Preparation and characterization of Nafion/SPEEK layered composite membrane and its application in vanadium redox flow battery

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1. Introduction

In the past several decades, much attention has been focused upon the research and development of vanadium redox flow battery (VRB) because of its long cycle life, flexible design, fast response time, deep-discharge capability, and low cost in energy storage [1,2,3]. It employs \(V^{2+}/V^{3+}\) and \(VO^{2+}/VO^{2+}\) redox couples in the negative and positive half-cell electrolytes which are separated by an ion exchange membrane. The function of the ion exchange membrane is to prevent cross mixing of the positive and negative electrolytes, while still allowing the transport of ions to complete the circuit during the passage of current. Consequently, an ion exchange membrane suitable for VRB application should exhibit low permeation rates of the active species to minimize self-discharge, and also should have low area resistivity to minimize losses in voltage efficiency. Finally, the membrane should possess good chemical stability and low cost.

Previous studies showed that most early types of commercial ion exchange membranes (e.g., Sellemion® CMV, CMS, AMV, DMV, ASS, DSV: Asahi Glass Co., Japan; Dow XUS1 3204.10: Dow Chemical Co., USA; K142: Asahi Chemical Co. Ltd., Japan) are unsuitable for VRB application due to their oxidation decomposition by the highly oxidizing pentavalent vanadium ions (\(VO_2^{2+}\)) in the positive half-cell electrolyte of VRB, which make them unable to offer long cycle life when used in the VRB system [2,4]. Up to now, the perfluorinated sulfonic acid membranes (e.g., Nafion membrane) have been generally used in practical VRB system due to its high ionic conductivity and excellent chemical stability in the positive electrolytes. However, as an indispensable component of VRB system, its high price (presently, $800 m^{-2}$) and the difficulty involved in its disposal still lie ahead before the successful commercial development of the VRB system. Furthermore, the crossover of vanadium ions through Nafion membrane will lead to a loss of electrochemical energy during the operation of VRB system [5]. Consequently, it is of great significance to seek for ion exchange membrane that can combine excellent chemical stability, high VRB performance and low cost for the VRB system.

In recent year, multilayered composite membrane containing a layer of non-fluorinated ionomer membrane and two outer layers of recast perfluorinated sulfonic acid membrane (e.g., Nafion membrane) has been fabricated and applied in proton exchange membrane fuel cells (PEMFC) and direct methanol fuel cells (DMFC) [6,7,8,9]. The perfluorinated sulfonic acid membrane layer of multilayered composite membrane was designed to prevent oxidation degradation of the non-fluorinated ionomer membrane. The non-fluorinated ionomer membrane layer of multilayered composite...
membrane could lead to significant cost reduction for the production of fuel cell system. Moreover, several non-fluorinated ionomer membrane such as sulfonated poly(ether ether ketone) (SPEEK) membrane could effectively block the fuel permeation. This multilayered approach to membrane fabrication may be a promising strategy to circumvent the contradictory problems of cost and chemical stability in fuel cell system.

Up to now, many efforts have been focused on hot-pressing methods or immersing the non-fluorinated ionomer membrane into the Nafion-containing solution in order to prepare multilayered composite membrane. In these methods, there are only physical adsorptions between different layers of multilayered composite membrane. Delamination phenomena occurred easily, which will increase the membrane resistance or sacrifice the mechanical strength of the multilayered composite membrane [10].

In this paper, integral Nafion/SPEEK layered composite membrane (N/S membrane) consisting of a thin layer of recast Nafion membrane and a layer of SPEEK membrane is fabricated and characterized. The choice of SPEEK as the non-fluorinated ionomer membrane is mainly based on its low cost, adequate conductivity, good thermal stability and mechanical strength. The thin layer of Nafion membrane is expected to prevent oxidation degradation of the SPEEK membrane by the highly oxidizing pentavalent vanadium ions (VO2+). In order to increase the combination of Nafion layer and SPEEK layer, diamine was used to crosslink the sulfonic acid groups of Nafion ionomer and SPEEK ionomer. Furthermore, its possible applications in VRB system were also investigated.

2. Experimental

2.1. Materials

Poly(ether ether ketone) (VICTREX, PEEK450 PF) were used as received. 5% Nafion® dispersion (Nafion® R-1100 resin) were used to prepare Nafion dry resin and purchased from DuPont Company. 1.1-Carbonyldiimidazole (CDI) and 1,6-hexane diamine (HDA) was used as received from Shanghai BangCheng Chemical Reagent Company and Sinopharm Chemical Reagent Co. Ltd., respectively. Other reagents used in the study such as dimethylsulfoxide (DMSO), NaOH and HCl were all reagent grades and were purchased from Tianjin JinDong TianZheng Precision Chemical Reagent Factory. All chemicals were used without further purification.

2.2. Preparation of sulfonated PEEK

SPEEK was prepared as previously reported [10]. PEEK (6 g) were poured into vigorously stirred 100 ml concentrated sulfuric acid (95–98 wt.%). The reaction was carried out at 50 ºC. The sulfonation reaction was terminated by precipitating the resulting acid polymer solution into ice-cold water under mechanical agitation. The polymer precipitate was filtered, washed several times with deionized water until pH was neutral. Then, the polymer was dried at room temperature for several days, and then dried in a vacuum oven at 100 ºC for 24 h.

2.3. Membrane preparation

The SPEEK membranes were prepared as following: SPEEK polymer was dissolved in DMSO to make a 10 wt.% SPEEK casting solution, which was then cast onto a flat glass. The cast membranes were dried at 60 ºC for 6 h to remove the solvents, and annealed at 120 ºC for 4 h. After cooling to room temperature, the resultant membranes were peeled from the glass in deionized water. Finally, the membrane was pretreated by boiling for over 1 h in 0.5 M H2SO4 and subsequently rinsed with deionized water several times. The thus-pretreated SPEEK membranes were kept in deionized water before testing. The thickness of the dried SPEEK membranes was about 80–120 µm.

Fig. 1 shows the reaction scheme of the preparation of N/S membrane. The cross-linking procedure was adapted from Nolte et al. [11,12]. The detailed procedures are as following: 5% Nafion® dispersion were dried at 60 ºC to form Nafion dry resin. Then SPEEK polymer and Nafion dry resin were dissolved in DMSO to form 10 wt.% SPEEK casting solution and 60–70 wt.% Nafion casting solution, respectively. Then CDI (0.25 mol equiv. with respect to sulfonic acids groups of SPEEK or Nafion) was added to the casting solution. The SPEEK casting solution was cast on a glass plate at 60 ºC to form SPEEK membrane. HDA (0.12 mol equiv. with respect to sulfonic acids groups of SPEEK or Nafion) was added to the Nafion casting solution. After stirring for 1 h at room temperature, the reaction mixture was cast on SPEEK membrane and allowed to evaporate for 12 h at 60 ºC to remove the solvents. After cooling to room temperature, the resultant membranes were peeled from the glass in deionized water. Finally, the membrane was immersed in 0.1 M H2SO4 for over 12 h to neutralize the remnant diamine. The final N/S membrane was kept in deionized water before testing.

2.4. Membrane characterization

The N/S membranes surface and cross-section were characterized with scanning electron microscope (SEM) using JEOL (JSM 6360LV SEM) for analyzing morphological appearance.

The IR spectra of Nafion 117 membrane, SPEEK membrane and N/S membrane were recorded as following: the ATR (attenuated total reflection) technique with a FT-IR spectrometer (Avatar 370 E.S.P., Nicolet Continuum Infrared Microscope) in order to confirm the formation of the Nafion layer on the surface of SPEEK membrane.

The IEC and the area resistance of the membranes were measured by using the methods described in literature [13]. For the IEC measurements, the membrane sample was immersed for 1 day in a large volume of 1 M HCl aqueous solution to give the membrane in the H-form. The membrane was then washed free of excess HCl with distilled water and for a further 4 h equilibrated with distilled water, with frequent changes of the distilled water to remove the last traces of acid.

The membrane was then equilibrated with exact 50 ml of 0.01 M NaOH aqueous solution for 24 h and the cation exchange capacity was determined from the reduction in alkalinity determined by back titration. The ion exchange capacity of the cation exchange membrane was calculated from the following equation:

$$\text{IEC} = \frac{M_{0,NaOH} - M_{E,NaOH}}{W}$$  (1)

where \( M_{0,NaOH} \) is the moles of NaOH in the flask at the start, \( M_{E,NaOH} \) is the moles of NaOH after equilibration, and \( W \) is the weight of the dry membrane (g).

For the area resistance measurements, the membrane was exposed to a solution of 1.5 M VOSO4 in 3 M H2SO4 on both sides in a conductivity cell. The electric resistances of the conductivity cell with membrane \((r_1)\) and without membrane \((r_2)\) were measured by electrochemical impedance spectroscopy (EIS) over a frequency range of 100 MHz to 100 kHz. The effective membrane area \( S \) of the cell was 1 cm². The area resistivity of the membrane \( r \) (Ω cm²) was calculated by the following equation:

$$r = (r_1 - r_2)S$$  (2)

The permeability of vanadium ions through the membrane were measured by using the methods described in literature [14]. The membrane was exposed to a solution of 1.5 M VOSO4 in 3 M H2SO4 on one side and a solution of 1.5 M MgSO4 in 3 M H2SO4 on the other
side. MgSO₄ was used to equalize the ionic strengths of the two solutions and to minimize the osmotic pressure effects. Both solutions were circulated through the cell compartments which were separated by the membrane sample. Before use, the membrane was immersed in distilled water. The effective area of the exposed membrane is 5 cm² while the volume of the solutions for each reservoir was 50 ml. Samples of solution from the right reservoir were taken at a regular time interval and analyzed for vanadium ions concentration by using an UV–vis spectrometer. The experiments were conducted at room temperature.

During the calculation of vanadium ions permeability, the change of vanadium ion concentration in the left reservoir (filled with 1.5 M VOSO₄ in 3 M H₂SO₄) is very small and can be negligible. Accordingly, pseudo-steady-state condition was used and the vanadium ion concentration in the right reservoir as a function of time is given by the following equation:

\[ \frac{c_B(t)}{c_A} = \frac{P}{L} (c_A - c_B(t)) \]  

where \( c_A \) is the vanadium ion concentration in the left reservoir, and \( c_B(t) \) 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 \( V_b \) is the volume of right reservoir, respectively. An assumption is also made here that \( P \) is independent of concentration.

For the VRB single cell used in the charge–discharge tests, the solutions of 1.5 M V²⁺/V³⁺ in 3.0 M H₂SO₄ and 1.5 M VO²⁺/VO₂⁺ in 3.0 M H₂SO₄ were employed as negative and positive electrolytes, respectively. The carbon felt was served as the current-collectors. The active area of the electrode was 5 cm² while the volume of electrolyte was 30 ml in each half-cell. The VRB single cell was charged and discharged with the constant current density of 50 mA/cm². To avoid the corrosion of the carbon felt electrode and graphite plates, the upper limit of charge voltage was 1.75 V, and the lower limit of discharge voltage was 0.8 V.

3. Results and discussion

3.1. SEM measurements

SEM of N/S membrane were recorded and representative micrographs of membrane surface and cross-section are presented in Fig. 2(a) and (b), respectively. SEM micrographs of the membrane surface showed that the surface morphology of N/S membrane is homogeneous. From the cross-sectional morphology, the N/S membrane was apparently composed of three layers (Fig. 2(b)): the Nafion layer, the SPEEK layer and the transition central layer. In transition central layer, Nafion was embedded in the SPEEK matrix to form partial polymer blends. The thickness of each layer was about 15, 35 and 50 μm, respectively.

There are two consideration concerning the structure and morphology of N/S membrane. Firstly, if layered structure and morphology has been formed instead of polymer blends structure and morphology. When the Nafion casting solution was cast on SPEEK membrane, SPEEK will dissolve in DMSO and blend with Nafion polymer inevitably. The content of DMSO in Nafion casting solution and the evaporate temperature will strongly affects the morphology of N/S membranes. The more SPEEK membrane dissolved, the more likely N/S layered polymer blend was formed. By controlling the evaporate temperature and concentration of Nafion casting solution, layered structure of N/S membrane was prepared. From the cross-sectional SEM of N/S membrane, the coating of Nafion layer was clearly viewed on the surface of the membrane.

A second aspect related to the membrane structure and morphology is that if crack exists between the Nafion layer and the SPEEK layer. In this work, we expect that the chemical bond in different layers can suppress the delamination phenomena and an integral layered membrane was formed. SEM images of the cross-sectional N/S membrane (Fig. 2(b)) confirm these considerations. In the N/S membrane, the formation of transition area where Nafion and SPEEK blend with each other was observed. Nafion layer and SPEEK layer was brought together by the transition central layer and a continuous membrane structure was formed.

3.2. FT-IR spectroscopy analysis

Fig. 3 shows the IR spectra of Nafion 117 membrane, SPEEK membrane, Nafion surface and SPEEK surface of N/S membrane. For the Nafion 117 membrane, the antisymmetric vibrations of C–F bonds in Nafion are present at 1148 and 1204 cm⁻¹. The doublet peaks at 978 and 983 cm⁻¹, and the peak at 1058 cm⁻¹ are characteristic peaks of the side chain in Nafion, and are assigned to the symmetric vibrations of C–O–C bonds and S–O stretching vibration of −SO₃⁻ groups, respectively [15]. The spectra for the Nafion surface of the N/S membrane are similar to that for Nafion membrane. The peak at 1478 cm⁻¹ may be assigned to the bending vibration of N–H bonds of sulfonamide group (−SO₂NH). For SPEEK membrane
and SPEEK side of N/S membrane, the absorption bands at 1020, 1076 and 1247 cm$^{-1}$ of SPEEK can be assigned to the symmetric and asymmetric stretching vibrations of the sulfonic acid group. The aromatic C–C band at 1486 cm$^{-1}$ for PEEK is observed to split into two peaks at 1470 and 1490 cm$^{-1}$ for SPEEK, due to the new substitute from sulfonation [16]. The spectra for SPEEK surface of the N/S membrane and for the SPEEK membrane is identical. All of these results confirm that layered Nafion perfluorinated sulfonic acid membrane was successfully deposited on the SPEEK membrane surface and complete Nafion/SPEEK polymer blends did not occur.

3.3. Permeability of vanadium ions

The choice of SPEEK as substitute for Nafion applied in VRB system was mainly based on cost considerations. However, the difference of microstructures of SPEEK with Nafion membrane can lead to different transport properties. Therefore, SPEEK are not only low cost alternative membrane materials for VRB applications, its use in VRB system may also help to alleviate the problems associated with high vanadium ions crossover in VRB system. Considering the high single cell performance of membrane in VRB application, we prepared SPEEK membrane with relatively higher degree of sulfonation and optimum thickness for test in our experiments. N/S membrane was also prepared by depositing Nafion layer on the surface of SPEEK membrane. As generally used membrane in practical VRB system, Nafion 117 membrane was chosen to contrast with SPEEK and N/S membrane.

In this study, the permeability of VO$^{2+}$ ion through Nafion 117, SPEEK and N/S membrane are measured at the same condition. The variations of the concentration of VO$^{2+}$ ion with time are illustrated in Fig. 4. As can be seen, the diffusion of VO$^{2+}$ ions through Nafion 117 membrane in the same time was more than those diffused through SPEEK membrane and N/S membrane. The VO$^{2+}$ ion permeability inside the membrane was calculated by using a pseudo-steady-state condition and listed in Table 1. From Table 1, it can be seen that the permeability of VO$^{2+}$ ion decreased to $2.432 \times 10^{-7}$ and $1.928 \times 10^{-7}$ cm$^2$/min for SPEEK membrane and N/S membrane from the value of $36.55 \times 10^{-7}$ cm$^2$/min for Nafion membrane. This shows that a significant reduction in vanadium ions crossover could be achieved by using SPEEK membranes and N/S membrane, which are much less permeable to vanadium ions.

The different vanadium ions permeability of SPEEK and Nafion membranes can be explained by the difference in their microstructures [17,18]. In Nafion membrane, the microstructures of polymers are composed of two parts: the extremely high hydrophobic fluorocarbon backbone and extremely high hydrophilic sulfonic functional groups. It would give rise to some hydrophobic/hydrophilic nano-separation, especially in the presence of water. The hydrophilic sulfonic groups cluster to form...
hydrophilic domains, which are well interconnected because of the high flexibility of the fluorocarbon of Nafion membrane. Not only proton and water can transport through these domains, but vanadium ions can also permeate through these domains. Compared with Nafion membrane, the backbone of the SPEEK membrane is less hydrophobic, and the sulfonic acid group is less acidic. This result in smaller hydrophilic/hydrophobic separation corresponding to highly dispersed sulfonic groups. Furthermore, the high rigidity of the SPEEK backbone to which the −SO₃H groups are attached also prevent the neighboring dispersed sulfonic groups from aggregating to bigger clusters. Thus, the water filled channels in SPEEK membrane are narrow and branched with more dead end pockets compared with those in Nafion membrane. This is perhaps the reason for the reduction of vanadium permeability in SPEEK membranes. In N/S membrane, chemically bond the Nafion layers and the SPEEK layers were introduced to suppress the delamination problem of layered N/S membrane. The form of sulfonamide linkages increases the combination of Nafion layers and SPEEK layers of the N/S membrane. However, the progressive introduction of secondary amine groups result in lower ion conductivity of N/S membrane because of the neutralization of sulfonic acid groups. The lower vanadium permeability of N/S membrane can be attributed to this.

3.4. IEC, area resistance and other properties of membrane

The IEC, area resistance and vanadium ion permeabilities of Nafion 117, SPEEK and N/S membrane were summarized in Table 1. It can be seen that SPEEK membrane exhibited relatively high IEC value (1.80 mmol/g) in comparison to that of Nafion membrane (0.91 mmol/g). However, the area resistance of SPEEK membrane is higher than Nafion membrane because of their difference in microstructures [17,18]. The less pronounced hydrophilic/hydrophobic separation of SPEEK compared to Nafion corresponds to narrower, less connected hydrophilic channels and to larger separations between the less acidic sulfonic acid functional groups. On one side, this leads to the favorable low vanadium ions diffusion and water transport; on the other hand, the relatively low conductivity and small effectual hydrophilic domains of membrane is inevitable. In the case of N/S membrane, the high area resistance and low IEC value can be attributed to the progressive introduction of amine groups and neutralization of sulfonic acid groups.

3.5. VRB single cell performance

The typical charge–discharge curves of VRB single cell using Nafion 117, SPEEK and N/S membrane were presented in Fig. 5. As can be seen, the average charge voltage of VRB single cell based on Nafion 117 membrane is a little bit lower than that of the VRB single cell based on SPEEK and N/S membrane. This is attributed to the larger IR drop caused by the higher area resistance of the SPEEK and N/S membrane. At the same time, the discharge time of the VRB single cell based on SPEEK membrane is a little longer than that of the VRB single cell with Nafion membrane. The reason for this may be the reduction of self-discharge of the VRB single cell by using the SPEEK membrane. In the case of N/S membrane, the relatively higher area resistances lead to the reduction of charge–discharge time due to the upper limit of charge voltage. But the discharge–charge time proportion of VRB using N/S membrane is the highest due to its low vanadium ions permeation. The performance of VRB single cell employing Nafion 117, SPEEK and N/S membrane at a charge–discharge current density of 50 mA/cm² was presented in Table 2. In general, the low area resistances of membrane lead to the high voltage efficiency when used in VRB. The high crossover of vanadium ions through the membrane result in a loss of electrochemical energy during the operation of VRB. As can be seen, the VRB single cell employing SPEEK and N/S membrane presented a coulombic efficiency of 97.1% and 97.6%, which are larger than the value of 93.8% for the VRB single cell employing Nafion 117 membrane. The voltage efficiency for VRB single cell based on Nafion, SPEEK and N/S membrane is 90.7%, 87.3% and 85.3%, respectively. This is in agreement with the conclusion present before. Compared with the energy efficiency value of 85% for Nafion membrane, the overall energy efficiency of VRB employing SPEEK and N/S membrane were 84.8% and 83.3%, respectively. Furthermore, the cycle performance of the VRB single cell employing N/S membrane at a current density of 50 mA/cm² was presented in Fig. 6. As shown, there is no efficiency decline after the cell was cycled for 30 cycles (more than 180 h). In a word, although N/S membrane delivered a little lower energy efficiency compared with Nafion membrane, its good chemical stability and low cost make it a suitable substitute for Nafion membrane used in VRB system.

Table 1
Comparison of the general properties between Nafion 117 membrane, SPEEK and N/S membrane

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Thickness (µm)</th>
<th>IEC (mmol.g⁻¹)</th>
<th>Area resistance (Ω cm²)</th>
<th>Permeability of VO²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion 117</td>
<td>175</td>
<td>0.91</td>
<td>1.06</td>
<td>36.55</td>
</tr>
<tr>
<td>SPEEK</td>
<td>100</td>
<td>1.80</td>
<td>1.27</td>
<td>2.432</td>
</tr>
<tr>
<td>N/S</td>
<td>100</td>
<td>1.67</td>
<td>1.6</td>
<td>1.928</td>
</tr>
</tbody>
</table>

Table 2
The single cell performance efficiency of VRB based on Nafion 117 membrane and modified Nafion membrane

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Nafion 117</th>
<th>SPEEK</th>
<th>N/S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coulombic efficiency (%)</td>
<td>93.8</td>
<td>97.1</td>
<td>97.6</td>
</tr>
<tr>
<td>Voltage efficiency (%)</td>
<td>90.7</td>
<td>87.3</td>
<td>85.3</td>
</tr>
<tr>
<td>Energy efficiency (%)</td>
<td>85.0</td>
<td>84.8</td>
<td>83.3</td>
</tr>
</tbody>
</table>
Integral N/S membrane consisting of a thin layer of recast Nafion membrane and a layer of SPEEK membrane is prepared by using chemically crosslink the sulfonic acid groups of Nafion ionomer and SPEEK ionomer. The Nafion layers of the N/S membrane serves as a shield preventing the oxidation degradation of the SPEEK membrane by VO2+ ions in the positive half-cell electrolyte of the VRB. Cross-sectional morphology of N/S membrane and IR analysis of the Nafion, SPEEK and N/S membranes all showed that Nafion layer was successfully deposited on the SPEEK membrane surface and an integral layered membrane structure was formed. The N/S membrane showed lower permeability of vanadium ions accompanied by higher area resistance compared with Nafion membrane. The VRB single cell employing N/S membrane exhibit lower voltage efficiency and higher coulombic efficiency compared with that employing Nafion membrane. Although the overall energy efficiency of VRB single cell with N/S membrane was a little lower, its good chemical stability and low cost make it a promising membrane used in VRB system.

4. Conclusions

References