Amphoteric ion exchange membrane synthesized by radiation-induced graft copolymerization of styrene and dimethylaminoethyl methacrylate into PVDF film for vanadium redox flow battery applications

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Abstract

Poly(vinylidene difluoride) (PVDF) film was grafted with styrene (St) and dimethylaminoethyl methacrylate (DMAEMA) using γ-irradiation techniques. Through subsequent sulfonation and protonation processes, a new kind of amphoteric ion exchange membrane (AIEM) was synthesized. The grafting yield (GY) increased with absorbed dose and leveled off at about 60 kGy. The composition of poly(St-co-DMAEMA) grafts was correlated to the ratio of St to DMAEMA monomer in the feed. Micro-FTIR and XPS analyses testified that the grafting and sulfonation of St unit in poly(St-co-DMAEMA) grafts had been carried out as designed. Further characterizations showed that the properties of the AIEM strongly depended on the composition and GY of the film, i.e. higher content of DMAEMA brought lower permeability of vanadium ions and conductivity, while higher GY led to higher water uptake, ion exchange capacity (IEC) and conductivity. Finally, an AIEM with a GY of 26.1% was assembled and tested in the vanadium redox flow battery (VRFB) system. It was found that the VRFB assembled with the AIEM maintained an open circuit voltage (OCV) higher than 1.2 V after placed for 68 h, which was much longer than that with the Nafion117 membrane. Therefore, this work provides a novel method to develop potential substitute of Nafion membranes to be applied in VRFB system.

1. Introduction

Since the vanadium redox flow battery (VRFB) was proposed by Skylas-Kazacos in 1985 [1,2], it has attracted more and more attention as a promising energy storage system. Ion exchange membrane (IEM) is the key component of the battery and should possess the following properties to obtain a high energy efficiency and long cycle life: high ionic conductivity; low permeability of vanadium ions; good chemical stability and low price. Unfortunately, up to now the commercial membranes cannot satisfy all of the above requirements. For instance, some of the membranes show poor stability in VRFB electrolyte solution due to the oxidation degradation induced by VO2+ [3], while some of the membranes with good stability suffer from the crossover of vanadium ions, which causes serious self-discharge of the battery [4]. Consequently, research on exploiting IEMs with improved properties is of great importance to the large-scale application of VRFB.

Radiation grafting technique has been widely used as an alternative route to prepare IEMs for electrochemical applications [5–9]. This technique has exhibited obvious advantages over traditional methods that the composition and resulting properties of the membrane can be easily controlled by applying appropriate grafting conditions. Various hydrocarbon and fluorocarbon films have been used as base films to prepare IEM using this technique. Comparing with the hydrocarbon polymers, the fluorocarbon polymers were much more favored due to their outstanding thermal and chemical stability, which makes them particularly suitable for preparing highly stable IEMs. PVDF [10], poly(tetrafluoroethylene) (PTFE) [11], poly(ethylene-co-tetrafluoroethylene) (ETFE) [5], poly(tetrafluoroethylene-co-hexafluoro-propylene) (FEP) [8], etc. have been grafted with different monomers to prepare a variety of IEMs, which have exhibited satisfying chemical stability in fuel cell or VRFB. Nevertheless, the application of these membranes in VRFB is still limited due to the respective shortcomings. For
instance, cation exchange membranes usually exhibit high conductivity but suffer from high permeability of vanadium ions [4], while anion exchange membranes effectively suppress the vanadium ions crossover but are simultaneously restricted by lower conductivity [12,13]. Accordingly, a novel IEM that combines high conductivity and low vanadium ions crossover is prerequisite for the industrialization of VRFB.

The amphoteric ion exchange membrane (AIEM) with both cation and anion exchange capabilities was first proposed by Sollner in 1932 [14]. Due to the controllability of the ion exchange property by adjusting the composition or the external conditions, the AIEM is expected to have potential applications in many fields [15–17]. Several kinds of IEMs by introducing anion exchange groups to the cation exchange membrane like Nafion117 have been applied in VRFB [18–21]. It has been found that the crossover of vanadium ions through these membranes has been suppressed as the anion exchange groups incorporated, and meanwhile these membranes maintain a rather high conductivity. Besides, the water transport through the membrane has been also reduced due to the decrease in vanadium ions permeation.

In this work, a novel AIEM is to be prepared via a handy radiation grafting approach. The parameters of the preparation procedure, as well as the characteristics of the resulting AIEM are to be investigated. The loading test of AIEM in the VRFB system is to be performed to evaluate the prospect for its application in VRFB systems.

2. Experimental

2.1. Materials

PVDF film with a thickness of 20 μm was supplied by Kureha Company (Japan) and used as the base film. St and DMAEMA (Acros) with a purity of more than 99% was used without further purification. Chlorosulfonic acid was purchased from Beijing Yili Fine Chemical Co. Ltd. VOSO₄·3H₂O (analytical reagent) was supplied by Shanghai Luyuan Fine Chemical Plant. Nafion117 membrane (Du Pont) was immersed into deionized water for 24 h prior to use.

2.2. Preparation of the AIEM

The preparation route of the AIEM is shown in Fig. 1. A piece of PVDF film was washed with acetone and dried to constant weight. Then the film with known weight was immersed into monomer solution of acetone. After bubbling with nitrogen for about 15 min and sealed, the sample was subjected to γ-ray irradiation from a 60Co source (Peking University). After irradiated with certain absorbed dose, the film was placed in a Soxhlet’s extraction device to remove the residue monomers and homopolymers by acetone for 24 h. Then the film was dried to constant weight in vacuum and weighed. GY was calculated as follows:

\[
GY (\%) = \frac{W_g - W_0}{W_0} \times 100
\]

where \(W_g\) and \(W_0\) are weights of the film after and before grafting, respectively.

To study the effect of the monomer ratio on the membrane properties, three monomer solutions (total concentration of 2 M) with St/DMAEMA mole ratios of 3:1, 1:1 and 1:3 were used. The grafted film was sulfonated in a 0.2 M chlorosulfonic acid solution of 1,2-dichloromethane at room temperature for 8 h, and then hydrolyzed with distilled water at 60 °C overnight. After that, the film was protonated in 1 M HCl for 6 h, and then kept in distilled water at room temperature prior to further characterization.

2.3. Micro-FTIR and elemental analysis of the grafted film

Micro-FTIR analysis was performed on a Nicolet (Magna-IR 750) spectrometer. The spectra were measured in absorbance mode in a wave number range of 4000–600 cm⁻¹.

To determine the content of St and DMAEMA, the grafted film was subjected to elemental analysis using an Elementar Analysensysteme GmbH (model: vario EL). The mole ratio of DMAEMA to St \(n_{\text{DMAEMA}}/n_{\text{St}}\) in poly(St-co-DMAEMA) grafts was determined according to the following equation:

\[
\frac{n_{\text{DMAEMA}}}{n_{\text{St}}} = \frac{104(100 + GY)P_n}{14G - (100 + GY)P_{157}}
\]

where \(P_n\) is the content of nitrogen; 14, 104 and 157 are molar mass of nitrogen, St and DMAEMA, respectively.

The X-ray photoelectron spectroscopy (XPS) analysis was performed with an AXIS-Ultra instrument from Kratos Analytical using monochromatic Al Kα radiation (225 W, 15 mA, 15 kV) and low-energy electron flooding for charge compensation. To compensate for surface charges effects, binding energies were calibrated using C

Fig. 1. Preparation route of the AIEM.
1s hydrocarbon peak at a binding energy (BE) of 284.8 eV. The data were converted into VAMAS file format and imported into CASA XPS software package for manipulation and curve fitting.

2.4. IEC, ion conductivity and water uptake of the AIEM

For anion exchange capacity measurement, a piece of dried AIEM with certain weight was immersed into 0.05 M HCl solution overnight and stirred occasionally. The anion exchange capacity was determined by titrating the above solution with 0.05 M NaOH solution.

In contrast, to determine the cation exchange capacity, a piece of dried AIEM with certain weight was immersed into 0.05 M NaOH solution for 24 h. Then the solution was titrated with 0.05 M HCl solution.

The proton conductivity of the AIEM was obtained by impedance spectroscopy measurement using a CHI660 electrochemical work station with an AC perturbation of 10 mV. The AIEM was hydrated for 24 h before determination and clamped between two Pt electrodes for recording of the impedance spectroscopy. The proton conductivity (σ) was calculated as

\[ \sigma = \frac{L}{R \cdot S} \]  

where R is the real impedance taken at zero imaginary impedance in the impedance spectroscopy, L and S are the thickness and area of the AIEM between the electrodes, respectively.

To evaluate the water uptake of AIEM, the sample with a certain weight was immersed into deionized water. After equilibrating for 24 h, the membrane was taken out and the water adhering to the surface was quickly wiped using filter paper, and then the membrane was weighed again. The water uptake was calculated according to the following equation:

\[ \text{Water uptake (\%) } = \frac{W_w - W_d}{W_d} \times 100 \]  

where \( W_w \) and \( W_d \) are the weights of the AIEM in the wet and dry state, respectively.

2.5. Permeability of vanadium ions through the AIEM

The permeability of vanadium ions through the AIEM was investigated using the equipment as shown in Fig. 2. 1.5 M V(IV) solution was prepared by dissolving VOSO\(_4 \cdot 3\)H\(_2\)O in 2 M H\(_2\)SO\(_4\) solution. As shown in Fig. 2, the left reservoir was filled with vanadium ion solution and the right one was filled with a 1.5 M MgSO\(_4\) in 2 M H\(_2\)SO\(_4\) solution. MgSO\(_4\) was used to balance the ionic strength and reduce the osmotic pressure. The area of the membrane exposed to the solution was 1.77 cm\(^2\) and the volume of solutions in both sides was 25 mL. The MgSO\(_4\) solution was taken for inductively coupled plasma atomic emission spectrometry (ICP-AES) (Leeman, Profile) analysis at a regular time and the concentration of vanadium ions in the solution was determined. The permeability of vanadium ions through the Nafion117 membrane was also tested using the same method for comparison.

2.6. VRFB performance of the AIEM

The VRFB was fabricated by sandwiching the membrane between two pieces of graphite carbon electrodes. 1.5 M V(II)/V(III) and V(IV)/V(V) in 2.5 M H\(_2\)SO\(_4\) solutions were used as the electrolytes in the positive and negative half cells, respectively. The membrane area was 5 cm\(^2\) and the volume of the electrolytes solution in each half cell was 40 mL. The artificial cell was charged to 1.6 V at a current density of 40 mA cm\(^{-2}\). The OCV was measured then at room temperature.

3. Results and discussion

3.1. Synthesis of the AIEM

Fig. 3 shows the effect of dose on the GY of grafted PVDF film. It can be seen that GY increases with dose and levels off after about 60 kGy. At a dose of 20 kGy, grafted PVDF film with a GY of about 30% can be prepared. Moreover, it can be seen from Table 1 that the initial monomer ratio has less effect on the total GY but strongly affect the \( n_{\text{DMAEMA}}/n_{\text{HS}} \) in poly(St-co-DMAEMA) grafts. Similar phenomenon has also been observed in radiation-induced graft copolymerization of St and DMAEMA into PTFE film [22]. One reason is that St and DMAEMA tend to react with each other to form a kind of alternate copolymer according to their reactivity ratios calculated using Fineeman-Ross method, \( r_1 = 0.510 \) and \( r_2 = 0.716 \) [23]. Another one is that the radical yield of St is higher than that of DMAEMA in the same condition [22,23]. Therefore, when DMAEMA/St increased from 1:3 to 3:1 in the feed, \( n_{\text{DMAEMA}}/n_{\text{HS}} \) only increased from ca. 0.4 to 1.4.

The grafted film is further sulfonated and protonated to synthesize a new kind of AIEM (Fig. 1). The composition of the AIEM can be easily modulated by controlling the initial monomer ratio, which is advantageous to the application in VRFB. Because the AIEM with higher content of DMAEMA may exhibit lower permeability of vanadium ions due to the Donnan exclusion effect between –R\(_n\)NH\(^+\) groups of protonated DMAEMA unit and vanadium ions, while higher content of St will lead to higher conductivity after subsequent sulfonation.
Table 1
Elemental analysis and conductivity of the AIEM with different compositions.

<table>
<thead>
<tr>
<th>DMAEMA/St in the feed</th>
<th>Dose (kGy)</th>
<th>GY (%)</th>
<th>Weight percent (%)</th>
<th>r_{DMAEMA}/n_{St} in the grafted film</th>
<th>Conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10</td>
<td>11.9</td>
<td>P_f (1.31) = 0.42</td>
<td>0.42</td>
<td>0.027</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>17.2</td>
<td>P_f (1.31) = 0.43</td>
<td>0.040</td>
<td>0.038</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>25.9</td>
<td>P_f (1.31) = 0.67</td>
<td>0.71</td>
<td>0.052</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>11.6</td>
<td>P_f (1.31) = 0.48</td>
<td>0.81</td>
<td>0.024</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>18.1</td>
<td>P_f (1.31) = 0.54</td>
<td>0.78</td>
<td>0.033</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>26.1</td>
<td>P_f (1.31) = 0.81</td>
<td>1.05</td>
<td>0.046</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>12.1</td>
<td>P_f (1.31) = 0.79</td>
<td>1.45</td>
<td>0.019</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>17.9</td>
<td>P_f (1.31) = 0.97</td>
<td>1.41</td>
<td>0.029</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>24.7</td>
<td>P_f (1.31) = 1.22</td>
<td>1.49</td>
<td>0.037</td>
</tr>
</tbody>
</table>

3.2. Effect of the membrane composition on the conductivity and permeability of vanadium ions

To evaluate the effect of membrane composition on the properties of the AIEM, the conductivity and permeability of vanadium ions of the AIEM with different composition was tested. It can be seen from Table 1 that conductivity of the AIEM increases with the content of St. The AIEM with r_{DMAEMA}/n_{St} of 0.42 and the GY of 25.9% gives a rather high conductivity, i.e. 0.052 S/cm. This can be attributed to the fact that the conducting of proton is mainly carried out by the sulfonic groups of the AIEM.

The crossover of vanadium ions through the IEM has been a serious problem to the VRFB as it causes serious self-discharge and results in low efficiency. In our previous work [13], a kind of anion exchange membrane has been prepared by radiation grafting of DMAEMA. Comparing with Nafion117 membrane, it was found that the permeability of vanadium ions through the anion exchange membrane with a GY of 40% has been reduced to only 1/20–1/40 of that through Nafion117 membrane, which is due to the Donnan exclusion effect between the cations in the membrane and the vanadium ions. Mohammadi and Skyllas-Kazacos [19] have prepared several kinds of IEMs by composing cation exchange membranes with anion exchange resin to obtain a better performance. However, the membrane stability is not satisfying according to the preparation procedure [19,30]. Recently, the IEMs prepared by introducing cation charged groups onto the Nafion117 membrane have also been proposed [18,20,21]. It was found that the permeability of vanadium ions through the membrane is evidently reduced because of the Donnan exclusion effect, meanwhile rather high conductivity was still maintained. These works are beneficial to the membrane design for VRFB in despite of the slightly decrement of conductivity after modification. Nevertheless, the high cost of the Nafion117 membrane will still be a problem making against to the commercialization of VRFB.

The permeability (P) of vanadium ions through the prepared AIEM was measured here. The change of the vanadium concentration in MgSO4 side with time is shown in Fig. 6. It can be seen that the concentration of vanadium ions in MgSO4 side for Nafion117 membrane increased much faster than that for the AIEM. As for the AIEM with different composition, it can be found that the concentration of vanadium ions decreases with increasing the content of DMAEMA, which can be explained that high content of DMAEMA leads to more significant Donnan exclusion effect and therefore lower permeability of vanadium ions. The concentration of vanadium ions in the MgSO4 side as a function of time can be defined according to the following equation:

\[
\frac{d c_v}{d t} = \frac{P}{L} (c_0 - c_t)
\]
where \( V \) is the volume of the solution in both sides; \( S \) is the area of the membrane exposed to the solution; \( P \) is the permeability of vanadium ions; \( L \) is the thickness of the membrane; \( c_0 \) is the initial concentration of the vanadium solution in the left reservoir; \( c_t \) is the vanadium concentration in the MgSO\(_4\) side at time \( t \). Assumption is made that \( P \) is independent on the concentration.

According to Eq. (5) and Fig. 6, the permeability \( P \) through the AIEM and Nafion117 membrane has been calculated and listed in Table 2. It can be found that the permeability of V(IV) through the AIEM is only about 1/10 of that through the Nafion117 membrane. Moreover, as \( n_{\text{DMAEMA}}/n_{\text{St}} \) increases from 0.42 to 1.45, \( P \) decreases by about 25%.

Accordingly, the AIEM has shown low permeability of vanadium ions as well as a rather high conductivity. The results were contributed to the fact that multivalent vanadium cations are difficult to be adsorbed onto the cationic charged AIEM compared to hydrogen proton because of Donnan exclusion effect [31]. Moreover, it can be concluded from the above results that the composition is of great importance to the membrane conductivity and permeability of vanadium ions. On the other hand, by controlling the grafting conditions, such as the initial monomer ratio or \( GY \), the AIEM with required properties can be prepared through a convenient approach. To further investigate the effect of \( GY \) on membrane properties, the AIEM prepared in the solution with monomer ratio of 1:1 was characterized in the following.

### 3.3. Effect of \( GY \) on IEC, ionic conductivity and water uptake

The effect of \( GY \) on the cation and anion exchange capacity of the AIEM is shown in Fig. 7. It can be seen that both of the cation and anion exchange capacities increase with \( GY \) of the AIEM. Moreover, the cation exchange capacity is higher than the anion exchange capacity at all \( GY \), which accords with the results obtained in the elemental analysis and further indicated that the sulfonation process has been completely carried out. For the AIEM with a \( GY \) of 26.1%, the AIEM has a cation exchange capacity of 0.83 mmol g\(^{-1}\) and an anion exchange capacity of 0.71 mmol g\(^{-1}\). The IEC of Nafion117 membrane is reported as 0.98 mmol g\(^{-1}\), which is a little higher than the cation exchange capacity of the AIEM with a \( GY \) of 26.1%.

The relationship between the conductivity and \( GY \) of the AIEM is shown in Fig. 8. Obviously, the conductivity of the AIEM increases with the \( GY \), which is attributed to the fact that more ion exchange groups are introduced into the membrane at high \( GY \). At a \( GY \) of 26.1%, the AIEM possesses a conductivity of 0.046 S cm\(^{-1}\), which is similar to that of Nafion117 membrane (0.05 S cm\(^{-1}\)). In our previous work [13], a kind of anion exchange membrane has been

### Table 2

Permeability of vanadium ions through the AIEM with different composition and Nafion117 membrane.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Thickness (µm)</th>
<th>( n_{\text{DMAEMA}}/n_{\text{St}} )</th>
<th>( P \times 10^{-7} \text{ cm}^2/\text{min} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion117</td>
<td>178</td>
<td>–</td>
<td>7.93</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0.42</td>
<td>0.91</td>
</tr>
<tr>
<td>AIEM</td>
<td>25</td>
<td>0.88</td>
<td>0.73</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>1.49</td>
<td>0.67</td>
</tr>
</tbody>
</table>
prepared using radiation grafting technique and it was found that the conductivity of the anion exchange membrane is lower than that of the AIEM at the same GY. The increase in conductivity is attributed to the sulfonic groups introduced by sulfonation of St unit in poly(St-co-DMAEMA) grafts, which is favored to the proton conducting.

Water uptake is an important property of the IEM as it relates to the conductivity and dimensional stability of the membrane. The water uptake of the AIEM in deionized water is also shown in Fig. 8. As expected, high GY leads to high water uptake, indicating the increase of hydrophilicity within the hydrophobic PVDF membrane, which is due to the incorporation of more ion exchange groups as a consequence of the increase in GY. As shown in Fig. 8, at ca. 26.1% GY, the water uptake of the AIEM is about 36%, which is slightly higher than that of the Nafion117 membrane (30%).

3.4. OCV of VRFB with the AIEM

The OCV result of VRFB with the AIEM is shown in Fig. 9. It has been found that OCV of the VRFB assembled with the Nafion117 membrane decreased rapidly after staying for about 14 h [13,18]. In contrast, the VRFB assembled with the AIEM with a 26.1% GY exhibits a much better performance: maintaining OCV above 1.2 V for about 68 h, which is much longer than that obtained with the Nafion117 membrane. The OCV performance indicates that the self-discharge of the VRFB with Nafion117 is more serious than that of the VRFB with the AIEM, which is corresponding to the permeability test, i.e. much lower permeability of vanadium ions through the AIEM than that through the Nafion117 membrane. Accordingly, due to much lower permeability of vanadium ions through the AIEM, the VRFB assembled with the AIEM is expected to have lower degree of self-discharge and higher energy efficiency, which will be investigated in further experiments.

4. Conclusions

A novel AIEM aiming for VRFB applications has been prepared through a radiation grafting approach. Further characterization shows that the AIEM with required properties can be conveniently prepared by choosing proper grafting conditions like the initial monomer ratio and the absorbed dose. The obtained AIEM has exhibited the advantages over both anion and cation exchange membranes in VRFB: much lower permeability of vanadium ions than cation exchange membranes due to the Donnan exclusion effect; higher conductivity comparing to the exchange membranes. We hope that this work provides a convenient method for preparing new kinds of IEMs for VRFB and other applications.

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References


