Structure and ionic conductivity of gel polymer electrolytes based on PVDF/P(AMPS-TFEMA) blend membranes

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Abstract. The copolymerization of 2-acrylamido-2-methylpropane sulfonic acid (AMPS) and trifluoroethyl methacrylate (TFEMA) was performed to synthesize the random copolymer P(AMPS-TFEMA). This polymer was blended with polyvinylidene fluoride (PVDF) to prepare the new blend membranes containing sulfonate. The blend membranes were activated with 1 M LiPF₆ solution to prepare gel polymer electrolytes. The thermal properties, morphology, mechanical properties, uptake electrolyte, and electrochemical properties of blend membranes were characterized. The effect of polymer on the membrane structure and performance was studied. At room temperature, the gel polymer electrolyte conductivity of P(AMPS-TFEMA) 30 wt% was up to 2.6 mS cm⁻¹ (uptake electrolyte 550%, swelling ratio less than 10%), and the electrochemical window was up to 4 V, which were acceptable for lithium ion batteries (LIBs).

1. Introduction
Lithium ion batteries (LIBs), as a convenient and clean energy storage device, play a vital role in mobile phones, automobiles and other fields. However, the commercial application of LIBs with large capacity and high energy and power density has been limited due to the use of liquid organic electrolytes, which suffer from safety problems during charging and discharging [1-2]. Therefore, polymer electrolytes have been widely studied as a safe and promising alternative to meet the challenges for application in LIBs during recent years. Polymer electrolytes mainly include solid polymer electrolytes and gel polymer electrolytes. For solid polymer electrolytes, it still needs a long way for their industrial application due to low ionic conductivity at ambient temperature [3-5]. Gel polymer electrolyte is a promising candidate by possessing the advantages of both solid and liquid electrolytes [6].

Gel polymer electrolytes can be obtained by embedding the organic solutions of lithium salt into a porous polymer membrane. The pore size, the volume fraction and interconnectivity of the pore domain, and the type of porous polymer matrix will determine the uptake of electrolyte and the ion conductivity of the final gel electrolytes. Many polymers, such as polyvinylidene fluoride (PVDF) [7-9], polymethylmethacrylate (PMMA) [10], polyethylene oxide (PEO) [11], perfluorsulfonic acid (PFSA) [12], have been used as matrices for gel polymer electrolytes. PVDF-based gel polymer electrolytes have been widely investigated for LIBs due to their excellent mechanical and chemical stability. But, their applications are limited by the poor uptake of the liquid electrolyte. Developing
dimensionally stable gel polymer electrolytes with high ionic conductivity is still an important research topic [13].

The fluorine-containing acrylate copolymer exhibits extremely low surface energy and good compatibility with the PVDF, which improves the thermal and chemical stability of the blend membranes [14]. 2-acrylamido-2-methylpropanesulfonic acid lithium (AMPS-Li), which has a good affinity for liquid electrolytes [15, 16]. In this work, the random copolymer P (AMPS-TFEMA) with sulfonate and fluorine has been synthesized by copolymerization of the sulfonate-containing monomer (AMPS) with and the fluorine-containing acrylate monomer, and then, were blended with PVDF to prepare the blend membrane by phase-inversion method. The PVDF-based gel electrolytes are prepared by filling and swelling the liquid electrolyte containing lithium salt into the PVDF/P(AMPS-TFEMA) blend membrane. In the paper, AMPS-Li was incorporated into the blend membrane to achieve high ionic conductivity [17]. TFEM was chosen to increase the mechanical properties and chemical stability [18].

2. Experimental materials
2-acrylamido-2-methylpropanesulfonic acid: ( Weifang Aorui Co.Ltd, AR). Trifluoroethyl methacrylate (Adamas Reagent Co.Ltd, 99.99%). N, N-dimethylformamide (DMF), potassium persulfate (K₂S₂O₈), Sodium bisulfite (NaHSO₃): (Sinopharm Group Chemical Reagent Co.Ltd, AR.) Ethanol ( Tianjin Fuchen Chemical Reagent Factory, AR). PVDF (Shanghai Organic Fluorine Material Factory), Dimethyl sulfoxide-d6 (DMSO-d6 Aladdin Co.Ltd, Shanghai, China. 99.9%), Lithium hexafluorophosphate (LiPF₆), Dimethyl carbonate (DMC), Ethylene carbonate (EC): (Shanghai Yien Chemical Technology Co.Ltd, 99% ). Lithium hydroxide (LiOH) : ( Tianjin xienxi Biochemical Technology Co. Ltd, 98% ).

2.1. Synthesis procedure
2.1.1. PAMPS and P(AMPS-TFEMA). The synthesis of polymer is shown in Scheme 1, Scheme 2, respectively. AMPS was dissolved in distilled water, stirred until completely dissolved at room temperature. It was bubbled with N₂ for 10 minutes to remove O₂. Then, the initiator potassium persulfate-sulfite sodium hydrogen (0.08% based on the mass of the monomer) was added into the solution. A temperature gradient heating method (heating method of 50 °C-2 h, 60 °C-5 h, 70 °C-1 h) was used for 8 hours to obtain a PAMPS polymer solution with a concentration of 20%. The transparent viscous polymer solution was precipitated with anhydrous ethanol. After three precipitations, the monomer AMPS could not be detected, and the precipitate was dried to constant weight under vacuum at 70 °C. The procedure of P(AMPS-TFEMA) was the same as the PAMPS, except the mass of AMPS: TFEMA was 6:4.

Scheme 1. The synthesis procedure of PAMPS from monomer AMPS.

Scheme 2. The synthesis procedure of P(AMPS-TFEMA) from AMPS and TFEMA.
2.2. Preparation of gel polymer electrolytes

Blend membranes were fabricated by the phase-inversion method. A certain amount of P(AMPS-TFEMA) (the content of P(AMPS-TFEMA) is 10 wt%, 20 wt%, 30 wt%, 40 wt% and 50 wt%) and PVDF were dissolved in DMF with stirring at 50 °C for 24 h to form a homogenous polymer solution of 20 wt%. The solution was cast on the glass plate. The membrane was dried under a vacuum at 50 °C for 24 h.

The obtained membranes were cut into rectangular shapes and immersed in a LiOH/ethanol solution at 75 °C for 2 h, washed with ethanol and dried under vacuum at 80 °C for 24 h, repeat the above process 2 times.

The gel polymer electrolytes with sulfonic acid lithium were achieved by immersing the dry blend membranes in the liquid electrolyte (1 M LiPF₆/EC/DMC(1:1, v/v)) solution. The opaque white membrane became transparent after the immersed. The activated procedure of PAMPS gel polymer electrolytes was the same as above.

2.3. Characterization

Nuclear magnetic resonance (¹H NMR) of the copolymer was completed on an NMR instrument (Agilent American). The scanning frequency was 400MHz. The powder sample was dissolved in DMSO-D6 reagent. Fourier transform infrared (FTIR) spectra were tested by instrument (Perkin Elmer Frontier 001 Fourier Infrared Analyzer), wavenumber range 4000 to 400 cm⁻¹. The morphology of the blend membrane was analyzed by S-3400 scanning electron microscope (SEM) (Hitachi Japan). The gel polymer electrolyte was quenched with liquid nitrogen before testing. The surface of the blend membrane was sprayed with gold.

The thermogravimetric analyzer (TGA) (Stapt Linseis Germany) was used to test the thermal stability of the polymer and membrane. The atmosphere was N₂, and the temperature was 10 °C min⁻¹. The temperature range was from room temperature to 800 °C.

The electrochemical stability of gel polymer electrolytes was tested in the electrochemical workstation (ChenHua CHI800D Shanghai) by the linear sweep voltammetry (LSV). The scanning range is 0-6 V and the scanning speed is 10 mV/s.

The ionic conductivity of gel polymer electrolytes was measured on an electrochemical workstation (ChenHua CHI800D Shanghai). The gel polymer electrolytes were sandwiched between two stainless steel electrolytic sheets to form a blocking battery. Electrochemical Impedance Spectroscopy (EIS) were determined over a frequency range of 0.01 Hz - 1 M Hz. Ionic conductivity (σ) can be calculated according to formula (1), d is the thickness, A is the area of the electrode and Rₑ is the membrane resistance.

\[ \sigma = \frac{d}{AR_e} \]  

The tensile strength and elongation at break of blend membrane were determined via DSA503A tester and the stretch rate of 5 mm min⁻¹. The size of the membrane was 5 cm × 3 cm. The thickness of the membrane was measured by a micrometer, and the sectional area of the membrane was 30 mm².

The electrolyte uptake (ΔW, wt%) and swelling ratio(SR, %) of gel polymer electrolytes were determined by comparing the change of dry and swelling membrane. The dry membrane was put into 100ml EC/DMC (1:1 v/v)solution, the additional solution on the membrane surface was removed with filter paper absorption and dry and swelling membranes were weighed. ΔW and SR were calculated by equation (2), (3), respectively.

\[ \Delta W = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \]  

\[ \text{SR} = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}} \times 100\% \]

W_wet is the weight of the swelled membrane, W_dry is the weight of the dry membrane. L_wet is the area of the swelled membrane, L_dry is the area of the dry membrane.
3. Result and discussion
The chemical structure of PAMS and P(AMPS-TFEMA) was confirmed by $^1$H NMR (Figure 1). Peak c at 5.6 ppm was assigned to the nitrogen hydrogen bond and peak a at 2.7 ppm was assigned to the sulfonic acid. Peak b at 4.7-4.9 ppm was assigned to -CH$_2$CF$_3$- of TFEMA [19].

![Figure 1. $^1$H NMR spectra of the TFEMA and P(AMPS-TFEMA).](image1)

![Figure 2. FTRI spectrum of PVDF, PAMS 30 wt% and P(AMPS-TFEMA) 30 wt% blend membranes.](image2)

As illustrated in Figure 2, polymer reaction is accompanied by the elimination of C=C bond at 1278 cm$^{-1}$ from AMPS segments adjacent to P(AMPS-TFEMA) to create C-C bond. Compared with the spectra of PVDF, C=O bond at 1685 cm$^{-1}$ was found. Furthermore, the band at 1041 cm$^{-1}$ is assigned to the SO$_3$ group of P(AMPS-TFEMA). In addition, there is a unique absorption peak at 840 cm$^{-1}$, which corresponds to the appearance of β crystal form in PVDF [20]. As we all know, the α crystal form in PVDF is more common, and the dipole moment is arranged in the reverse direction, so there is no polarity. In addition, the β crystal form has polarity and exhibits electrochemical activity.

![Figure 3. Surface SEM micrographs of blend membranes with P(AMPS-TFEMA) ( a 10 wt%, b 30 wt%, c 50 wt% ).](image3)

![Figure 4. Cross-section SEM micrographs of blend membranes with P(AMPS-TFEMA)(a’ 10 wt%, b’ 30 wt%, c’ 50 wt% ).](image4)
SEM images (Figure 3-4) showed that the addition of P(AMPS-TFEMA) can form uniform pores and the network structure in gel polymer electrolytes, as well as increase with the growth of copolymer content. The network structure was mainly derived from the typical structure formed by the phase separation process and the process prevented the formation of PVDF spherulite [21]. The presence of finger pores and the network structure in blend membranes will increase the liquid content, which means that lithium ions can conduct faster in blend membranes.

Also, the thermal stability of blend membranes can be characterized by the TGA analysis in Figure 5. PAMPS loses more than 5% at 125-175 °C, when TFEMA can still maintain good stability. The stable C-F bond of TFEMA in molecules plays an important role and improves the thermal stability of the polymer. The heat resistance of the gel polymer electrolytes is greatly improved, the blend membrane remains stable at 250 °C, which can meet the requirements of LIBs.

Figure 5. Thermogravimetric curves of polymers (a. PAMPS, b. P(AMPS-TFEMA) and blend membranes (c PAMPS 30 wt%, d P(AMPS-TFEMA) 30 wt%).

In Figure 6, the electrochemical stability of the blend membranes was measured by LSV. In general, the working environment of LIBs requires that the ion exchange membrane has certain electrochemical stability. Manuel et al. supported that the electrochemical stability window depends on the polymer [22]. Compared with the PAMPS blend membrane, the addition of 30 wt% P(AMPS-TFEMA) can make the electrochemical window wider, reached 4 V, which was due to the higher content of the fluoride in P(AMPS-TFEMA).

Figure 6. Electrochemical stability window of blend membranes (PAMPS 30 wt%, P(AMPS-TFEMA) 30 wt%).

Figure 7. Uptake electrolyte of blend membranes with PAMPS (10-50 wt%) and P (AMPS-TFEMA) (10-50 wt%).

Bohnke et al. and Capiglia et al. assumed that two ion-conducting mechanisms in the polymer electrolyte are mainly based on the amorphous region and the pore structure [23, 24]. Ionic transport plays a decisive role in gel polymer electrolyte, uptake electrolyte is a critical parameter for ionic conductivity.

Figure 8. Ion conductivity of gel polymer electrolytes with PAMPS (10-50 wt%) and P(AMPS-TFEMA) (10-50 wt%).
conductivity. Therefore, the process of exchanging protons for lithium ions is necessary, it was a method to improve the Li\(^+\) content in the blend membrane. In addition, the uptake electrolyte was calculated with eq.(2) and is shown in Figure 7. The uptake electrolyte increased with an increase of the copolymer in the blend membranes. The result indicated that uptake electrolyte in the membrane was more dependent on the P(AMPS-TFEMA) content than on the PAMPS content. Moreover, those could be ascribed to the excellent affinity for the liquid electrolyte of AMPS-Li.

Ionic conductivity is an important parameter of gel polymer electrolytes for LIBs. The room temperature ionic conductivity of gel polymer electrolytes are shown in Figure 8. It is clear that the trend of the ionic conductivity change of the gel polymer electrolyte is similar to the uptake electrolyte. Generally, the ionic conductivity depends on the content of carrier ions and their mobility[25]. SEM in Figure 3-4 has proved that the addition of copolymer changed the morphology of the membrane, and a large number of pores structure appeared. The pore structure resulted that the liquid electrolyte trapped in pores increased, which increased the content of carrier ions and enhanced conductivity of the electrolyte accordingly[25]. With the increase of the copolymer P(AMPS-TFEMA) in the blend membrane, the conductivity of gel polymer electrolytes increases up to the maximum conductivity of 2.6 mS cm\(^{-1}\) in 30 wt% P(AMPS-TFEMA). However, when the amount of the copolymer in the blend membranes is more than 30 wt%, the conductivity of the gel polymer electrolytes decreases due to the electrostatic repulsion between sulfonate, which hinders the migration of lithium ions. The P(AMPS-TFEMA)/PVDF blend porous membrane swelled with LiPF\(_6\)/EC/DMC solution may be more suitable for LIBs.

In general, the blend membrane should be strong enough and keeping a minor swelling ratio to meet the request of the gel polymer electrolyte. The mechanical properties and swelling ratio of the membrane were shown in Table 1 and Table 2. By comparing the change of tensile strength and elongation at break, the copolymer P(AMPS-TFEMA) significantly could improve the mechanical properties of the membranes. And the PVDF-based blend membranes showed a low swelling ratio and exhibited excellent dimensional stability, which is important for LIBs [26].

| P(AMPS-TFEMA)/wt% | Tensile strength /MPa | Elongation at break /% | Swelling ratio /% |
|-------------------|-----------------------|------------------------|------------------|
| 10 %              | 3.64                  | 13.16                  | 3.3              |
| 20 %              | 2.44                  | 15.33                  | 4                |
| 30 %              | 2.29                  | 19.29                  | 6.7              |
| 40 %              | 1.89                  | 5.26                   | 7.3              |
| 50 %              | 1.24                  | 4.31                   | 7.3              |

**Table 1.** The results of the mechanical and swelling ratio test of blend membranes with P(AMPS-TFEMA) (10-50 wt%).

| PAMPS /wt% | Tensile strength /MPa | Elongation at break /% | Swelling ratio /% |
|------------|-----------------------|------------------------|------------------|
| 10 %       | 2.35                  | 2.89                   | 2                |
| 20 %       | 2.99                  | 3.97                   | 3.3              |
| 30 %       | 4.31                  | 4.83                   | 4                |
| 40 %       | 2.67                  | 2.46                   | 6                |
| 50 %       | 0.24                  | 0.45                   | 6.3              |

**Table 2.** The results of the mechanical and swelling ratio test of blend membranes with PAMPS (10-50 wt%).
4. Conclusion
In summary, the copolymer P(AMPS-TFEMA) was synthesized and blended with PVDF to prepare the blend membrane. Besides, its potential as a gel polymer electrolyte was evaluated. The uptake electrolyte and ionic conductivity performance were improved due to the microporous structure and affinity of AMPS-Li. The thermal stability of the blend membrane was mainly dependent on the TFEMA. Similarly, good mechanical properties and swelling ratio of the blend membrane could be achieved by the P(AMPS-TFEMA) and PVDF. The electrochemical stability was mainly dependent on the content of the fluoride of the membrane. When the blend membrane was activated by the LiPF$_6$ solution, a transparent gel polymer electrolyte was obtained. For the gel polymer electrolyte containing 30 wt% P(AMPS-TFEMA), the maximum ionic conductivity at room temperature reached 2.6 mS cm$^{-1}$ (uptake electrolyte 550%, swelling ratio less than 10%) and electrochemical window reached 4 V. And the P(AMPS-TFEMA) blend membrane had more excellent mechanical properties. In short, the P(AMPS-TFEMA) blend membrane was more suitable for LIBs.

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