Modification of Nafion membrane using interfacial polymerization for vanadium redox flow battery applications

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Abstract

In order to reduce the permeation of vanadium ions across the ion exchange membrane during the operation of vanadium redox flow battery (VRB) based on Nafion membrane, the interfacial polymerization was applied to form a cationic charged layer on the surface of Nafion 117 membrane. The area resistance and the permeability of vanadium ions were measured. The results indicate that comparing with the unmodified Nafion membrane, the modification of Nafion membrane results in a dramatic reduction in crossover of vanadium ions across the membrane and a little higher area resistance of the membrane. As a result, the columbic efficiency for the VRB single cell based on the modified Nafion membrane (VRB-modified Nafion), which is related to the concentration of the incubation solution of polyethylenimine (PEI), was increased significantly. The value is 96.2–97.3%, which is higher than that obtained with the VRB single cell based on unmodified Nafion membrane (VRB-Nafion) (around 93.8%). Due to the little higher area resistance caused by the modification, the voltage efficiency of VRB-modified Nafion is lower than that of VRB-Nafion. Furthermore, the water transfer across the modified membrane was also reduced. The ion exchange capacity (IEC) of the modified Nafion membrane was also evaluated. The formation of the thin cationic charged layer on the membrane surface was confirmed by IR spectra analysis.

Keywords: Vanadium redox flow battery; Interfacial polymerization; Membrane modification; Self-discharge phenomena

1. Introduction

The vanadium redox flow battery (VRB) proposed by Skyllas-Kazacos and co-workers \cite{1} has attracted many attentions worldwide due to its long cycle life, flexible design, fast response time, deep-discharge capability, and low cost in energy storage. It employs $V^{2+}/V^{3+}$ and $VO_{2}^{+}/VO_{2}^{2+}$ redox couples in the negative and positive half-cell electrolytes, respectively, which are separated by an ion exchange membrane. The function of the membrane is to prevent cross mixing of the positive and negative electrolytes, while still allowing the transport of ions, such as proton in the case of VRB-Nafion, to complete the circuit during the passage of current. The ideal membrane should possess low permeability of vanadium ions, high proton conductivity, good chemical stability, and low cost \cite{2,3}.

Nafion membrane is generally served as VRB membranes due to its high proton conductivity and excellent chemical stability in $VO_{2}^{2+}$ solution \cite{2,4}. However, the selectivity of Nafion membrane between proton and vanadium ions is not high enough. So that it will lead to the undesired transport of vanadium ions across the membrane during the charge–discharge processes of VRB. If vanadium ions with different oxidation states transport to the opposite half cell and react with each other, electrochemical energy loss and energy efficiency reduction of the battery cannot be prevented \cite{5}. Moreover, a significant amount of water transfers across Nafion membrane during charge–discharge processes of VRB, causing the undesired preferential volumetric change as one half cell is flooded and diluted while the other becomes more concentrated, adversely affecting the overall operation of the VRB. Although the detail mechanism of water transfer across the membrane is not understood comprehensively, some researches indicated that the transfer of hydrate vanadium ions between the two half-cell solutions is the main reason of water transfer \cite{6,7}.

In order to reduce the permeation of multivalent vanadium ions through the membrane and maintain the conductivity of...
proton simultaneously, the ion exchange membrane with monovalent cation permselectivity is required. In general, multivalent cations are difficult to be adsorbed on the cationic charged layer compared to monovalent cations because of Donnan exclusion effect. Accordingly, it is expected that when cationic charged layer is formed on the cation exchange membrane, the permeation of multivalent cations through the membrane should be decreased. Many efforts to prepare cation exchange membranes with permselectivity for monovalent cation have been made [8–10].

In this study, the interfacial polymerization was applied for the formation of an ultra-thin cationic charged layer on the surface of Nafion membrane for the application in VRB. Polyethylenimine (PEI) with a great deal of amino groups was selected as polyelectrolyte to form the cationic charged layer. For getting a better adsorption of PEI, chlorosulfonyl (–SO2Cl) groups were introduced as reactive groups onto the surface of Nafion membrane in advance. The ion exchange capacity (IEC), area resistance, water transfer properties and vanadium ions permeability of the modified Nafion membrane was tested in comparison with unmodified Nafion membrane. The performances of VRB single cells using modified and unmodified Nafion membrane were tested. IR spectra analysis was used to confirm the formation of a cationic charged layer on Nafion membrane surface after modification.

2. Experimental

2.1. Materials

Nafion membranes were purchased from DuPont Company. Phosphorus pentachloride and phosphorus oxychloride from Beijing Chemical Reagent Company were reagent grade and used for the chlorosulfonation reaction. PEI was purchased from Shanghai ShengYu Chemical Reagent Company. Isophthaloyl dichloride was purchased from Jiangxi LianKe Chemical Co. Ltd. Other reagents used in the study such as Hexane and carbon tetrachloride were all reagent grades and purchased from Tianjin JinDong TianZheng Precision Chemical Reagent Factory. All chemicals were used without further purification.

2.2. Membrane preparation

Mechanism of the modification of Nafion 117 membrane is shown in Fig. 1. Nafion 117 membrane was employed in this work. Firstly, chlorosulfonation reaction was carried out to introduced the chlorosulfonyl (–SO2Cl) groups onto the surface of Nafion 117 membrane (a). Then PEI was adsorbed on the membrane surface through acid–amide bonds between Nafion membrane and PEI (b). Finally, interfacial polymerization reactions were carried out by submerging the above membrane in isophthaloyl dichloride hexane solution to form cationic charged layer on the surface of Nafion 117 membrane (c).

The Nafion membrane was converted into sulfonil chloride form as described in literature [11]. A piece of Nafion 117 membrane was immersed in a mixture of phosphorus pentachloride/phosphorus oxychloride (1:2, w/w) in a three-neck round-bottomed flask with a cooler to carry out chlorosulfonation reaction for about 4 h at 90 °C. Then, the liquid was poured off while hot and carbon tetrachloride was added. Following a brief reflux, the carbon tetrachloride was decanted. Twice more fresh carbon tetrachloride was added, refluxed and decanted. By controlling the reaction temperature and time, the chlorosulfonyl (–SO2Cl) groups were partially introducted onto the surface of membrane.

The resulting Nafion sulfonyl chloride membrane was soaked in PEI aqueous solutions for about 2 h. Then, the treated membrane was taken out of the solution. After the excessive solution drained off, the membrane was submerged in isophthaloyl dichloride hexane solution. Thus the reaction occurs at the interface between the two solutions to form a very thin dense polymer layer on the surface of membrane. After the reaction, the composite membrane was taken out and air-dried at 100 °C for 1 h.

2.3. Membrane characterization

The IEC and the area resistance of the membrane were measured by using the methods described in literature [12]. 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 is calculated from Eq. (1).

\[
\text{IEC} = \frac{M_{0,\text{NaOH}} - M_{E,\text{NaOH}}}{W}
\]  

(1)

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

For the area resistance a measurement, the membrane was exposed to a solution of 1.5 M VOSO\(_4\) in 3 M H\(_2\)SO\(_4\) on both sides in a conductivity cell (scheme is same with Fig. 1 in ref. [12]). 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 cm\(^2\). The area resistivity of the membrane (\(\Omega / \text{cm}^2\)) is calculated by Eq. (2).

\[
\frac{1}{r} = \left(\frac{1}{r_1} - \frac{1}{r_2}\right)S
\]  

(2)

The device used for the measurement of the permeability of vanadium ions through the membrane was illustrated in Fig. 2. The left reservoir was filled with the solution of 1.5 M VOSO\(_4\) in 3 M H\(_2\)SO\(_4\), and the right reservoir was filled with the solution of 1.5 M MgSO\(_4\) in 3 M H\(_2\)SO\(_4\). MgSO\(_4\) 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 samples. Before use, the membrane was immersed in distilled water. The effective area of the exposed membrane is 5 cm\(^2\) 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.

The static water transfer across the membranes was evaluated by the methods described in literature [6]. Negative and positive electrolytes at 50% state of charge (SOC) [0.75 M V\(^{2+}\) + 0.75 M V\(^{3+}\) on one side and 0.75 M VO\(^{2+}\) + 0.75 M VO\(^{2+}\) on the other side] were used to evaluate the water transport behavior of the membranes. The membrane area exposed to the electrolytes was 15 cm\(^2\). The tube connected to each compartment had an internal diameter of 3.76 mm. The change of 9 cm in the height of the solution is equivalent to 1 mL solution transferring from one side to the other.

For the VRB single cell (Fig. 2) used in the charge–discharge tests, the solutions of 1.5 M V\(^{2+}/V^{3+}\) in 3.0 M H\(_2\)SO\(_4\) and 1.5 M VO\(^{2+}/VO^{2+}\) in 3.0 M H\(_2\)SO\(_4\) were employed as negative and positive electrolytes, respectively. The carbon felt was served as the electrodes and the graphite plates were served as the current-collectors. The active area of the electrode was 5 cm\(^2\) 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/cm\(^2\). 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.

The IR spectra were recorded by using 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 cationic charged layer on the surface of Nafion membrane.

### 3. Results and discussion

#### 3.1. IEC, area resistance and other properties of membrane

The properties of Nafion 117 membrane and the modified Nafion membranes were tested and summarized in Table 1. The Nafion-PEI-2.5 membrane and Nafion-PEI-5 membrane corresponded to the Nafion membrane treated by soaking in 2.5% and 5% PEI aqueous solutions, respectively.

It can be seen from Table 1 that the unmodified Nafion membrane presented the highest IEC value. Comparing with Nafion membrane, the IEC values of the modified Nafion membrane decreased. It can also be seen clearly from Table 1 that the modified Nafion membrane treated with higher concentration PEI aqueous solutions presented lower IEC value. For example, the IEC value decreased to 0.89 mmol g\(^{-1}\) for Nafion-PEC-2.5 membrane and 0.87 mmol g\(^{-1}\) for Nafion-PEC-5 membrane from the value of 0.91 mmol g\(^{-1}\) for the unmodified Nafion membrane. The reduction of the IEC value can be attributed to
the formation of acid–amide bonds between Nafion membrane and PEI achieved by forming chlorosulfate groups in advance.

From Table 1, it can also be seen that the modification of Nafion membrane increased the area resistance of the modified membrane. The unmodified Nafion membrane presented the smallest area resistance of 1.06 \( \Omega \) cm\(^2\). This value corresponding to Nafion-PEI-2.5 membrane and Nafion-PEI-5 membrane is 1.24 and 1.34 \( \Omega \) cm\(^2\), respectively. The increase of the area resistance was caused by the formation of an ultra-thin cationic charged layer that was obtained with the adsorption of PEI and following interfacial polymerization. The cationic charged layer acts as an electrical repulsion barrier for not only vanadium ions but also protons to permeate the membrane, leading to a higher, but still acceptable area resistance.

3.2. Permeability of vanadium ions

Another important characteristic for the ion exchange membrane for VRB application is that the membrane should provide an effective separation of the positive and negative electrolytes. Diffusion or leakage of vanadium ions with different oxidation states across the membrane lead to self-discharge of the battery and other undesirable consequences. From the point of view of membrane applying in the VRB, low permeability of vanadium ions of the ion exchange membrane is required.

In this study, the vanadium ions permeability of the Nafion membrane before and after modification is compared at the same condition. The device applied in this work is presented in Fig. 2. The amount of vanadium transferring across the membrane was monitored by detecting vanadium concentration in MgSO\(_4\) solution. The concentration of VO\(^{2+}\) in the solution of MgSO\(_4\) with the time is illustrated in Fig. 3. It was clear that the vanadium ions diffusion through the unmodified Nafion membrane was considerably faster than those diffusion through the modified Nafion membrane. Due to the increase of PEI adsorbed on the surface of Nafion membrane when the membrane was treated with higher concentration of PEI solution, the permeability of vanadium ions across the modified Nafion membrane decreased.

The permeability of vanadium ion through the membrane was calculated by using the pseudo-steady-state condition and listed in Table 1. From Table 1, it can be seen that the permeability of vanadium ion decreased significantly to \(5.23 \times 10^{-7}\) cm/min and \(1.70 \times 10^{-7}\) cm/min corresponding to Nafion-PEI-2.5 membrane and Nafion-PEI-5 membrane from the value of \(36.55 \times 10^{-7}\) cm/min for the unmodified Nafion membrane. It can be concluded that the modification of Nafion membrane by PEI provides a barrier to vanadium ions permeation. These phenomena can be mainly attributed to the Donnan exclusion effect of the cationic charged layer on the surface of Nafion membrane [9].

3.3. Water transport measurements

The transfer of water across the membrane during the process of charge–discharge, which is caused by several processes, can severely affect the performance of VRB. When selecting the suitable membranes for VRB, therefore, one of the most important requirements is that the membrane should be able to prevent excessive transfer of water from one half cell to the other. In this work, the water transporting across the unmodified Nafion membrane and the modified Nafion membrane were measured. The results obtained at 50% SOC are presented in Fig. 4. It can be seen that a significant amount of water transferred across Nafion membrane from the negative half-cell electrolyte to the positive half-cell electrolyte under the experimental condition of this work. This is in agreement with that reported in the previous literature [6]. The direction of water transfer in the device based on the modified Nafion membrane was the same as that based on the unmodified Nafion membrane. Furthermore, the amount of water transferred across the modified Nafion membrane was approximately 1 mL, which is just half of the value of water transfer across the unmodified Nafion membrane. From the results above-mentioned it can be concluded that the modification of Nafion membrane can effectively minimize the water transfer across the membrane in a VRB single cell.
Some studies [6,7] indicated that the transfer of water across the membranes during the charge–discharge cycling of VRB is determined by the hydration shells of the different vanadium ions and the osmosis pressure difference between the two half-cell solutions. Under the certain condition, for a VRB using cation exchange membrane the net water transfer is toward the positive half cell, whereas for a VRB using anion exchange membranes the net water transfer is toward the negative half cell. As shown in Fig. 4, under the work condition in this work the net transfer of water across Nafion membrane is from the negative half cell to the positive half cell. This is in accord with the results obtained under the same work conditions by [6]. The authors indicated the transfer of water from the negative half cell to the positive half cell was caused by the hydration shells of V^{2+} and V^{3+} ions which carry a large amount of water and can easily permeate through the cation exchange membrane [6]. In the case of the modified Nafion membrane, the amount of water transferred across the membrane was reduced obviously. This may due to the fact that the transfer of V^{2+} and V^{3+} ions across the membrane is significantly reduced by employing the modified Nafion membrane.

3.4. Performance of VRB single cell

The transfer of vanadium ions across the membrane will result in the self-discharge of VRB, representing the decrease of open circuit voltage (OCV) [13]. Thus the value of OCV can be used to indicate the degree of self-discharge of a VRB. In this work, the measurements of OCV were performed by pumping the electrolyte solutions through the cell unceasingly after the VRB single cells were charged to a SOC value of 50%. The OCV values were recorded unceasingly too. The OCV value obtained with VRB single cell based on different Nafion membrane were illustrated in Fig. 5. As can be seen, the OCV value gradually decreased from the initial value of 1.43 V with the experimental time at first and then decreased sharply. For VRB-modified Nafion, the time for OCV value remaining larger than 1.0 V extended to 265 h. But for VRB-Nafion, this value was only 96 h. It indicated that the self-discharge of VRB caused by the crossover of vanadium ions can be reduced significantly by using the modified Nafion membrane.

The charge–discharge curves of VRB-Nafion and VRB-modified Nafion were presented in Fig. 6. The average charge voltage of VRB-Nafion is a little bit lower than that of VRB-modified Nafion. This is due to the larger IR drop caused by the higher area resistance of the modified Nafion membrane. Besides, the charge–discharge capacity (Ah) of VRB-modified Nafion is a little larger than that of VRB-Nafion. This may be caused by the reduction of self-discharge of the VRB single cell by employing the modified Nafion membrane.

The performances of VRB-Nafion and VRB-modified Nafion at a current density of 50 mA/cm² were presented in Table 2. As can be seen, the VRB single cell employing Nafion-PEI-2.5 and Nafion-PEI-5 membrane presented a columbic efficiency of 96.2% and 97.3%, which are larger than the value of 93.8% for VRB-Nafion. This is due to the reduction of self-discharge of VRB by employing the modified Nafion membrane. The voltage efficiency for VRB single cell based on Nafion, Nafion-PEI-2.5 and Nafion-PEI-5 membrane is 90.7%, 88.4% and 83.3%, respectively. The lower voltage efficiency obtained with VRB-modified Nafion is resulted from the higher area resistance of the modified membrane, Although Nafion-PEI-5 membrane presented the best capability for reducing the crossover of vanadium ions, and the proton conductivity of it is also reduced obviously. So in order to meet the requirements for VRB application, the modified Nafion membrane with low permeability of vanadium ions and high conductivity of proton should be developed.

![Graph showing OCV decrease over time for VRB single cell based on Nafion 117 and Nafion-PEI-2.5 membrane.](image)

![Graph showing charge–discharge curves for VRB single cell based on Nafion and modified Nafion membrane.](image)
3.5. FT-IR spectroscopy analysis

To further confirm the introduction of chlorosulfonyl (–SO2Cl) groups and then the presence of cationic charged layer on the surface of the modified Nafion membrane, FT-IR spectra of Nafion membrane, Nafion sulfonyl chloride membrane, and the modified Nafion membrane were determined by attenuated total reflectance (ATR) analysis. In Fig. 7, the typical FT-IR spectra for the membranes above-mentioned were presented. For Nafion membrane, the antisymmetric vibration of C–F bonds in Nafion are presented 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 [14]. After the chlorosulfonylation reaction, new peaks appeared at 1427 cm−1 which is assigned to –SO2Cl groups introduced on the membrane surface, as shown in Fig. 7(b). In the case of the modified Nafion membrane, as shown in Fig. 7(c), two new absorption bands at 1659 and 1454 cm−1 appeared. The former is attributed to the presence of C=O bonds and the latter is due to the stretching vibration of C–N bonds. These results all confirm that a cationic charged layer was successfully formed on the surface of Nafion membrane.

4. Conclusions

Surface modification of Nafion membrane using interfacial polymerization has drastically reduced the permeation of vanadium ions across the membrane accompanied by a little higher area resistance. The self-discharge of the VRB single cell significantly decreased by employing the modified Nafion membrane as an alternative of Nafion membrane. As a result, the columbic efficiency for the charge–discharge cycle performed with VRB-modified Nafion is obviously higher than that obtained with VRB-Nafion. However, due to the higher area resistance of the modified Nafion membrane, the voltage efficiency obtained with VRB-modified Nafion is lower than that obtained with VRB-Nafion. The overall energy efficiency (columbic efficiency × voltage efficiency) did not change significantly. Furthermore, the amount of water transferred across the modified Nafion membrane was minimized to just half of the value that transferred across the unmodified membrane. IR spectra analysis also confirmed the formation of cationic charged layer on the surface of membrane after modification. It has shown that the interfacial polymerization can be used successfully to modify Nafion membrane to improve the operation of VRB.

References