to form a homogeneous solution under N_2 flow at 65°C for 30 min. Then KPS and DAP were added in the solution. The polymerization was continued for 8 h under vigorous stirring. The resulting solution was poured into 2–3 wt% Al_2O_3 solution to yield the precipitate. The precipitate was subsequently filtered, washed with ethanol and dried in vacuum at 60°C to constant weight. Fourier transform infrared (FTIR) of the copolymer was carried out with FTIR-8400S (Japan) in the range of $450\text{--}4000 \text{ cm}^{-1}$ (resolution: 2 cm^{-1}).

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The prepared P(AN-VAc) copolymer was dissolved in dimethylformamide (DMF). The resulting viscous solution was cast with a doctor blade onto a glass plate, then immersed in deionized water for 30 min at room temperature. After the exchange of DMF and water by phase inversion, a substantial number of pores were formed in the films. The resulting P(AN-VAc) porous membranes were dried at 60 °C under vacuum for 24 h. The dried membrane typically has a thickness of 50 μm .

PMMA (>99.9%) was dissolved in a mixed solution of DMF and diethylene carbonate (DEC) to form a homogeneous solution of 3 wt% PMMA. The prepared P(AN-VAc) membranes were then immersed in the PMMA solution for 30 min, then taken out and dried in vacuum at 60 °C for 24 h. The morphology of the P(AN-VAc) and P(AN-VAc)/PMMA membranes were examined with scanning electron microscope (JEOL, JSM-6380LV, JAPAN). The thermal stability of the polymers was analyzed with thermogravimetric analyzer (NETZSCH STA 409 PC/PG). Mechanical strength measurements were carried out with a Gotech GT-TS-2000 apparatus, at a crosshead speed of 10 mm min^{-1} , using standard dumb bell type tensile bars as the testing samples. The tests were carried out at room temperature.

To prepare gel polymer electrolyte (GPE), the P(AN-VAc)/PMMA membranes were transferred into a glove box (Supper1220/750, Belgium) and soaked with 1 M LiPF_6 in dimethyl carbonate (DMC)/DEC/ethylene carbonate (EC) (1:1:1, v/v/v, Guangzhou Tinci Materials Technology Co. Ltd., battery grade) for 30 min. After wetting, the excess liquid electrolyte on the surface was removed by pressing lightly between two sheets of filter papers. The ionic conductivity and the interfacial stability of the GPE were determined by ac impedance spectroscopy on electrochemical instrument (CHI650B, Shanghai). In the determination of ionic conductivity, the GPE was sandwiched between two stainless steel (SS) electrodes to form SS/GPE/SS cell. In the determination of the interfacial stability, the GPE was sandwiched between two lithium electrodes to form a symmetrical Li/GPE/Li cell. The electrochemical stability of the GPE was examined on the cell Li/GPE/SS by linear sweep voltammetry at 1 mV s^{-1} . To determine the battery performance, a cell Li/GPE/LiCoO₂ was set up and tested on PCBT-138-64D (WUHAN LISUN).

3. Results and discussion

3.1. FTIR spectra

Fig. 1 presents the FTIR spectra of AN, VAc and P(AN-VAc). The AN shows its characteristic absorption at 2240 cm^{-1} and 1623 cm^{-1} , corresponding to $-\text{C}\equiv\text{N}$ and $\text{C}=\text{C}$ groups, respectively. The VAc shows its characteristic absorption at 1739 cm^{-1} and 1627 cm^{-1} , corresponding to $-\text{C}=\text{O}$ and $-\text{C}=\text{C}$ groups, respectively. Compared with the FTIR spectra of AN and VAc, the copolymer P(AN-VAc) is

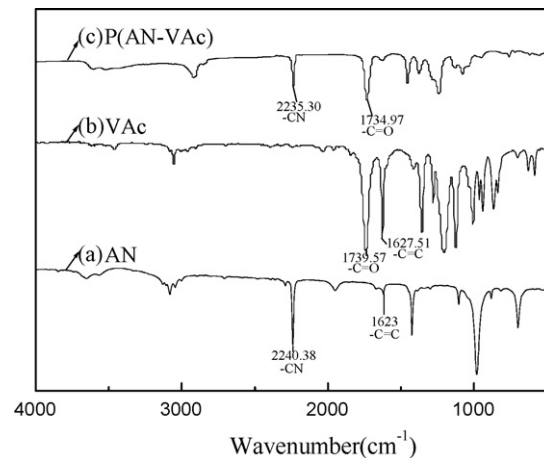


Fig. 1. FTIR spectra for AN (a); VAc (b) and P(AN-VAc) (c) in the range of 450–4000 cm^{-1} .

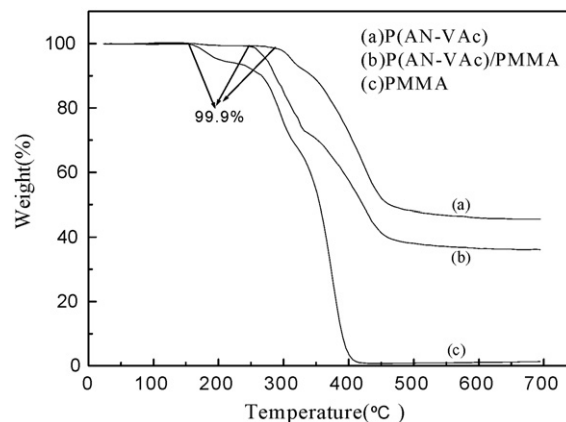


Fig. 2. TGA curves for P(AN-VAc) (a); P(AN-VAc)/PMMA (b) and PMMA (c) from room temperature to 600 °C at a heating rate of 10 °C min^{-1} .

characteristic of vibrational bands of PAN [22] and PVAc [23]. P(AN-VAc) keeps the absorptions at 1734 cm^{-1} for $\text{C}=\text{O}$ and 2235 cm^{-1} for $-\text{C}\equiv\text{N}$ and loses the absorption at 1623 cm^{-1} or 1627 cm^{-1} for $\text{C}=\text{C}$. This indicates that $\text{C}=\text{C}$ is transformed to $\text{C}-\text{C}$ completely and the copolymer, P(AN-VAc), is obtained [19].

3.2. Thermal stability

The thermal stability was analyzed by thermogravimetry under N_2 atmosphere, from room temperature to 600 °C at a heating rate

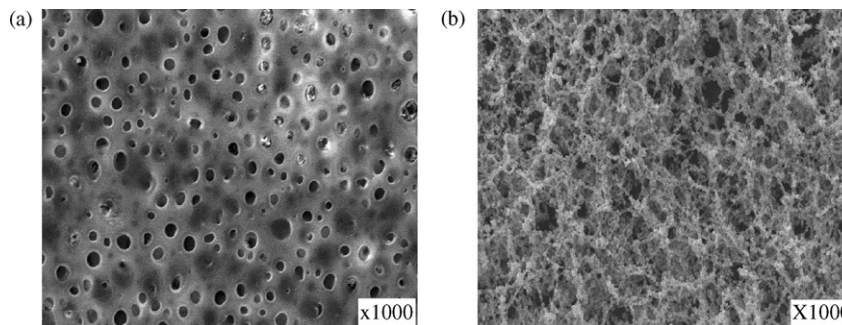


Fig. 3. SEM images of P(AN-VAc) matrix (a) and P(AN-VAc)/PMMA (b) membrane.

Table 1
Electrolyte uptake and conductivity of the P(AN-VAc)-based GPE

Molar ratio (AN/VAc)	Uptake (%)	Conductivity ($\times 10^{-3} \text{ S cm}^{-1}$)
(90AN/10VAc)/PMMA	177.77	1.25
(80AN/20VAc)/PMMA	242.85	1.72
(70AN/30VAc)/PMMA	300	1.88
(60AN/40VAc)/PMMA	250	1.69
(50AN/50VAc)/PMMA	133.3	1.18
70AN/30VAc	188	1.4

of $10^\circ\text{C min}^{-1}$. Fig. 2 presents the TGA curves for P(AN-VAc), P(AN-VAc)/PMMA and PMMA. The PMMA and P(AN-VAc) show their thermal stability up to 160°C and 300°C , respectively. Compared with the TGA curves of PMMA and P(AN-VAc), P(AN-VAc)/PMMA has no mass loss for the temperature up to 250°C , which is better than that of PMMA and poorer than that of P(AN-VAc). This indicates that the thermal stability of PMMA can be improved by P(AN-VAc).

3.3. SEM images

Fig. 3a presents the SEM image of P(AN-VAc) membrane. It can be seen that the P(AN-VAc) membrane has uniform porous structure. Fig. 3b presents the SEM image of P(AN-VAc)/PMMA membrane. It can be seen that the P(AN-VAc)/PMMA membrane has uniform network-like microporous structure, which should result from the presence of polar functional groups in PMMA [20]. This structure is very different from that of the P(AN-VAc) and helps to improve the electrochemical stability of P(AN-VAc). The cross-linked micropores on the surface of the activated membrane may increase the efficient uptake of the liquid electrolyte and help to improve the ionic conductivity of the GPE.

3.4. Electrolyte uptake and Ionic conductivity

The variation of electrolyte uptake and conductivity in P(AN-VAc) and P(AN-VAc)/PMMA for the GPE preparation are listed in Table 1. The electrolyte uptake (A) is obtained by:

$$A (\%) = \frac{(W_2 - W_1)}{W_1} \times 100\% \quad (1)$$

where W_1 and W_2 are the mass of the dry and the wet copolymer, respectively.

In the determination of the ionic conductivity, the GPE was sandwiched between two parallel SS discs (diameter $\Phi = 16 \text{ mm}$). The ionic conductivity was calculated from the bulk electrolyte resis-

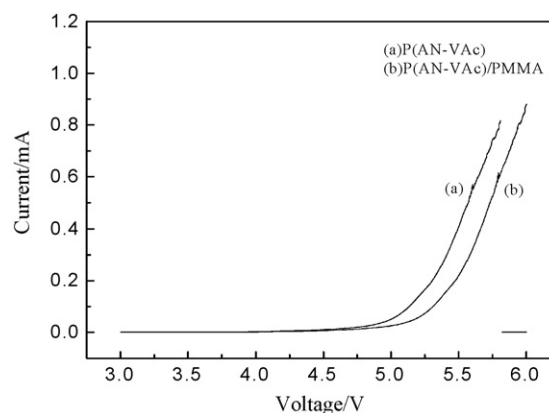


Fig. 4. Linear voltammograms on stainless steel for GPE with P(AN-VAc) (a) compared with P(AN-VAc)/PMMA; (b) scan rate: 1 mV s^{-1} .

tance (R) according to:

$$\sigma = \frac{l}{RS} \quad (2)$$

where l is the thickness of the GPE, and S is the contact area between GPE and SS disc.

It can be seen from Table 1 that the uptake and the ionic conductivity of the P(AN-VAc)/PMMA are related to the mole ratio of AN to VAc in the copolymer and the ionic conductivity of the gel based on P(AN-VAc)/PMMA is proportional to its electrolyte uptake. The ionic conductivity increases with the mole ratio of AN to VAc increasing when the ratio is smaller than 7:3 and then decreases when the ratio increases further. The maximum ionic conductivity of the GPE based on P(AN-VAc)/PMMA is $1.88 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature for the copolymer with the mole ratio of AN to VAc 7:3, which is larger than that of the GPE based on P(AN-VAc). This indicates that the activation of P(AN-VAc) with PMMA can improve its ionic conductivity. The improvement of ionic conductivity can be ascribed to the carbonyl groups in PMMA, which are more compatible with the carbonate solvents than other groups in P(AN-VAc). Thus the activation of P(AN-VAc) with PMMA increases the uptake of the liquid electrolyte and the mobility of the charge carrier, resulting in higher ionic conductivity [24–27].

3.5. Electrochemical stability

Fig. 4 presents the linear voltammogram obtained for the cell SS/GPE/Li. It can be seen from the curve (a) of Fig. 4 that the P(AN-VAc) electrolyte decomposes at about 4.8 V (vs. Li/Li^+). However, the P(AN-VAc)/PMMA does not decompose until 5.2 V , as shown by

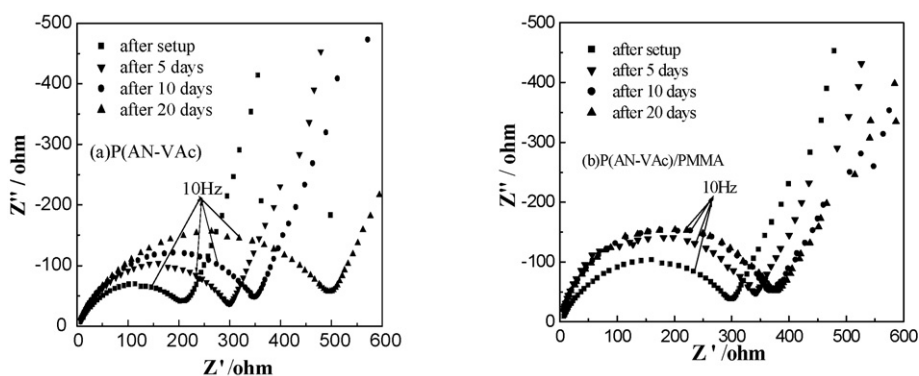


Fig. 5. Impedance spectra of cell Li/GPE/Li at open circuit potential with the P(AN-VAc) (a) and P(AN-VAc)/PMMA (b).

the curve (b) of Fig. 4. This indicates that the GPE based on P(AN-VAc)/PMMA is more stable than the GPE based on P(AN-VAc) and thus has better compatibility with high-voltage electrode materials.

Interfacial stability with electrode is an essential factor to guarantee acceptance performance in the lithium ion batteries [28–31]. To understand the stability of the interface between Li and GPE, a cell Li/GPE/Li was set up and ac impedance spectroscopy was used to monitor the change in impedance with time. Fig. 5 shows the impedance spectra for the cells based on the GPEs of P(AN-VAc) and P(AN-VAc)/PMMA at different time. It can be seen from Fig. 5a that the interfacial resistance of P(AN-VAc)-based GPE increases rapidly with storage time. However, the interfacial resistance of P(AN-VAc)/PMMA-based GPE is relatively stable during the same storage time, keeps almost unchanged after the fifth day, as shown in Fig. 5b. This suggests that passive film forms on Li at the beginning and does not change as soon as it has formed for the P(AN-VAc)/PMMA-based GPE. The semi-circle at high frequencies reflects the charge transfer resistance at the lithium/electrolyte interface [32]. Apparently, the activation of P(AN-VAc) with PMMA improves its compatibility with anode of lithium ion battery.

3.6. Battery performance

Fig. 6 presents the cyclic stability of the battery Li/P(AN-VAc)/PMMA/LiCoO₂ compared with the battery Li/P(AN-VAc)/LiCoO₂. The batteries were charged and discharged with a constant current of 0.48 mA cm⁻² (C/5 rate) between 4.2 V and 3.0 V. From Fig. 6, it can be seen that the battery Li/P(AN-VAc)/PMMA/LiCoO₂ has the initial capacity as high as and the cyclic stability better than the battery Li/P(AN-VAc)/LiCoO₂. After 50 cycles, the battery Li/P(AN-VAc)/PMMA/LiCoO₂ keeps 90.3% of its initial discharge capacity but the battery Li/P(AN-VAc)/LiCoO₂ keeps only 86.5% of its initial discharge capacity.

3.7. Mechanical strength

The stress curves obtained from P(AN-VAc) and P(AN-VAc)/PMMA membranes are shown in Fig. 7. It can be seen from Fig. 7 that there is less difference in fracture strength between P(AN-VAc) and P(AN-VAc)/PMMA. This suggests that the activation of PMMA on P(AN-VAc) does not change the mechanical strength of P(AN-VAc). Both P(AN-VAc)/PMMA and P(AN-VAc) with the same mole ratio of AN to VAc (7:3 (AN:VAc) have the strongest fracture strength, about 15 MPa at ambient temperature. This value is far

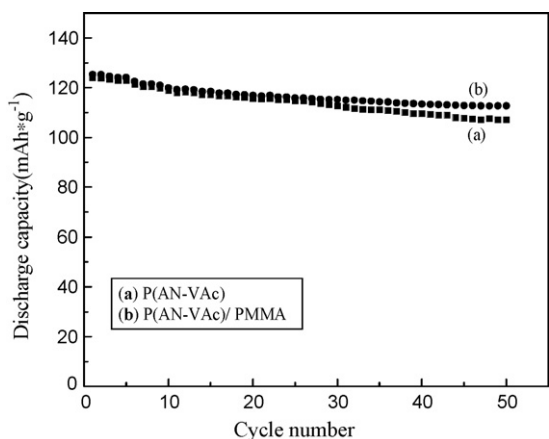


Fig. 6. Comparison of cyclic stability between polymer electrolyte P(AN-VAc) (a) and P(AN-VAc)/PMMA (b).

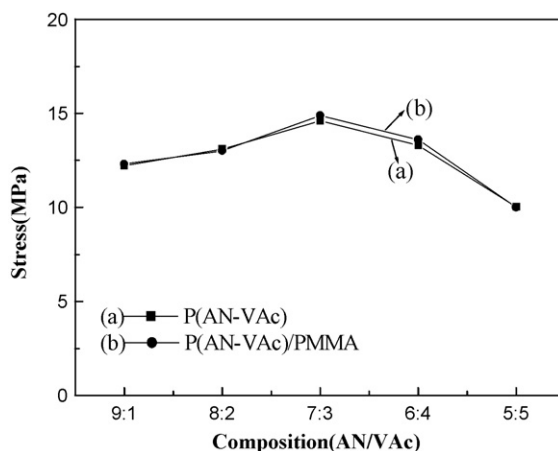


Fig. 7. Comparison of tensile strength between polymer electrolyte membranes of P(AN-VAc) (a) and P(AN-VAc)/PMMA (b).

higher than other copolymer, such as poly(acrylonitrile-co-methyl methacrylate) (P(AN-co-MMA)) [33], whose fracture strength is only 4.88 MPa.

4. Conclusion

The performance of P(AN-VAc) as matrix of gel polymer electrolyte for lithium ion battery can be improved by the activation of PMMA. The gel polymer electrolyte based on this activated polymer, P(AN-VAc)/PMMA, has high ionic conductivity and better electrochemical compatibility than the gel polymer electrolyte based on P(AN-VAc). The performance improvement can be ascribed to the compatibility of PMMA with carbonate electrolyte, cathode and anode.

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