



Short communication

A significantly improved membrane for vanadium redox flow battery

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ABSTRACT

A novel sandwich-type sulfonated poly(ether ether ketone) (SPEEK)/tungstophosphoric acid (TPA)/polypropylene (PP) composite membrane for a vanadium redox flow battery (VRB) has been developed with improved properties: the permeability of vanadium ions is greatly reduced and the performance of the VRB cell is greatly increased. The membrane is based on a traditional SPEEK membrane embedded with TPA but PP is used to enhance the membrane for the first time. Although its voltage efficiency (VE) is a little lower than that of a Nafion 212 membrane, it is expected to have good prospects for VRB systems because of its low cost and good performance.

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1. Introduction

The vanadium redox flow battery (VRB) proposed by Skyllas-Kazacos et al. shows great promise as a new, highly efficient and reliable energy storage system for a wide range of applications such as wind turbine generators, remote area power systems, emergency back-up applications and uninterruptable power sources (UPS) [1–2]. The ion exchange membrane which effectively separates the anode and cathode electrolytes while allowing the transport of ions to complete the reaction is crucial for a VRB. An ideal membrane for a VRB should possess good chemical stability, low permeability for vanadium ions and low cost. Most of the early types of commercial ion exchange membranes are unsuitable for a VRB system due to their high cost and high permeability for vanadium ions [3]. In order to reduce this permeability, various modifications of Nafion membranes have been proposed [4–6].

Nafion/SPEEK membranes have low permeability for vanadium ions when they are used in a VRB [7]. The layer of poly(ether ether ketone) (SPEEK) reduces the permeation of vanadium ions effectively and also has other advantages, including low cost, excellent chemical and thermal stability. In order to improve the properties of the membrane used in VRB systems, a novel sandwich-type SPEEK/tungstophosphoric acid (TPA)/PP (S/T/P) composite membrane has been prepared which consists of a layer of polypropylene (PP) membrane between two layers of SPEEK/TPA (S/T) membrane. Its properties and performance in a VRB single cell have been studied in this work.

2. Experimental

2.1. Preparation of S/T/P composite membrane

For sulfonating the PEEK (Victrex, PEEK450 PF), 16 g were slowly added to H₂SO₄ (98 wt%, 200 mL) and stirred at 30 °C for 16 h. The solution was cooled to room temperature and poured into ice-cold water under mechanical agitation. After stirring for 3 h, the solution was stored overnight. After filtered, washed with distilled water until pH 7, the SPEEK was dried at room temperature for 48 h and then heated at 60 °C until the color changed from white to yellow.

For preparation of S/T/P composite membrane, 3 g SPEEK was dissolved in DMSO, which was mechanically stirred at 30 °C for 1–3 h to form a 5 wt% solution. TPA (3 g) was added and the resulting solution was stirred at 30 °C for 6–9 h. Half of the solution was poured onto a purpose-made grooved glass plate and PP (thickness = 140 μm and for a Ni-MH battery) membrane was immersed in it. The cast membrane was dried at 30 °C for 6 h, heated for a further 16 h at 70 °C and then the other half of the solution was poured onto the PP. After dried and cooled to room temperature, the resulting cast membrane was peeled from the glass plate in deionized water and dipped in deionized water before testing. For comparison of the permeability of V(IV) ions, S/T membrane (thickness = 245 μm) with the similar thickness as the S/T/P membrane was also prepared.

2.2. Characterizations of S/T/P composite membrane

The schematic device for area resistance of the membrane measurement is shown in Fig. 1. The electrolytes in the two sides of the membrane were 1.5 mol L⁻¹ VOSO₄ in 2.0 mol L⁻¹ H₂SO₄ and

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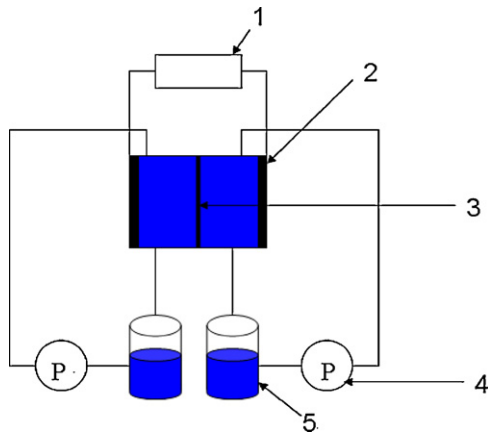


Fig. 1. The schematic setup for measuring the proton conductivity of the membrane: (1) DME-20 Battery Internal Resistance Tester; (2) conductivity cell; (3) membrane; (4) pump; (5) 1.5 mol L⁻¹ VOSO₄/2.0 mol L⁻¹ H₂SO₄ solution.

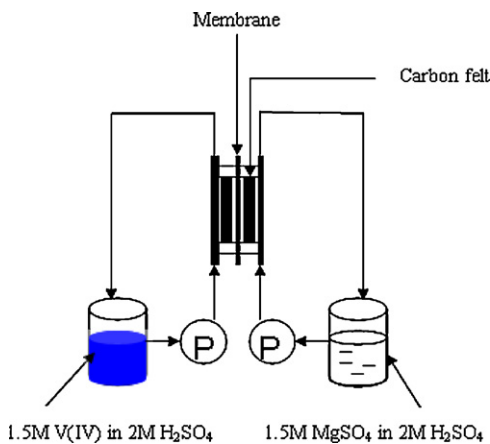


Fig. 2. Schematic illustration of the device for the measurement of V(IV) ion permeability across the membrane.

their volumes were 80 mL. The active area (S) of the membrane was 28 cm² and its thickness (L) was measured. The resistances of the cell with and without (defined as R_1 and R_2) membrane were measured by DME-20 Battery Internal Resistance Tester (test with AC signal and over a frequency of 1 kHz. it can ensure the stability and accuracy even when reading at 10 $\mu\Omega$ level). The area resistances of the membranes $R = (R_1 - R_2) \times S$ (Ω cm²) was shown in Table 1. It can be seen that the area resistance of S/T/P membrane (1.3 Ω cm²) is higher than that of Nafion 212 (0.6 Ω cm²), but is close to the area resistance of Nafion 117 (1.06 Ω cm²) [7]. So the area resistance of S/T/P membrane is proper for VRB cell.

Fig. 2 shows the schematic equipment used for studying the permeability of V(IV) ions in the membranes. The left reservoir was filled with 1.5 mol L⁻¹ VOSO₄ in 2.0 mol L⁻¹ H₂SO₄, while the right one was filled with 1.5 mol L⁻¹ MgSO₄ in 2.0 mol L⁻¹ H₂SO₄, and the

Table 1
Comparison of the general properties between Nafion 212 membrane and S/T/P membrane.

Membrane	Nafion 212 membrane	SPEEK/TPA/PP membrane
Thickness (μ m)	50	240
Area resistance (Ω cm ²)	0.6	1.3
Permeability of V(IV) (10^{-7} cm ² min ⁻¹)	8.23	4.78
Coulombic efficiency (%)	89.2	95.9
Voltage efficiency (%)	91.3	86.2
Energy efficiency (%)	81.5	82.6

volume of each solution was 70 mL. MgSO₄ in the right reservoir was used to balance the intensity of ions of the solutions in both sides and to minimize the osmotic pressure [7]. Both solutions were circulated simultaneously through the cell compartments which were separated by membranes with an effective surface area of 28 cm². Samples (5 mL) of the solution from the right reservoir were taken at regular time intervals and the concentration of vanadium ions was analyzed by a UV-vis spectrometer. The experiments were carried out at room temperature. The surface and cross-section of the membranes were observed using scanning electron microscope (SEM) JSM-6360LV after being freeze-fractured in liquid nitrogen.

2.3. VRB single cell tests

For the VRB single cell used in the charge-discharge tests, carbon felt served as electrodes, and conductive plastic plates served as current collectors. The active area of the electrode was 28 cm². The negative and positive electrolytes consisted of 1.5 mol L⁻¹ VOSO₄ in 2.0 mol L⁻¹ H₂SO₄. To avoid over-charging the positive electrolyte, the negative electrolyte volume was 80 mL but the positive one was 170 mL. The VRB single cell was charged and discharged with a constant current density of 35.7 mA cm⁻². To avoid corrosion of the carbon felt and the conductive plastic plates, the upper limit of the charge voltage was 1.65 V, and the lower voltage limit for discharge was controlled to be 0.85 V.

3. Results and discussion

3.1. Membrane morphology study

Fig. 3(a) and (b) shows the SEM pictures of the surface and cross-section of S/T/P membrane, respectively. It can be seen that TPA particles are well dispersed in the SPEEK membrane. The good dispersion of the TPA particles in the SPEEK membrane can reduce the area resistance and increase the V(IV) ions permeability. From the cross-sectional morphology of the sandwich-type structure of the S/T/P membrane could be seen clearly: the double S/T layers and the transition central layer. In the transition central layer S/T resins are dispersed in the holes of PP membrane. There is no delamination throughout the whole membrane cross-section. This indicates that the S/T resins have completely filled the holes of the PP membrane and are linked together by the PP membrane. The thickness of each layer is about 64, 135 and 34 μ m, respectively. In this study, it is found that the bottom S/T layer is always thicker than the upper S/T layer. This may due to the different quantity of S/T resins dispersed in hole of the PP membrane when preparing the double S/T layers.

3.2. Permeability of V(IV) ions

Permeability of V(IV) ions was measured under the same conditions as mentioned above. The dependence of concentration of V(IV) ions with time is presented in Fig. 4. The diffusion of V(IV) ions is much slower in the S/T/P membrane than those in Nafion 212 and S/T membrane. It is supposed that the change in vanadium ion concentration in the left reservoir (1.5 mol L⁻¹ VOSO₄ in 2.0 mol L⁻¹ H₂SO₄) is very small and can always be negligible during the calculation of permeability. Inside the membrane, a pseudo-steady-state condition is used. Accordingly, the vanadium ion concentration in the right side as a function of time is given by the equation [7]:

$$V_B \frac{dc_B(t)}{dt} = A \frac{P}{L} (c_A - c_B(t)) \quad (1)$$

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

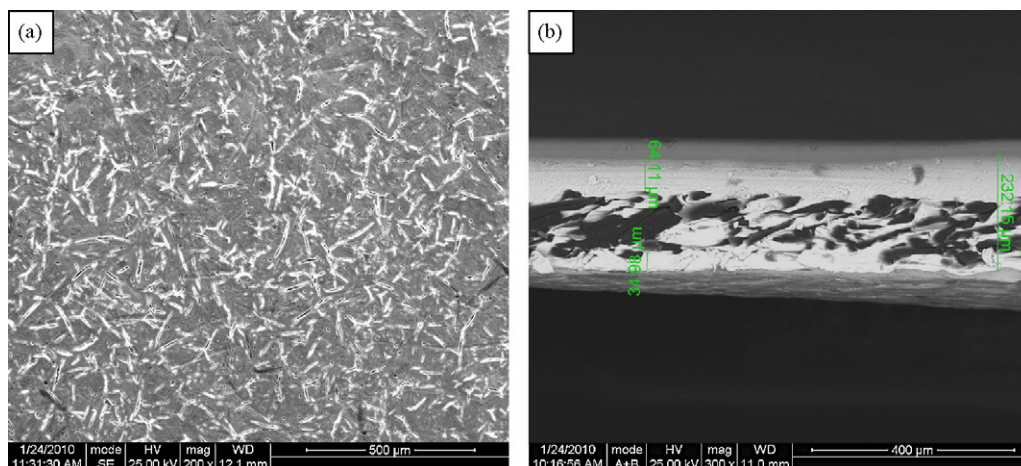


Fig. 3. SEM images of the S/T/P membrane: (a) surface; (b) cross-section.

membrane. P is the permeability of vanadium ions, and V_B is the volume of the right reservoir.

The permeabilities of V(IV) ions in the membranes are also listed in Table 1. The permeability of the S/T/P membrane is only $4.78 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$ compared with $8.23 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$ for the Nafion 212 membrane because the former is based on SPEEK which has a different microstructure from that of the Nafion membrane [7,8]. The perfluorinated backbone of the Nafion membrane is highly hydrophobic and its sulfonic groups are highly hydrophilic. These sulfonic groups are well interconnected because of the high flexibility of the fluorocarbon of the Nafion membrane. The hydrophobic/hydrophilic domains of the Nafion membrane enhance the interconnections between the sulfonic groups, especially in the presence of water. However, in the S/T/P membrane the small hydrophobic/hydrophilic separation and the high rigidity of the polymer backbone of SPEEK results in narrow proton channels and a branched structure with many dead end pockets. The lower permeability of Nafion 212 than the Nafion 117 ($36.55 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$) [7], which is probably due to the differences of the facilities and experimental conditions used during the permeability test. The permeability of V(IV) ions in S/T membrane is calculated to be ($18.6 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$), which is larger than the value of S/T/P membrane. This may be resulted from a decrease in the pore size after SPEEK/TPA particles being embedded in the hole

of the PP membrane and thus reduce the channel size for V(IV) ions diffusion. In normal condition, the inorganic particles will act as barrier to reduce the V(IV) ions permeability. But in this study, it is found that the V(IV) ions permeability of S/T membrane is more than that of Nafion 212 membrane. This was most likely due to the hygroscopic of TPA that absorbs water.

3.3. Performance of VRB single cell

The charge–discharge curves of the second cycle of VRB with an S/T/P membrane and a Nafion 212 membrane, respectively, are presented in Fig. 5. The second cycle is the real first cycle of a single VRB cell, because in the first cycle the negative electrolyte is V(IV) ions rather than V(III) ions at the beginning of the test. A higher average charge voltage and a lower voltage efficiency (VE) of a VRB single cell with an S/T/P membrane than that with a Nafion 212 are found, due to the large IR drop caused by the high area resistance of an S/T/P membrane. However, the discharge capacity, columbic efficiency (CE), and energy efficiency (EE) with the S/T/P membrane are higher because the lower permeability for vanadium ions will reduce the self-discharge of the VRB single cell. Table 1 shows the VE, CE, and EE of a VRB single cell with a Nafion 212 membrane and an S/T/P membrane, respectively.

The charge capacity decay of VRB single cell during the charge–discharge cycles was illustrated in Fig. 6. The charge

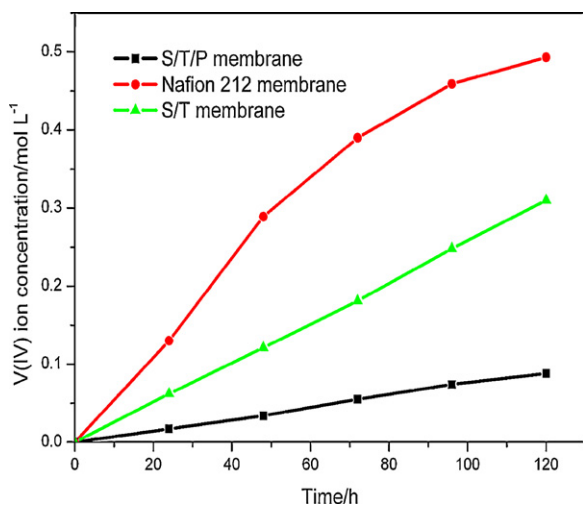


Fig. 4. Vanadium ion concentration in the right reservoir of a VRB single cell with a Nafion 212 membrane, S/T membrane and an S/T/P membrane, respectively.

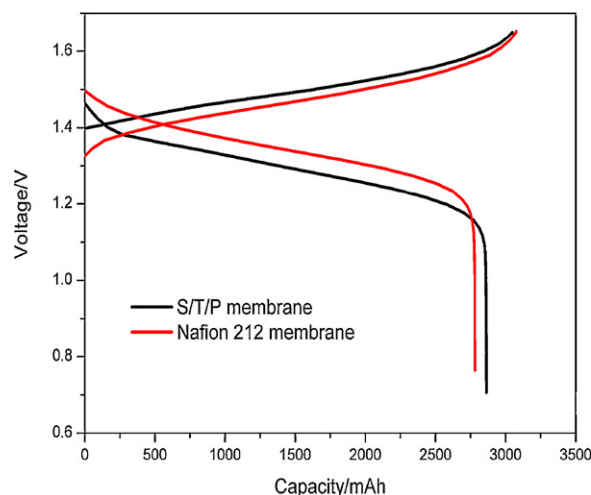


Figure 5. Charge–discharge curves of a VRB single cell with a Nafion 212 membrane and an S/T/P membrane respectively, at current density of 35.7 mA cm^{-2} .

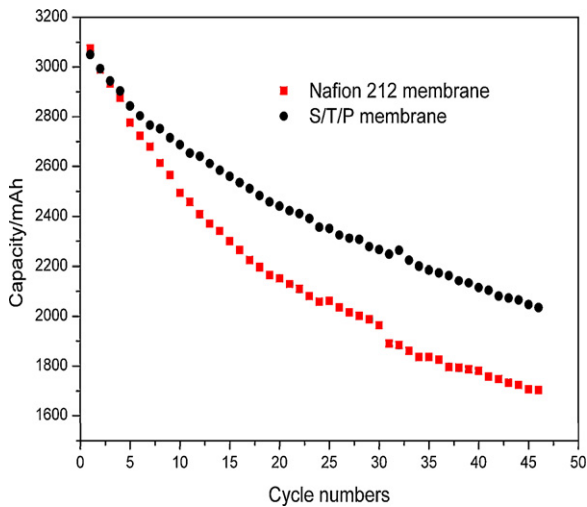


Fig. 6. The charge capacity decay of a VRB single cell with a Nafion 212 membrane and an S/T/P membrane, respectively.

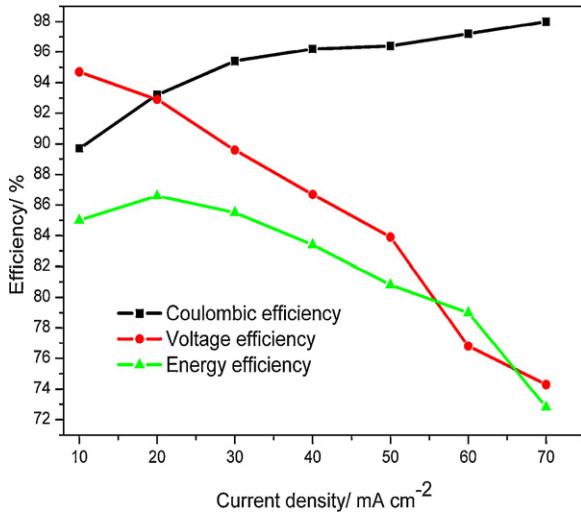


Fig. 7. Effect of current density on coulombic efficiency (CE), voltage efficiency (VE), and energy efficiency (EE) of the VRB with S/T/P membrane.

capacity of VRB single cell with the S/T/P membrane (3049 mAh) and Nafion 212 membrane (3075 mAh) in the second cycle are a little lower than the theoretical value of 3216.6 mAh ($96,485 \text{ C mol}^{-1} \times 1.5 \text{ mol L}^{-1} \times 80 \text{ mL} \times 3600^{-1} \text{ Ah C}^{-1}$). The decay rate of charge capacity of VRB single cell with the S/T/P membrane is lower than that with a Nafion 212 membrane. This is caused by the reduction of self-discharge of the VRB single cell with the S/T/P membrane.

The relationships of the CE, VE and EE with different charge-discharge current density are illustrated in Fig. 7. An increase of CE can be observed with increasing current density, while the VE shows the completely opposite trend. The EE is found to have a maximum at about 20 mA cm^{-2} . As the current density increases, the charge-discharge cycle becomes shorter. This decreases the amount of the penetrated vanadium ions, thus reduces the self-discharge of the cell, which can be reflected in an increased CE.

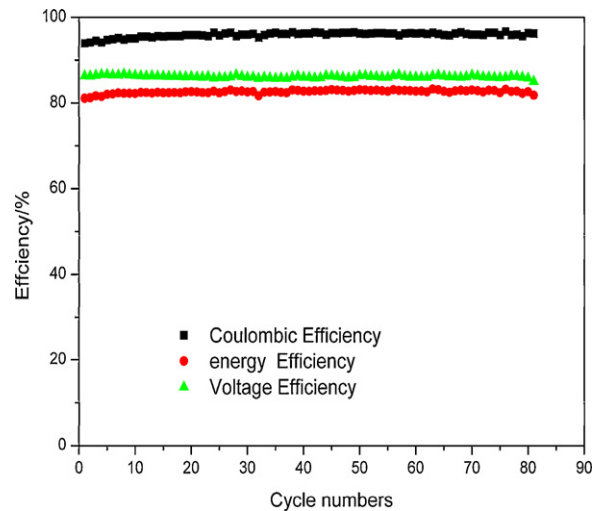


Fig. 8. The cycle performance for VRB single cell with S/T/P membrane at current density of 35.7 mA cm^{-2} .

The cyclic performance of a VRB single cell with an S/T/P membrane with a charge-discharge current density of 35.7 mA cm^{-2} is presented in Fig. 8. There is no decrease in VE, CE and EE even after the cell has undergone more than 80 cycles (>350 h). It reveals that the membrane has good chemical stability in strong acidic vanadium solutions. The special sandwich-type structure of the S/T/P membrane will increase its working life in a VRB system, because when one outer layer breaks the other outer layer can continue to work. The cost of the S/T/P membrane is much lower than Nafion 212 membrane. The high chemical stability and low cost make the S/T/P membrane very suitable as an ion exchange membrane in a VRB system.

4. Conclusions

A novel sandwich-type S/T/P composite membrane has been prepared by hybrid solution casting. The vanadium ion permeability of the S/T/P composite membrane was significantly lower than that of a Nafion 212 membrane. A VRB single cell with an S/T/P membrane has higher CE, EE and a lower self-discharge rate than the cell with a Nafion 212 membrane. Therefore, with the good performances and low cost, the S/T/P membrane is expected to have excellent commercial prospects as an ion exchange membrane for VRB systems.

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