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## Sulfonated poly(ether ether ketone)/TiO<sub>2</sub> double-deck membrane for vanadium redox flow battery application

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**Abstract:** A novel sulfonated poly(ether ether ketone) (SPEEK)/TiO<sub>2</sub> double-deck membrane which consists of a layer of SPEEK and a layer of TiO<sub>2</sub> was prepared and investigated for vanadium redox flow battery (VRB) application for the first time. The physicochemical properties of the SPEEK/TiO<sub>2</sub> membrane, including the water uptake, swelling ratio, ion exchange capacity, proton conductivity, VO<sup>2+</sup> permeability and ion selectivity are evaluated in detail, compared to the pristine SPEEK membrane and Nafion 117 membrane. The scanning electron microscopy images reveal its double-deck structure and the structural stability with no delamination, and thermogravimetric analysis (TG) identifies its thermal stability. Among all membranes, the SPEEK/TiO<sub>2</sub> double-deck membrane possesses lowest vanadium ion permeability ( $6.66 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$ ) and highest ion selectivity ( $9.46 \times 10^4 \text{ S min cm}^{-3}$ ). The VRB single cell with SPEEK/TiO<sub>2</sub> double-deck shows higher coulombic efficiency (97.0 % vs 93.3 %) and energy efficiency (85.8 % vs 83.7 %) compared to that with Nafion 117 membrane at  $60 \text{ mA cm}^{-2}$ . Furthermore, the SPEEK/TiO<sub>2</sub> double-deck exhibits

highly stable cell performance after 60 times of cycling tests at  $60 \text{ mA cm}^{-2}$  and lower capacity decay rate than that of Nafion 117 membrane. Therefore, the SPEEK/TiO<sub>2</sub> double-deck exhibits good potential usage in VRB systems.

**Keywords:** Vanadium redox flow battery; Sulfonated poly(ether ether ketone); Titanium dioxide; Double-deck membrane

## 1. Introduction

The vanadium redox flow battery (VRB), originally proposed by Skyllas-kazacos et al.[1], has received considerable attention as a large-scale energy storage system due to its fast response time, long cycle life, flexible design and deep-discharge capability[2-4]. As one of the key components of VRB, ion exchange membrane is used to separate the positive and negative electrolyte effectively while allowing the transport of ions to complete the circuit. An ideal membrane for VRB should possess low permeability for vanadium ions, good proton conductivity, high stability and low cost[5]. Currently, Nafion 117 membrane, produced by DuPont company, is the most commonly used in VRB. Even though the Nafion 117 membrane shows good chemical stability and high proton conductivity, the extremely high vanadium ion permeability and cost have limited its further application[6, 7]. In order to reduce the permeation of the vanadium ions and improve the performance of VRB, various modifications of Nafion 117 membrane including composites, surface modification and introduction of thin layer have been reported with lower vanadium ion permeability and better VRB performance than the pristine Nafion 117 membrane[8-13]. However, the modified membranes are still too expensive which

would hinder the commercialization of VRB. Hence new alternative ion exchange membrane materials are being sought.

To date, sulfonated aromatic polymer membranes, such as sulfonated poly(ether ether ketone) (SPEEK), sulfonated poly(fluorenyl ether ketone) (SPFEK), sulfonated polyimide(SPI), and sulfonated polysulfone (SPSF) have been widely researched as candidates for VRB application[14-24]. In these membranes, sulfonated poly(ether ether ketone) (SPEEK) is paid more attention for its low cost, good mechanical property, low vanadium ion permeability and easy preparation. The properties of SPEEK membrane are determined by its degree of sulfonation (DS). Although SPEEK membrane with high DS exhibits high proton conductivity which is desired for VRB application, the high DS also result in poor mechanical property and high vanadium ion permeability, which greatly hinder its further application in VRB[25]. Layered membrane is regarded as an effective way to modify and improve the membrane performance. Yan et al. prepared sandwich-type S/T/P multilayered membrane[26] and sandwich-type S/P/P multilayered membrane[27], which show low vanadium ion permeability and good VRB performance.

In this paper, a novel SPEEK/TiO<sub>2</sub> double-deck membrane which consists of a layer of SPEEK and a layer of TiO<sub>2</sub> was prepared by solution casting method and used in VRB for the first time. TiO<sub>2</sub> was used due to its good stability, easy availability, and low price. TiO<sub>2</sub> can enhance the antioxidant ability of non-fluoropolymer based proton conductive membranes and effectively improve proton transport ability of the proton conductive membranes owing to it is a kind of

mesoporous material[28]. To fabricate successfully  $\text{TiO}_2$  layer on SPEEK layer, Poly(vinylidene fluoride) (PVDF) was used as binder[29, 30].  $\text{TiO}_2$  layer reduces the permeation of vanadium ion effectively and also provides good antioxygenic property, while SPEEK layer affords good proton conductivity. When used in VRB, the SPEEK and  $\text{TiO}_2$  layer are in contact with negative and positive half-cell electrolytes, separately. The morphology and physicochemical properties of the SPEEK/ $\text{TiO}_2$  double-deck membrane accompanied with its performance in VRB single cell were evaluated in detail.

## **2. Experimental**

### **2.1. Materials**

Poly(ether ether ketone) (PEEK) (Viktrex, PEEK 450PF) was dried under vacuum at 100 °C overnight before use. Nafion 117 membrane and PVDF were purchased from DuPont company. All the other analytical reagents, including  $\text{TiO}_2$ , N,N-Dimethylacetamide (DMAC),  $\text{H}_2\text{SO}_4$  (98wt.%), NaCl, NaOH,  $\text{VOSO}_4$  and  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  were provided by local chemical suppliers and used as received without further purification.

### **2.2. membrane preparation**

For preparing sulfonated poly(ether ether ketone) (SPEEK), 5 g PEEK were added to  $\text{H}_2\text{SO}_4$  (98 wt.%, 100 ml) with stirring at 40 °C for 5 h. Then the reaction was terminated by pouring into ice-cold water under mechanical agitation. After washed with distilled water until the pH reached neutrality, the SPEEK was dried at 80 °C for 24 h under vacuum environment. The DS of SPEEK was 64 % determined by titration method[31].  $\text{TiO}_2$  slurry was prepared by milling a mixture containing 225 mg  $\text{TiO}_2$

with 37.5 mg PVDF (mass ratio of  $\text{TiO}_2/\text{PVDF}=6/1$ ) in mortar and then dispersing in 10mL DMAC. The slurry was homogenized by a treatment in ultrasonic bath for 1h.

The preparation of membrane followed two steps. First, 1.5 g SPEEK was dissolved in 10mL DMAC at 60 °C for 4 h to form a 15 wt./vol.% casting solution which was cast onto a stainless steel plate and dried at 80 °C for 10 h, then dried at 100 °C for 8 h. In the second step,  $\text{TiO}_2$  slurry with an mass ratio of  $\text{TiO}_2/\text{SPEEK} = 1/10$  was poured onto the SPEEK membrane after SPEEK membrane was cooled to room temperature. Then the membrane was dried at 80 °C for 8 h. The membrane was peeled off from the stainless steel plate by immersing in deionized water and then soaked in 1 mol  $\text{L}^{-1}$   $\text{H}_2\text{SO}_4$  solution for 24 h. Afterwards, the membrane was rinsed with deionized water and soaked in deionized water for 24 h to remove any  $\text{H}_2\text{SO}_4$  residues, and stored in deionized water before it was used. SPEEK/ $\text{TiO}_2$  membrane was denoted as S/Ti membrane. The Nafion 117 membrane served as reference membrane was pretreated by the standard procedure according to the literature[11].

## **2.3. Membrane characterization**

### **2.3.1. membrane morphology**

The sample for cross-sectional view was fractured in liquid nitrogen and then coated with gold before the cross-section morphology of membrane was observed by a Hitachi S-4800 (Japan) scanning electron microscope (SEM).

### **2.3.2. Water uptake and swelling ratio**

The water uptake and swelling ratio of membrane were conducted by following procedures. The weight and length of wet membrane were immediately measured

after quickly wiping off the water adhered to the surface of membrane with absorbent paper. Afterwards, the wet membrane was dried under vacuum at 100 °C for 24 h and dry membrane were measured. The water uptake and swelling ratio of membrane were calculated according to the following equations:

$$\text{Water uptake (\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{wet}}} \times 100\% \quad (1)$$

$$\text{Swelling ratio (\%)} = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}} \times 100\% \quad (2)$$

where  $W_{\text{wet}}$  and  $W_{\text{dry}}$  are the weight of wet and dry membrane, respectively;  $L_{\text{wet}}$  and  $L_{\text{dry}}$  are the length of wet and dry membrane, respectively. Three parallel tests were conducted and the average values were calculated.

### 2.3.3. Ion exchange capacity (IEC) and proton conductivity

The IEC of membrane was determined by a titration method. The membrane was firstly soaked in 50 mL 1 mol L<sup>-1</sup> NaCl solution for 24 h so that the H<sup>+</sup> in the membrane was exchanged by the Na<sup>+</sup> in the solution. The H<sup>+</sup> concentration in the solution was titrated with 0.01 mol L<sup>-1</sup> NaOH, using phenolphthalein as indicator. Subsequently, the membrane were dried and weighted. The IEC was calculated by the following equation:

$$\text{IEC (mmol g}^{-1}\text{)} = \frac{C_{\text{NaOH}} \times V_{\text{NaOH}}}{W_{\text{dry}}} \quad (3)$$

where  $V_{\text{NaOH}}$  is the volume of the consumed NaOH solution,  $C_{\text{NaOH}}$  is the concentration of the NaOH solution and  $W_{\text{dry}}$  refers to the dried weight of membrane.

The proton conductivity of membrane was measured by electrochemical impedance spectroscopy (EIS) using a Solartron 1287+1260 electrochemical station (USA,

AMETEK, Inc.). The measurement was conducted between frequencies of 1 MHz and 1 Hz with amplitude of 10 mV. The proton conductivity ( $\sigma$ ) of membrane was calculated by the following equation:

$$\sigma \text{ (S cm}^{-1}\text{)} = \frac{L}{A \times R} \quad (4)$$

where L is the distance between two electrodes, A is the cross-sectional area of membrane, R is membrane resistance obtained from the EIS data.

#### 2.3.4. Permeability of $\text{VO}^{2+}$ and selectivity

The permeability of  $\text{VO}^{2+}$  of membrane was measured as previously described[32]. The membrane with effective area of  $2.54 \text{ cm}^2$  was sandwiched between two reservoirs. 28 mL  $1 \text{ mol L}^{-1} \text{VO}^{2+}$  in  $2 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$  solution was filled in the left reservoir and 28 mL  $1 \text{ mol L}^{-1} \text{MgSO}_4$  in  $2 \text{ mol L}^{-1} \text{H}_2\text{SO}_4$  solution was filled in the right reservoir.  $\text{MgSO}_4$  was used to equalize the ionic strengths of the two solutions and to minimize the osmotic pressure effects[17]. To avoid the concentration polarization, the two solutions were continuously magnetically stirred throughout the measurement. Samples from the  $\text{MgSO}_4$  reservoir periodically were taken out and measured by a UV-vis spectrometer (TU-1900, Beijing Purkinje General Instrument Co., Ltd., China) at a wavelength of 762 nm. The taken out  $\text{MgSO}_4$  solution was put back into the right cell after each measurement. It was supposed that the change in vanadium ion concentration in the left reservoir can 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 as the formula[26, 33-35]:

$$V_R \frac{dC_R(t)}{dt} = A \frac{P}{L} [C_L - C_R(t)] \quad (5)$$

Where  $V_R$  is the volume of right reservoir,  $C_R(t)$  refers to the vanadium ion concentration in the right reservoir as a function of time,  $t$  is time,  $A$  is the effective area of membrane,  $P$  is the  $VO^{2+}$  permeability,  $L$  is the thickness of membrane, and  $C_L$  is the concentration of the  $VO^{2+}$  in the left cell. An assumption is also made here that  $P$  is independent of concentration.

The ion selectivity ( $S$ ) of membrane is defined as the ratio of proton conductivity divided by  $VO^{2+}$  permeability, which can be calculated by following equation:

$$S = \frac{\sigma}{P} \quad (6)$$

### 2.3.5. Thermal analysis

The thermal property of membrane was characterized by a NETZSCH STA 2500 Regulus (Germany) with a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  from  $100\text{ }^{\circ}\text{C}$  to  $800\text{ }^{\circ}\text{C}$  under a nitrogen atmosphere.

### 2.3.6. VRB single cell performance

The VRB single cell was assembled by sandwiching a membrane between two pieces of 5mm thickness graphite felt electrodes, which served as the electrodes. Two flexible graphite polar plates and two copper foils were served as current collectors, and the effective reaction area of membrane and electrodes were  $25\text{ cm}^2$ . 40 mL of  $1.5\text{ mol L}^{-1} VO^{2+}$  in  $3\text{ mol L}^{-1} H_2SO_4$  solution and 40 mL of  $1.5\text{ mol L}^{-1} V^{3+}$  in  $3\text{ mol L}^{-1} H_2SO_4$  solution were applied as positive and negative starting electrolytes respectively, which were cycled using peristaltic pump (BT100L, LEAD FLUID, China) at a flow

rate of 40 mL min<sup>-1</sup>. All the cell tests were performed by a battery test system (Land-CT2001A, Wuhan Sanland Electronic Technology Co., Ltd., China). To avoid the corrosion of the graphite felt electrodes and flexible graphite polar plates, the upper limit of charge voltage was 1.65 V and the lower limit of discharge voltage was maintained at 0.8 V. The coulombic efficiency (CE), voltage efficiency (VE) and energy efficiency (EE) of the cell are calculated by following equations:

$$CE (\%) = \frac{\int I_d dt}{\int I_c dt} \times 100\% \quad (7)$$

$$EE (\%) = \frac{\int V_d I_d dt}{\int V_c I_c dt} \times 100\% \quad (8)$$

$$VE (\%) = \frac{EE}{CE} \times 100\% \quad (9)$$

where  $I_d$  and  $I_c$  are the current of the discharging and the charging, respectively;  $V_d$  and  $V_c$  is the voltage of the discharging and the charging, respectively.

### 3. Results and Discussion

#### 3.1. Membrane morphology

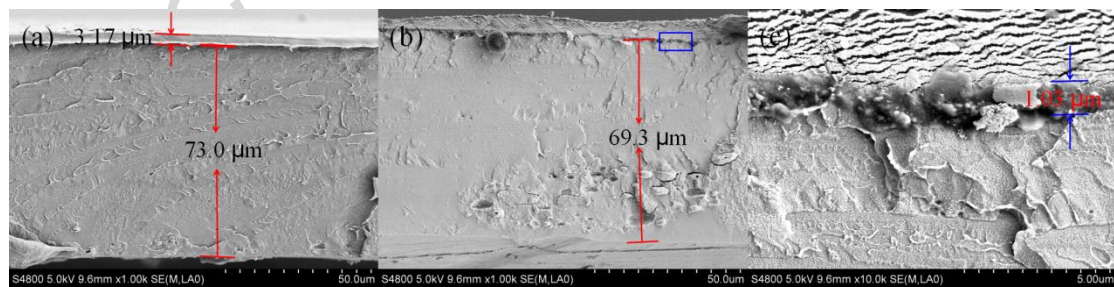


Fig.1. SEM images of the cross-section of S/Ti membrane: (a) before test, (b) and (c) after 60 cycles charge-discharge test.

Fig. 1(a-c) show the SEM images of the cross-section of S/Ti membrane before and after cycle testing, which are given a comparison to examine the microstructure and

confirm the composition of the S/Ti membrane. As shown in Fig. 1a, the double-deck structure of the S/Ti membrane can be observed clearly. No cracks are found throughout the whole membrane, indicating that the  $\text{TiO}_2$  layer is successfully deposited into holes of the SPEEK membrane. The thickness of  $\text{TiO}_2$  layer and SPEEK layer is about 3  $\mu\text{m}$  and 73  $\mu\text{m}$ , respectively. Fig. 1c is the high-resolution SEM image of the region encircled by blue line in Fig. 1b. From Fig. 1c, there is no delamination through the whole membrane cross-section after 60 cycles charge-discharge test, which also indicates that the  $\text{TiO}_2$  layer is successfully deposited into holes of the SPEEK membrane and is well attached to the SPEEK layer. The results further confirm that the bonding effect of the PVDF avoids the delamination of the SPEEK layer from the  $\text{TiO}_2$  layer. The thickness of the SPEEK layer and  $\text{TiO}_2$  layer has change before and after the 60 cycles charge-discharge test. This may be due to the non-uniformity of the SPEEK layer or  $\text{TiO}_2$  layer.

### 3.2. Physicochemical properties

Table 1 Physicochemical properties,  $\text{VO}^{2+}$  permeability and selectivity of Nafion 117, SPEEK and S/Ti membranes.

Membrane	Thickness ( $\mu\text{m}$ )	Water uptake(%)	Swelling ration(%)	IEC ( $\text{mmol g}^{-1}$ )	Proton Conductivity ( $\text{S cm}^{-1}$ )	$\text{VO}^{2+}$ permeability ( $10^{-7} \text{ cm}^2 \text{ min}^{-1}$ )	Selectivity ( $10^4 \text{ S min cm}^{-3}$ )
Nafion 117	220	28.5	16.3	0.91	0.097	36.5	2.66
SPEEK	107	56.6	20.5	1.81	0.067	19.1	3.51
S/Ti	90	40.4	10.5	1.58	0.063	6.66	9.46

Detailed comparisons of the physicochemical properties,  $\text{VO}^{2+}$  permeability and selectivity of all membranes are listed in Table 1. The thickness of the SPEEK and S/Ti membranes retain in the range of 90 to 110  $\mu\text{m}$ , which is much thinner than the Nafion 117 membrane (220  $\mu\text{m}$ ). Moreover, S/Ti membrane reveals lower water uptake than that of the pristine SPEEK membrane, but higher than that of Nafion 117 membrane. The swelling ratio of S/Ti membrane is the lowest of the three membranes. This may be resulted from the decreased pore number with the existence of  $\text{TiO}_2$  layer on SPEEK membrane and thus reduce the channel number for  $\text{H}_2\text{O}$  diffusion, decreasing the absorption of  $\text{H}_2\text{O}$ . The IEC of S/Ti membrane is higher than Nafion 117 membrane, but lower than SPEEK membrane, which is in good accordance with the result of water uptake, because the increased water uptake would facilitate the dissociation of  $-\text{SO}_3\text{H}$  groups and the migration of protons in the membrane. The S/Ti

membrane has lower proton conductivity compared to the pristine SPEEK membrane, which can be explained by the blocking effect of the proton-nonconductive  $\text{TiO}_2$  layer. Although the proton conductivity of S/Ti membrane is lower than that of Nafion 117 membrane, the double-deck membrane still possess effective VRB cell performances, which can be verified by the following results.

### 3.3. Vanadium permeability and selectivity

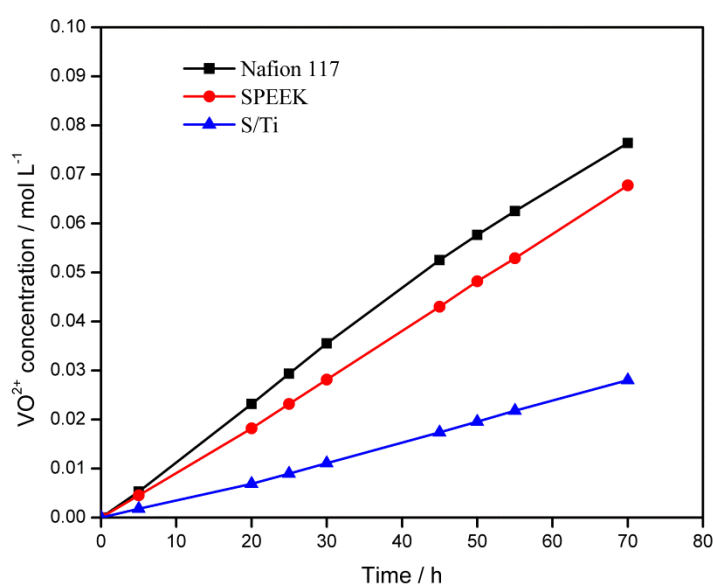


Fig. 2. Concentration change of  $\text{VO}^{2+}$  in  $\text{MgSO}_4$  solution across Nafion 117, SPEEK and S/Ti membranes.

As shown in Table 1, the  $\text{VO}^{2+}$  permeability of SPEEK membrane and S/Ti membrane are lower than that of the Nafion 117 membrane, which exhibit obviously in Fig. 3. Fig. 2 clearly indicates a linear relation between time and the concentration of V(IV) in  $\text{MgSO}_4$  solution for various membranes, illustrating the  $\text{VO}^{2+}$  ion diffusion speed of SPEEK membrane and S/Ti membrane is slower than Nafion 117 membrane. Former is due to their different microstructures. The microstructure of the

SPEEK membrane has smaller hydrophobic/hydrophilic separations compared to Nafion 117, resulting from the backbone is less hydrophobic and the sulfonic acid groups are less acidic. Furthermore, the high rigidity of the backbone of SPEEK also prevents the neighboring dispersed  $\text{-SO}_3\text{H}$  groups to form aggregating to hydrophilic domains. Thus, the water filled channels in SPEEK membrane are narrow and branched with more dead end pockets compared with those in Nafion membrane. The S/Ti membrane demonstrates lower  $\text{VO}^{2+}$  permeability than that of the Nafion 117 membrane, which is owing to two respects. On one hand, S/Ti membrane is based on SPEEK. On the other hand,  $\text{TiO}_2$  layer distributing throughout SPEEK membrane decrease the channel number for ion crossing and increase the number of the dead pores, which result in signally restraining the crossover of vanadium ion.

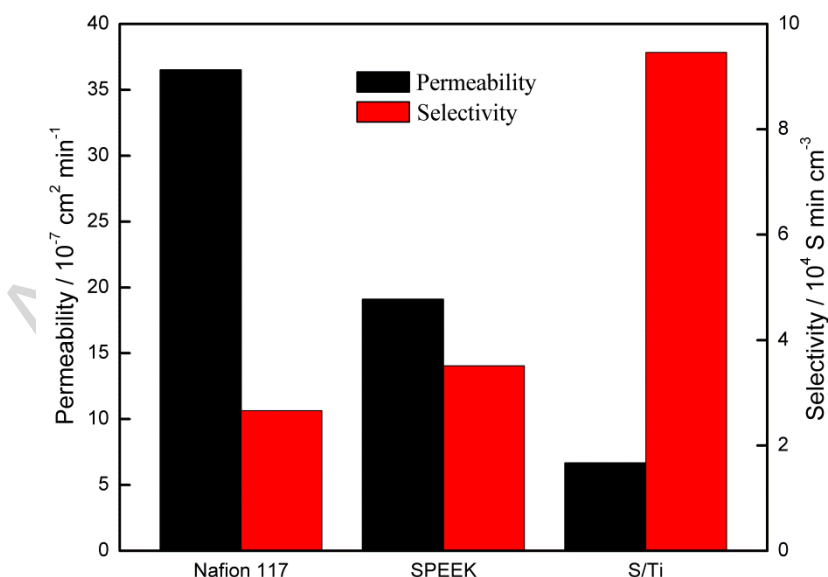


Fig. 3.  $\text{VO}^{2+}$  permeability and selectivity of Nafion 117, SPEEK and S/Ti membranes.

Selectivity is a comprehensive factor for evaluating the balance of proton conductivity and vanadium ion permeability. Generally, a higher selectivity value indicates better performance in VRB. The  $\text{VO}^{2+}$  permeability and selectivity of various membranes are calculated and shown in Fig. 3, and the corresponding data are listed in Table 1. It can be seen that the selectivity value of S/Ti membrane is  $9.46 \times 10^4 \text{ S min cm}^{-3}$ , which is about three times higher than that of Nafion 117 membrane ( $2.66 \times 10^4 \text{ S min cm}^{-3}$ ) due to the permeability value of the S/Ti membrane is much lower than that of Nafion 117 membrane. From Fig. 3, it is observed that the S/Ti membrane exhibits the better selectivity among these membranes, suggesting that the VRB assembled with the S/Ti membrane will show the better VRB performance.

### 3.4. Thermal analysis

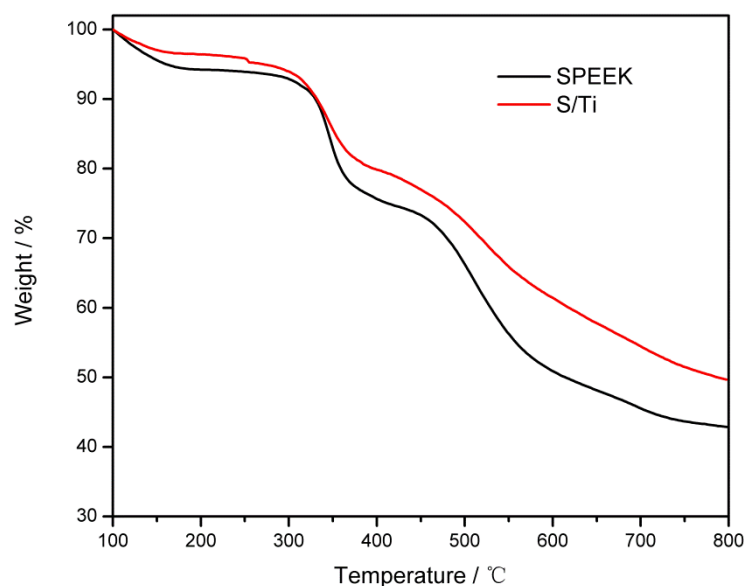


Fig. 4. TG curves of SPEEK and S/Ti membranes.

Fig. 4 shows the TG curves of SPEEK and S/Ti membranes. Two distinct weight loss process of all membranes can be observed. The first weight loss in the range of

290-330 °C can be attributed to the degradation of sulfonic acid groups in SPEEK polymer. The second one in the range of 420-520 °C is caused by the decomposition of the SPEEK backbone. The TG curve of the S/Ti membrane with the existence of TiO<sub>2</sub> layer shift obviously toward higher temperature as shown in Fig. 4, indicating a higher thermal stability of the S/Ti membrane.

### 3.5. VRB single cell performance

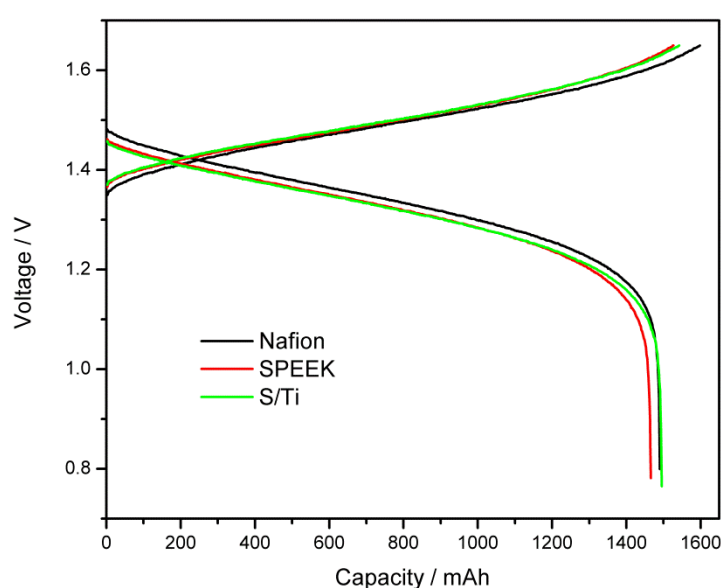


Fig. 5. Charge-discharge curves for VRB with Nafion117, SPEEK and S/Ti membranes at a current density of 60 mA cm<sup>-2</sup>.

The charge-discharge curves of VRB single cell employing Nafion 117, SPEEK and S/Ti membranes at 60 mA cm<sup>-2</sup> are presented in Fig. 5. It can be seen that the VRB with S/Ti membrane show higher charge capacity and discharge capacity than that with SPEEK membrane, which is ascribed to a good balance between proton conductivity and vanadium ion permeability. Moreover, the charge capacity of the VRB with S/Ti membrane is lower than that of Nafion 117 membrane, which is



assigned to lower proton conductivity. A little higher discharge capacity of S/Ti membrane is obtained due to its lower vanadium ion permeability and higher ion selectivity compared with Nafion 117 membrane. The CE and EE of VRB with S/Ti membrane (97.0 % and 85.8 %) are higher than that of Nafion 117 membrane (93.3 % and 83.7 %).

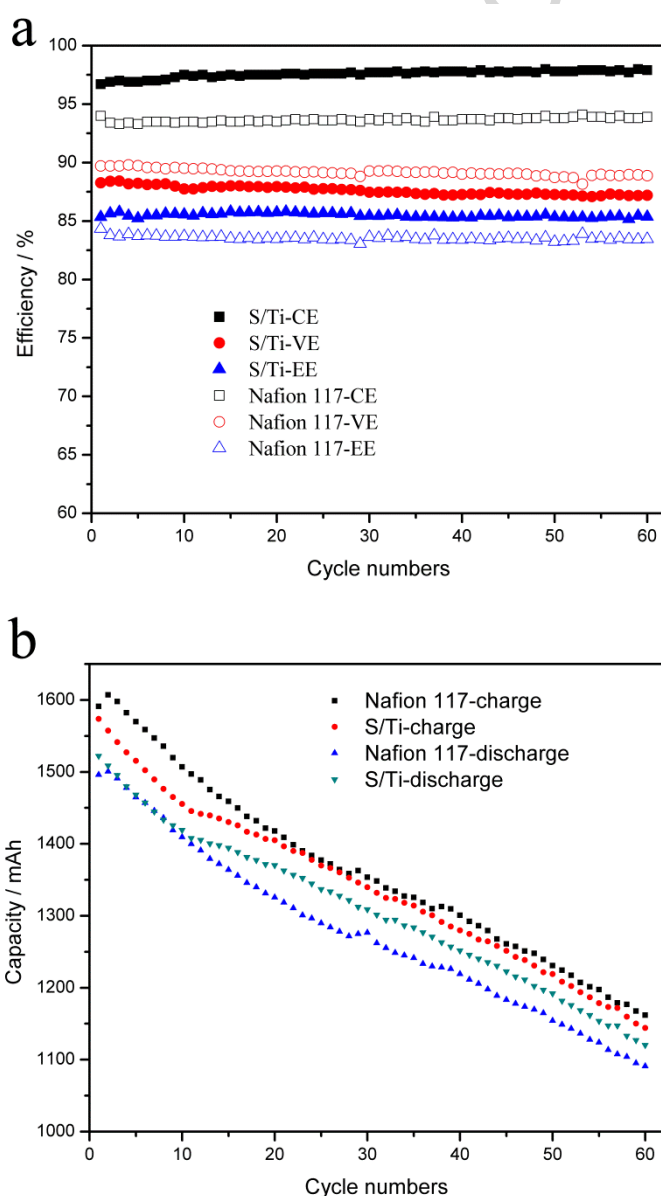


Fig. 6. Cycle performance of VRB with Nafion 117 and S/Ti membranes at a current

density of  $60 \text{ mA cm}^{-2}$ : (a) efficiency and (b) capacity decay.

Fig. 6a shows the cycle performance of VRB single cell with S/Ti and Nafion 117 membranes at a current density of  $60 \text{ mA cm}^{-2}$ , respectively. It is found that both S/Ti and Nafion 117 membranes exhibit good stability after 60 cycles on the parameters of CE, VE and EE. Furthermore, it is worth mentioning that S/Ti membrane displays higher CE and EE value than those of Nafion 117 membrane. The charge and discharge capacities fading of VRB with S/Ti and Nafion 117 membranes are illustrated in Fig. 6b. It can be seen that both the decay rates of charge and discharge capacities of VRB with S/Ti membrane are lower than that with Nafion 117 membrane. Furthermore, the discharge capacity of S/Ti membrane is higher than Nafion 117 membrane throughout the cycle life test. The higher capacity decay rate of Nafion 117 membrane can be ascribed to the higher crossover of vanadium ions and the resulting high self-discharge. As shown in Fig. 1c, the SEM image of the S/Ti membrane even after 60 cycles test proves its structural stability under the strong oxidizing and acid situation,. The above results demonstrate that the S/Ti membrane presents good cycle performance and chemical stability in VRB operating environment.

#### 4. Conclusions

A novel SPEEK/TiO<sub>2</sub> double-deck membrane which consists of a layer of SPEEK and a layer of TiO<sub>2</sub> was prepared by solution casting method and investigated for VRB application for the first time. The TiO<sub>2</sub> layer of the SPEEK/TiO<sub>2</sub> double-deck reduces the permeation of vanadium ion effectively and also enhances antioxygenic

property, while SPEEK layer affords good proton conductivity. As a result, the permeability of vanadium ion of the SPEEK/TiO<sub>2</sub> double-deck membrane is significantly lower than that of Nafion 117 membrane. The VRB single cell with the SPEEK/TiO<sub>2</sub> double-deck membrane exhibits higher CE, EE and smaller capacity decay rate than that with Nafion 117 membrane, and excellent cycle performance. Considering its excellent cell performance and low cost, the SPEEK/TiO<sub>2</sub> double-deck membrane is a promising candidate for application in VRB system.

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