BaTiO₃/PVDF-g-PSSA composite proton exchange membranes for vanadium redox flow battery

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Abstract

Poly(vinylidene fluoride) membranes with BaTiO₃ powders were grafted with styrene monomer and then sulfonated in concentrated sulfuric acid. The composite proton exchange membranes were characterized by Fourier Transform Infrared Spectrometer and X-ray diffraction. The results showed chemical absorption formed between poly(vinylidene fluoride) and BaTiO₃. The proton conductivity and vanadium ion permeability of the membranes were determined by two-electrode AC impedance and

UV-visible spectrophotometry, respectively. The experimental results showed that the addition of BaTiO₃ decreased the permeability of V (IV) ions significantly. Proton conductivity reached 1.11S/cm when the BaTiO₃ content of composite proton exchange membranes was at 5%. Upon the introduction of 15% BaTiO₃, tensile strength increased from 30.20 Mpa to 37.35 Mpa and Young's modulus increased from 324.62 Mpa to 385.9 Mpa.

Keywords: BaTiO₃; PVDF-g-PSSA; Proton exchange membrane

1. Introduction

The vanadium redox flow battery (VRB) is a kind of new rechargeable battery with excellent advantages, such as low cost, high capacity, long cycle life [1]. Proton exchange membrane (PEM) is one of the most important materials for VRB. It is usually used to separate the anode and cathode electrolytes. The ideal exchange membranes should be equipped with high ionic conductivity, low permeability of vanadium ions, good chemical stability and low cost [2]. However, the present widely used PEM materials, such as Nafion series, are very expensive. Therefore, much work has been devoted to develop new proton exchange membranes, including inorganic-organic composite membranes [3, 4], graft membranes [5-7], blend composite membranes [8] etc. It is evident that composite membranes have many advantages: reducing ion permeability, increasing mechanical properties, reducing cost.

Poly(vinylidene fluoride) (PVDF) is one of ferroelectric polymer materials with low cost, good chemical stability and mechanical properties [9]. To achieve various performance objectives, ferroelectric ceramics such as BaTiO₃ (BT) [10], Pb(Zr,Ti)O₃ (PZT) [11] and LTNO [12] have been used as fillers in polymers. The ferroelectric ceramic/PVDF composite materials overcome the defect of polymeric materials and the ferroelectric ceramics. In this study, BaTiO₃/Poly(vinylidene fluoride) (BT/PVDF)

membrane was prepared. Moreover, we attempted to modify BT/PVDF membrane to make it to be PEM with high performance. Therefore, BT/PVDF membrane as base membrane were grafted with styrene monomer and then sulfonated in concentrated sulfuric acid. A series of BaTiO₃/poly(vinylidene fluoride)-g-polystyrene sulfonated acid (BT/PVDF-g-PSSA) composite proton exchange membranes were prepared. Solution uptake, proton conductivity, the permeability of V (IV) Ions and mechanical properties of composite membranes were tested.

2. Experimental method

x BT/PVDF (x=0, 1 %, 3 %, 5%, 10 %, 15 %) membranes were prepared by tape casting. The x was the weight percentage of BaTiO₃. BaTiO₃ was dispersed in 30 mL of N, N-dimethyl formamide in a round bottom flask and dispersed in an ultrasonic bath for 1 h. Then PVDF powder was added to the suspension. The mixture was stirred at 60 °C for 2 h. An appropriate amount of the casting polymer solution was uniformly dumped on a silicon wafer at room temperature for 10 min to remove air bubble and then dried at 80 °C under vacuum for 1 h. These membranes were washed with acetone to remove impurity on its surface and dried at 50 °C under vacuum for 24 h. Then the membranes were immersed into 0.07 mol/L KOH in ethanol at 80 °C for 45 min. Before grafting, the membranes were washed with deionized water until reaching a constant pH, then, they were quickly immersed into 20% (v/v) styrene in tetrahydrofuran. Benzoyl peroxide, with a concentration of 0.4 g/100 mL, was added as the radical initiator. The mixture was bubbled by Nitrogen gas for 20 min to remove dissolved oxygen. And the grafting reaction was performed at 80 °C under nitrogen atmosphere. Then, the membranes were sonicated with dichloromethane for 2 h to remove the unreacted monomer and homopolymer. The sulfonation was conducted by immersing the membranes which were swelled in 1, 2-dichloroethane at 60 °C for 2 h in

concentrated sulfuric acid for 4 h at 70 °C. Finally, the membranes were washed with deionized water for several times to remove the remaining sulfuric acid.

The degree of grafting was determined according to equation 1

$$DG = \frac{m_1 - m_0}{m_0} \times 100\%$$

1

Where m_0 and m_1 are the weights of BT/PVDF and BT/PVDF-g-PS.

Solution uptake was measured by immersing the membrane into 1 mol/L H_2SO_4 at room temperature for 24 h. It can be calculated from equation 2

$$SU = \frac{m_2 - m_1}{m_1} \times 100\%$$

2

Where m_1 and m_2 are the weights of wet and dried BT/PVDF-PSSA membranes.

Fourier transform infrared spectra (FTIR) of the membranes were measured using a Nicolet Avatar 380 operated by Attenuated Total Reflectance (ATR). The morphology of membrane was observed by scanning electron microscope (JEOL JSM-6460 LV). XRD measurements of the blend membranes were recorded on X-ray Diffractometer (Rigaku D/Max II B).

Proton conductivity in plane direction of the membrane was determined by measuring the impedance spectroscopy on PARSTAT2273 electrochemical workstation (AMETEK, Inc.) at 25 °C. The measurement used 2-point probe AC impedance method in the frequency region 1 Hz to 1 MHz with oscillating voltages of 5 mV. Before using, the membrane was immersed in 1.0 mol/L H_2SO_4 for 24h. Proton conductivity can be calculated from equation 3

$$\sigma = \frac{d}{A} \left(\frac{1}{R} - \frac{1}{R_0} \right) = \frac{d}{A} \cdot \frac{1}{R}$$

Where σ (S/cm) is proton conductivity, d (cm) is the thickness of the membrane, A (cm²) is the effective area of the membrane, R_1 (Ω) is the resistance of solution, R_0 (Ω) is the resistance of 1.0 mol/L H₂SO₄, and R_2 (Ω) is the resistance of membrane.

The equipment used for the measurement of the permeability of vanadium ions (IV) had two reservoirs. The left reservoir was filled with 0.5 mol/L VOSO₄ in 1.0 mol/L H₂SO₄. The right reservoir was filled with 0.5 mol/L MgSO₄ in 1.0 mol/L H₂SO₄. The membrane was between two solutions. Samples of solution from the right reservoir were taken at a regular time interval and analyzed for vanadium ion concentration with UV-Vis spectrophotometer (Hitachi U-3900). It was supposed that the change in vanadium ion concentration in the left reservoir could always be negligible during the calculation of permeability, due to the fact that the concentration of the vanadium ion in the right reservoir is low. Inside the membrane, a pseudo-steady-state condition was used. Accordingly, the flux of the vanadium ion is constant, and its concentration in the right reservoir as a function of time is given by equation 4

$$V_R \frac{dC_R}{dt} = APLC_L - CRt$$

4

Where C_L is the vanadium ion concentration in the left reservoir, and $C_R(t)$ refers to the vanadium ion concentration in the right reservoir as a function of time. A and L are the area and thickness of the membrane, P is permeability of the vanadium ions, and V_R is the volume of right reservoir, respectively. An assumption is also made here that P is independent of concentration.

Hardness and strength of the materials are the important factors to evaluate the value of the materials.

The standard membrane was stretched in 50 mm/min on Electronic Universal Material Testing Machine to test its stress and strain.

3. Results and discussions

As shown in Fig. 1, the infrared spectra of BT/PVDF revealed the C-F stretching vibration in the range of 1164-1172 cm^{-1} , and a slight move of C-F stretching vibration to higher wavenumber with the increase of BaTiO_3 . The reason for that was chemical absorption, which reduced the polarity of C-F and increased bond force, formed since it is easy for F to enter into oxygen vacancies existed in BaTiO_3 crystal [13].

The FTIR spectra of PVDF, retreated PVDF, PVDF-g-PS, PVDF-g-PSSA were presented in Fig. 2. The peak at 1404 cm^{-1} was designated to CH_2 formation vibration. The peak at 1240 cm^{-1} was designated to CF_2 stretching vibration and CH_2 out-of-plane bending vibration. The peak at 1168.5 cm^{-1} was the stretching vibration of CF_2 . The absorption peak of C-C appeared at 1068 cm^{-1} . The asymmetrical stretching vibration of C-C was at 870 cm^{-1} . The peak at 836 cm^{-1} was formed due to C-C skeletal deformation vibration. The formation vibration of CF_2 was located at 746 cm^{-1} . As shown in the FTIR spectroscopy of retreated PVDF, the weak absorption peak at 1592 cm^{-1} was C=C stretching vibration. Meanwhile, the peak at 1240 cm^{-1} disappeared. The in-plane bending vibration and out-of-plane bending vibration of C-H in benzene ring from PSSA was located at 744 cm^{-1} and 697 cm^{-1} . At the same time, the S-O bond in sulfonic acid ester could be also located at about 1004 cm^{-1} .

The XRD patterns of the membranes were presented in Fig. 3. The peak at 20.3° corresponded to the (110) and (200) planes in the pure PVDF membrane which was the characteristic peak of β crystal phase. The peaks at 17.6 ° and 18.3 ° corresponded to the (100) and (020) planes which were the characteristic

peaks of α crystal phase [9]. It suggested that PVDF is semi-crystal. For PSSA, there was only a wide peak with a low intensity. This implied that PSSA was amorphous. With the increase of BT, the peak at 20.3° became stronger in the blend membranes. This meant that the membrane crystallinity increased after the addition of BT.

With the increase of BT, the graft ratio was gradually decreased, as shown in table 1. Because it was more prone to form chemical adsorption between PVDF and BT. Higher content of BT was in the membrane, more oxygen vacancies would occur in the system, and more F^- would enter into oxygen octahedron of the BT. It led to the reduction of double bonds in the pretreatment of PVDF with KOH and the degree of grafting. Moreover, this phenomenon resulted in the decrease of strongly hydrophilic sulfonic acid groups on the branched chain. So solution uptake had a downward trend with the increase of BT. However, solution uptake reached 161.16% when BT content was at 5%. The reason was that a microphase separation could be formed between highly hydrophobic C-F skeleton and sulfonic acid group [14], so appropriate C-F skeleton in PVDF-g-PSSA membranes could increase solution uptake.

As shown in Fig. 4, the semi-circular which represented the charge transfer resistance (R_{ct}) in the IF region disappeared because of the quick transfer of the electric charge on platinum electrode, while the straight line which represented the mass transfer process in the IF region still exists. This showed that this system was controlled by the mass transfer process. In the Niquist impedance plots, the intersection of the curve with the real axis is called solution resistance (R_s). It was observed from table 2 that the results of proton conductivity increased gradually with the increase of BT until the content of BT reached 5%. The jump was due to hydrophobic / hydrophilic phase separation which provided favorable channels for protons.

Fig. 5 showed the relationships of the concentration of vanadium ions in the right reservoir with time. It can be seen that the concentration of vanadium ions in the right reservoir for PVDF-g-PSSA membrane increased faster than that for the BT/PVDF-g-PSSA membranes. The vanadium ion permeability P inside the membrane was listed in table 2. With the increase of BT, the permeability of V (IV) Ions decreased. This is because chemisorption was formed between BT and PVDF which made the channel in the membrane narrow, making it more difficult for vanadium ions to pass.

Mechanical properties of the membranes, such as tensile strength and modulus, strongly influence the fabrication conditions of IPMCs and also have an effect on the blocking force and durability of the final actuators [15]. The rigid fillers commonly tend to increase the stiffness of the material but they may decrease its strength and strain at break [16]. The mechanical properties of BT/PVDF-g-PSSA dry membranes were measured in room temperature. Table 3 showed the comparison of the mechanical properties with average values of the experimental data. We could observe that 1%BT/PVDF-g-PSSA membranes had the max value of Young's modulus. But its value reduced when content of BT reached 3% and then a nearly linear increased with nanoparticle content, with an overall improvement in modulus for nanocomposites. Tensile strength behaved similarly. The PVDF-g-PSSA membrane had higher values of elongation at break than the other membranes. With the increase of BT, the values of elongation at break became lower and lower. Further addition of BT reduced elongation at break of the composites. The crystallinity of the composite membranes improved due to the addition of BT. Crystal makes the molecular chain close and orderly, reduces porosity and enhances intermolecular forces. But the filler was equivalent to the introduction of impurities and defect. It will accelerate the destruction once cracks are triggered.

4. Conclusions

BaTiO₃/PVDF-g-PSSA composite membranes structures test by related methods. The proton conductivity and vanadium ion permeability of the membranes were determined by two-electrode AC impedance and UV-visible spectrophotometry, respectively. Proton conductivity reached 1.11 S/cm when BT content of composite proton exchange membranes was at 5%. This is because a micro phase separation, which provides favorable channels for protons, forms between highly hydrophobic C-F skeleton and sulfonic acid group. The infrared spectra illustrate that the channel in membrane narrows due to chemisorption between BT and PVDF. So the addition of BT can reduce the permeability of vanadium ions in vanadium battery during operation. Meanwhile, the tensile strength and Young's modulus of the composite membranes improved when BT content was at 15%. The results showed BaTiO₃/PVDF-g-PSSA membranes possessed the potential for use as proton exchange membranes in vanadium redox flow battery.

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Fig.1 The FTIR spectra of BT/PVDF membranes

Fig. 2 The FTIR spectra of PVDF, retreated PVDF, PVDF-g-PS, PVDF-g-PSSA.

Fig. 3 The XRD patterns of the membranes

Fig. 4 Nquist impedance plots for the membranes

Fig. 5 $V(IV)$ concentrations in the right reservoir of the cell with BT/PVDF-PSSA membranes.

Table1 DG and SU of the membranes

Sample	BT (wt %)	DG (%)	SU (%)
PVDF-g-PSSA	0	63.94	160.47
1% BT/PVDF-g-PSSA	1	62.01	111.91
3% BT/PVDF-g-PSSA	3	57.54	114.07
5% BT/PVDF-g-PSSA	5	53.15	161.16
10% BT/PVDF-g-PSSA	10	25.72	102.35
15% BT/PVDF-g-PSSA	15	19.54	90.56

Table 2 Results of proton conductivity and the permeability of V(IV) Ions

Sample	$R_0 (\Omega)$	$R_1 (\Omega)$	R_2 (Ω)	d (cm)	σ (S/cm)	Permeability of VO^{2+} (cm^2/min)
PVDF-g-PSSA	14.17	14.63	0.46	0.08	0.054	9.02×10^{-5}
1%BT/PVDF-g-PSSA	14.17	14.43	0.26	0.08	0.095	7.13×10^{-5}
3%BT/PVDF-g-PSSA	14.17	14.26	0.09	0.08	0.27	7.03×10^{-5}
5%BT/PVDF-g-PSSA	14.17	14.19	0.02	0.07	1.115	5.76×10^{-5}
10%BT/PVDF-g-PSSA	14.17	14.51	0.34	0.04	0.037	2.84×10^{-5}
15%BT/PVDF-g-PSSA	14.17	14.60	0.43	0.05	0.0366	1.99×10^{-5}

Table 3 The mechanical properties of BT/PVDF-g-PSSA membranes

Sample	Tensile strength (Mpa)	Elongation at break (%)	Young's modulus (Mpa)
PVDF-g-PSSA	30.20	115.80	324.62
1%BT/PVDF-g-PSSA	30.52	95.76	381.66
3%BT/PVDF-g-PSSA	27.40	94.64	284.50
5%BT/PVDF-g-PSSA	29.58	89.08	291.93
10%BT/PVDF-g-PSSA	33.31	87.96	291.37
15%BT/PVDF-g-PSSA	37.35	52.33	385.9