

## A super thin polytetrafluoroethylene/sulfonated poly(ether ether ketone) membrane with 91% energy efficiency and high stability for vanadium redox flow battery

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**ABSTRACT:** In order to further decrease the cost and enhance the durability of sulfonated poly(ether ether ketone) membrane for vanadium redox flow battery, a super thin (40  $\mu\text{m}$ ) polytetrafluoroethylene (PTFE)/SPEEK (PS) membrane is prepared. The physico-chemical properties and single cell performance of PS membranes prepared with different casting solvents including NMP (*N*-methyl-2-pyrrolidone), DMF (*N,N'*-dimethylformamide), and DMAc (*N,N'*-dimethylacetamide) have been investigated. Results show that the energy efficiency of VRB with PS/DMF can reach up to 91.2% at the current density of 40  $\text{mA cm}^{-2}$ , which is 11.1% and 6.4% higher than that of the commercial Nafion 212 and pristine SPEEK membrane, respectively. In addition, charge–discharge test over 150 times proves that the PS/DMF membrane possesses high stability and thus it is suitable for VRB application. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43593.

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### INTRODUCTION

With the rapid development of modern society, the energy shortage and environmental pollution are becoming more and more serious because of the detrimental effects of traditional fossil fuels. Consequently, many efforts have been focused on the renewable and sustainable energy resources such as solar and wind energy to solve the problem. However, the solar and wind energy are intermittent and volatile and thus require energy storage systems.<sup>1</sup> To date, a lot of energy storage technologies including physical and chemical methods are developed, such as pumped hydro, compressed air, fly-wheel, capacitors, batteries, etc. Among the batteries being used for energy storage, all vanadium redox flow battery (VRB) invented by Skyllas-Kazacos *et al.*<sup>2</sup> is considered to be one of the most suitable technologies for medium to large scale energy storage. VRB consists of one piece of membrane, two electrolyte tanks, carbon electrodes, etc. The unique advantage of VRB is that its energy capacity and power output are independent because of the separation of energy storage part (electrolyte tanks) and VRB stack. Furthermore, the VRB possesses many advantages of excellent energy efficiency, long cycle life, safety, fast response time, deep-discharge capability, and so on. The ion exchange membrane is a key component of VRB and it has been extensively explored in recent years. Because of the strong acid and

oxidative condition of the VRB electrolyte, perfluorosulfonated ion exchange membrane such as Nafion (register of DuPont) has been the reference membrane for VRB for its superior chemical stability and excellent proton conductivity. However, extremely high cost and relatively low vanadium/proton selectivity have limited its wide application in VRB. In this regard, nonperfluorinated membranes including cation and anion exchange membranes are developed because of their high chemical and thermal stability.<sup>3–8</sup> Among these membranes, sulfonated poly(ether ether ketone) (SPEEK) is considered to be the most promising alternative to Nafion membrane for its low cost, acceptable stability, and good electrochemical activity in VRB. Studies show that the properties of SPEEK membranes depend on the degree of sulfonation (DS),<sup>1,9,10</sup> and higher proton conductivity can be obtained via prolonging sulfonation time and increasing temperature. However, with the increasing DS of the SPEEK, it could be easily dissolved in water and unfavorable for the membrane mechanical performance.<sup>11,12</sup> Furthermore, study by Xi *et al.* shows that the solvents used to prepare the SPEEK membranes have important effect on the performances of VRB.<sup>9</sup>

Recently, ultra-thin membranes based on polytetrafluoroethylene/Nafion (P/N) have exhibited great potential in VRB application.<sup>13–15</sup> The P/N membrane possesses higher stability and

lower cost than that of Nafion membrane. Because of the super-chemical and mechanical stability of PTFE (polytetrafluoroethylene), the P/N membrane can be controlled to be as thin as 25–30  $\mu\text{m}$ . With the decrease of the membrane thickness, the cost of the membrane has been greatly reduced because of the less consumption of Nafion resin. Moreover, the P/N membranes also possess good mechanical strength both in swollen and unswollen states, good thermal stability as well as low membrane resistance.<sup>16</sup>

In this article, super-thin PTFE/SPEEK (PS) membranes were prepared by using PTFE as substrate to further decrease the consumption of SPEEK resin while still keeping its ductility and stability. Furthermore, different casting solvents including NMP, DMAc, and DMF were chosen to investigate their influence on the properties of PS membrane. The physico-chemical properties including water uptake, proton conductivity, and vanadium ion permeability were investigated. And the properties of the PS membrane such as Fourier transform infrared spectra (FTIR), scanning electron microscope (SEM), small angle X-ray scattering (SAXS) as well as VRB single cell performances were studied.

## EXPERIMENTAL

### PS Membranes Preparation

Porous PTFE membranes ( $\sim 20 \mu\text{m}$ ) were treated by ethanol at 55 °C for 2.5 h to improve its hydrophilicity and compatibility with SPEEK resin. Dried PEEK powder (Victrex, 450 PF) was sulfonated by using concentrated  $\text{H}_2\text{SO}_4$  at 60 °C for 5 h. The degree of sulfonation of PEEK was 56% as determined by using  $^1\text{H}$  NMR method.<sup>17</sup> Dried SPEEK powder was dissolved in different solvents to form a 6 wt % casting solution. The solvents were NMP (*N*-methyl-2-pyrrolidone), DMF (*N,N'*-dimethylformamide), and DMAc (*N,N'*-dimethylacetamide), respectively. Afterwards, the three kinds of casting solvents were cast on the pretreated PTFE membranes mounted on a glass plate and subsequently annealed at 130 °C to enhance the crystallinity and mechanical property. Finally, the membranes were immersed in 1.0 mol  $\text{L}^{-1}$   $\text{H}_2\text{SO}_4$  solution until they can be easily peeled off from the glass plate. Consequently, the membranes were denoted as PS/DMF, PS/DMAc, and PS/NMP to represent the membrane made by DMF, DMAc, and NMP, respectively. A pristine SPEEK membrane with 40  $\mu\text{m}$  was also prepared by the similar procedure as a control sample.

### Membrane Characterizations

Water uptake (WU) was measured by weighing method. Membranes were first dried at 80 °C for 24 h and cooled naturally to room temperature. After being measured for dry weight, the membranes were immersed in the deionized water for 24 h to be fully hydrated. The wet membranes were weighed again after removing immediately the excess water on the membrane surface and the WU can be calculated according the following equation:

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

where  $W_{\text{wet}}$  and  $W_{\text{dry}}$  are the weights of wet and dry membranes, respectively.

The in-plane proton conductivity ( $\sigma$ ) of the membranes was determined by the electrochemical impedance spectroscopy (EIS) method using a CHI600e electrochemical station (Chenhua, China) over a frequency range from 1 to 1 MHz with an oscillating voltage of 10 mV to record the ionic resistance of the samples. The proton conductivity can be calculated by the following equation:

$$\sigma = \frac{L}{R \times S} \quad (2)$$

where  $\sigma$  (mS  $\text{cm}^{-1}$ ) is the membrane proton conductivity,  $L$  (cm) is the distance between the two Pt electrodes,  $R$  ( $\Omega$ ) is the resistance value obtained from EIS curves, and  $S$  ( $\text{cm}^2$ ) is the cross-section area of the membranes.

Fourier transform infrared (FTIR) spectra of the membranes were measured by a Nicolet 380 spectrometer (Thermo Scientific, USA) equipped with a diamond crystal accessory. Each spectrum was recorded at the range of 4000–650  $\text{cm}^{-1}$  (32 scans, 4  $\text{cm}^{-1}$  resolution) using attenuated total reflectance (ATR) method.

The microstructure and morphology of the membranes were analyzed by two types of scanning electron microscope instruments. One is a TESCAN VEGA II (Czech Republic) SEM, and the other is a MERLIN Compact field emission environmental SEM (Zeiss, Germany). All the samples surfaces were coated with gold powder before SEM observations. The small-angle X-ray scattering (SAXS) measurements were analyzed using SAXSess  $\text{mc}^2$  (Anton Paar GmbH, Austria) equipped with a Cu anode X-ray tube ( $\lambda K\alpha = 1.5418 \text{ nm}$ ).

The  $\text{VO}^{2+}$  permeability was measured by using a diffusion cell made by acrylic with two chambers. The left chamber was filled with 18 mL of 1.5 mol  $\text{L}^{-1}$   $\text{VOSO}_4$  in 2.5 mol  $\text{L}^{-1}$   $\text{H}_2\text{SO}_4$ , and the right one was filled with 18 mL of 1.5 mol  $\text{L}^{-1}$   $\text{MgSO}_4$  in 2.5 mol  $\text{L}^{-1}$   $\text{H}_2\text{SO}_4$ .  $\text{MgSO}_4$  was used to balance the ionic strengths and minimize the osmotic pressure effects.<sup>18</sup> The effective area of the membranes was 1.77  $\text{cm}^2$  and the solution in  $\text{MgSO}_4$  side was taken regularly and determined by a 721 UV-vis spectrometer (Shanghai Jinghua, China). The  $\text{VO}^{2+}$  permeability ( $P$ ) was calculated according to the following equation:

$$V_r \frac{dC_r(t)}{dt} = A \frac{P}{D} [C_l - C_r(t)] \quad (3)$$

where  $P$  is  $\text{VO}^{2+}$  permeability,  $C_r(t)$  and  $C_l$  are the  $\text{VO}^{2+}$  concentration in the right and left chambers, respectively.  $A$  and  $D$  are the active area and thickness of the samples,  $V_r$  is the volume of right reservoir.

The mechanical properties of prepared membranes were investigated on a universal testing machine (Instron-5965, USA) with a tensile rate of 10  $\text{mm min}^{-1}$  at ambient temperature. The samples were cut into rectangular shape and the size is about 25  $\times$  10 mm.

### Chemical Stability Test

In order to investigate the chemical stability of the PS membranes, they were immersed in 1.5 mol  $\text{L}^{-1}$   $\text{VO}_2^+$  in 2.5 mol  $\text{L}^{-1}$   $\text{H}_2\text{SO}_4$  solution for 3 weeks to determine the membrane

**Table I.** Water Uptake and Proton Conductivity of Three PS Membranes

Membrane	Water uptake (%)	Proton conductivity (mS cm <sup>-1</sup> )
PS/DMF	17.2	47.4
PS/NMP	20.1	49.6
PS/DMAc	17.9	48.4

weight loss and vanadium permeability change. All the VO<sub>2</sub><sup>+</sup> solutions used in the experiment were prepared by electrochemical oxidation of the VO<sup>2+</sup> solution. The weight loss and the vanadium permeability are calculated by the eqs. (4) and (3), respectively.

$$\text{Weight loss (\%)} = \frac{W_0 - W}{W_0} \times 100\% \quad (4)$$

where  $W_0$  and  $W$  are the weight of the membranes before and after being immersed in VO<sub>2</sub><sup>+</sup> solution for 3 weeks, respectively.

### Single Cell Test

A sandwiched single cell was assembled to perform the charge-discharged test. Two graphite plate graved with serpentine flow field were used as polar plates. The PS membranes with effective area of 9 cm<sup>2</sup> were clamped by two pieces of carbon felt with 5 mm thickness. Forty mL 1.5 mol L<sup>-1</sup> V<sup>3+</sup>/VO<sup>2+</sup> in 2.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> were employed as initial electrolyte which was prepared by electrolytic method. Cell tests were controlled by a CT2001C (Wuhan Land Electronics, China) battery analyzer at various current densities. In order to avoid the corrosion of graphite plate, battery charge and discharge voltage was set between 1.65 and 0.8 V, respectively. The cell was charged at 50% state of charge and left at open circuit state to conduct the self-discharge process as reported.<sup>10</sup> The test was stopped until the open circuit voltage (OCV) of the cell dropped to 0.8 V. The cycle life test of the membrane was evaluated at constant current density of 80 mA cm<sup>-2</sup> with cutoff voltages limited between 1.65 and 0.8 V for charge and discharge, respectively. The coulombic efficiency (CE), voltage efficiency (VE), and energy efficiency (EE) of the cell were calculated by the method as we have reported.<sup>19</sup>

## RESULTS AND DISCUSSION

### Basic Physico-chemical Properties of Different PS Membranes

Basic physico-chemical properties including WU and proton conductivity of the PS membranes prepared by DMF, NMP, and DMAc are presented in Table I.

It can be seen that the WU and proton conductivity of the PS membranes are all slightly affected by the solvents. For the PS/NMP membrane, it possesses the highest WU and proton conductivity among the three membranes. Studies by Robertson *et al.* show that the proton conductivity of the SPEEK membrane is affected by both casting solvents and temperature.<sup>17</sup> When the heating temperature is 130 °C in membrane treatment process, the membrane prepared with NMP solvent has the highest proton conductivity. The reason may be that NMP is easier to be removed than DMAc and DMF because there is no strong hydrogen-bonding between SPEEK and NMP, since the presence of retained solvents may cause the low conductivity of

these membranes.<sup>17</sup> Furthermore, the retained solvents in the membrane caused by hydrogen-bonding between SPEEK and DMF/DMAc also prevent the SO<sub>3</sub>H groups from absorbing water, which makes the PS/NMP has the highest water uptake.<sup>20</sup>

### FTIR

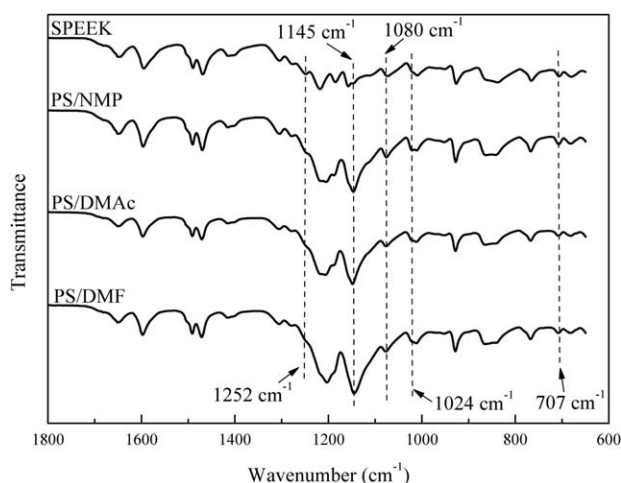
Figure 1 shows the FTIR spectra of pristine SPEEK, PS/NMP, PS/DMAc, and PS/DMF. The characteristic bands of PTFE include C-F asymmetric stretching mode (1155 cm<sup>-1</sup>), C-F symmetric stretching mode (1218 cm<sup>-1</sup>), and three other peaks at lower wavenumbers.<sup>21</sup> While for SPEEK membrane, its characteristic bands are O=S=O asymmetrical stretching (1252 cm<sup>-1</sup>), O=S=O symmetrical stretching (1080 cm<sup>-1</sup>), S=O stretching (1024 cm<sup>-1</sup>), and S-O stretching (709 cm<sup>-1</sup>), respectively.<sup>1,22</sup> It can also be observed that both the characteristic bands of PTFE (~1145 cm<sup>-1</sup>) and SPEEK (~1080, ~1024, ~707 cm<sup>-1</sup>) have been found in all the PS membranes, indicating the SPEEK resin can be successfully impregnated in PTFE matrix by all the solvents.

### Membrane Morphology

As shown in Figure 2(a), the structure of PTFE membrane is highly porous just like a spider web. But for the PS composite membranes, the pores of PTFE are all fully filled and covered with SPEEK resin with no obvious PTFE pores. However, different from the smooth and clean surface of the SPEEK membranes [Figure 2(b)], the surface of all the PS membranes is not so smooth and there has some pits. One reason may be that the pores of PTFE substrate are not even, and there should have small or big pores existed in the membrane. The other reason is that SPEEK layer is not thick enough since the total thickness of the PS membranes is only ~40 μm, and the PTFE substrate itself is 20 μm. Therefore, in some areas, the SPEEK resin layer cannot smoothly fill the pores of PTFE substrate and form the pits on the surface of the membrane.

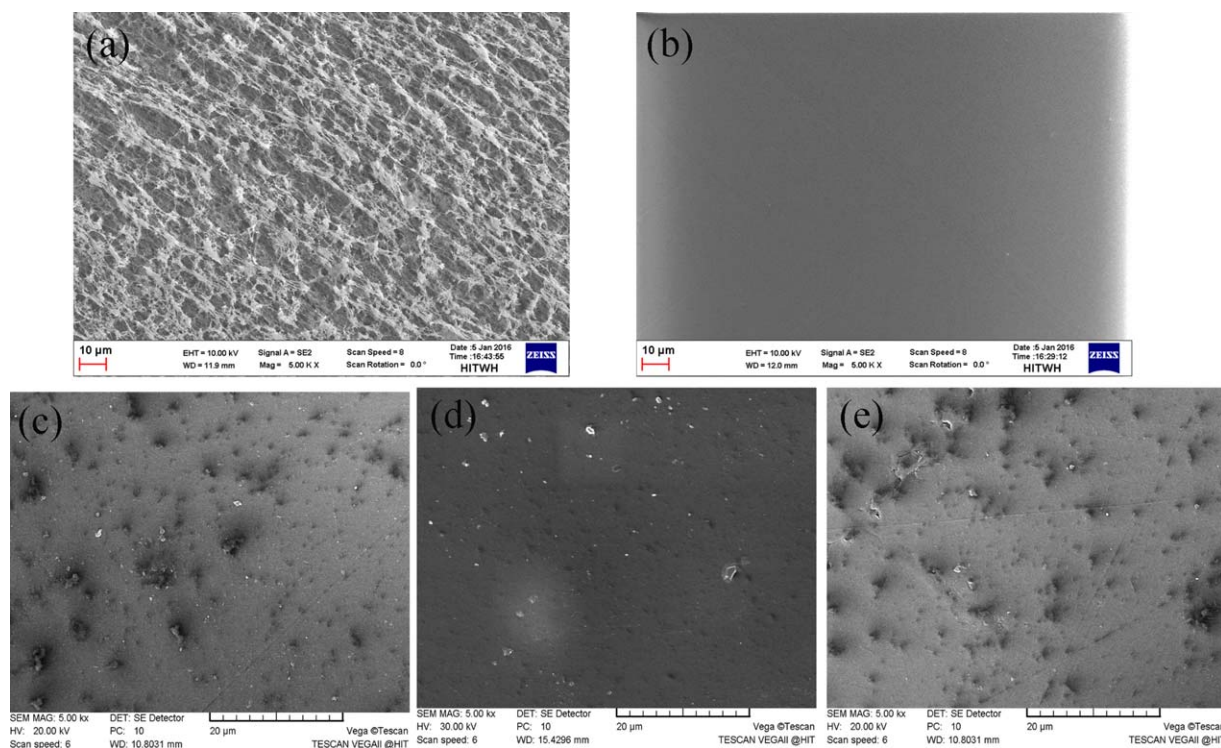
### SAXS

The membrane properties including water uptake, proton conductivity, and vanadium ion permeability are closely related to



**Figure 1.** FT-IR spectra of SPEEK and PS membranes casted with different solvents.





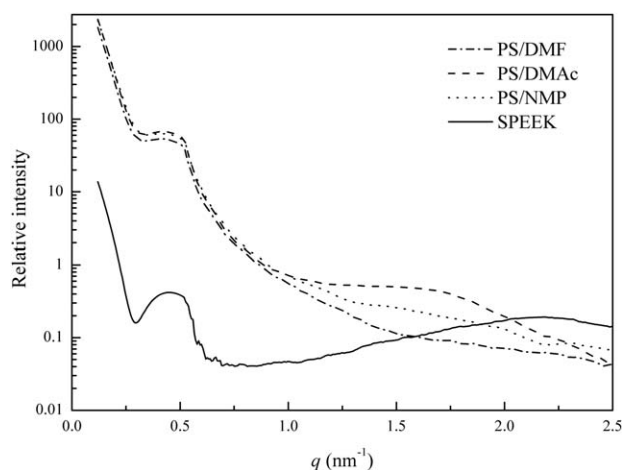
**Figure 2.** SEM images of (a) PTFE, (b) SPEEK, (c) PS/DMAc, (d) PS/NMP, and (e) PS/DMF. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

the ionic cluster structure of the membrane. In order to reveal the effect of casting solvents on the microstructure of PS membranes, the ionic cluster structures of three kinds of PS membranes are investigated using a SAXS technique and compared with that of pristine SPEEK membrane. Figure 3 shows the SAXS patterns of SPEEK and three PS membranes prepared with different solvents. Although affected by the sulfonation level,<sup>23</sup> SPEEK membrane generally presents two wide peaks at about  $0.8$  and  $2.0 \text{ nm}^{-1}$  because of the presence of the hydrophilic and hydrophobic domains.<sup>24,25</sup> It can be seen from Figure 3 that all the membranes have shown two distinct scattering regions, which implied the existence of the nanophase separation and the ionic clusters. But for the PS membranes incorporating with the PTFE, the higher peak of SPEEK at  $q = \text{about } 2.2 \text{ nm}^{-1}$  has been shifted to lower  $q$  values. Furthermore, the intensity of ionic peaks for PS membranes at higher  $q$  value change in the sequence of  $\text{PS/DMAc} > \text{PS/NMP} > \text{PS/DMF}$ . Especially for PS/DMF membrane, the ionic peak at high  $q$  value almost disappears compared with that of PS/NMP membrane, suggesting that the ionic clusters at this region should be very small or nonexistent. Consequently, it should have the smallest vanadium ion permeability when applied in VRB system. And it should also be noted that the position at higher  $q$  value for PS membranes is much smaller than that of SPEEK membrane, the reason should be attributed to the interaction between PTFE substrate and SPEEK polymer chain.

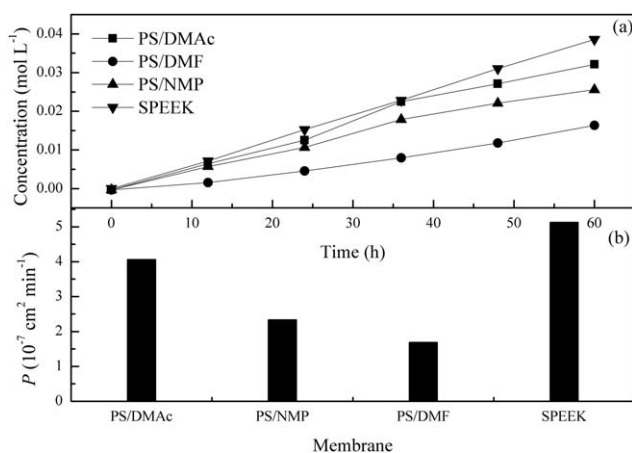
#### $\text{VO}^{2+}$ Permeability

The concentration of  $\text{VO}^{2+}$  change with time is presented in Figure 4(a). As can be seen, the concentration of  $\text{VO}^{2+}$  for all varies linearly with time. At the same interval, the sequence of

$\text{VO}^{2+}$  concentration transporting across the four kinds of membranes is  $\text{SPEEK} > \text{PS/DMAc} > \text{PS/NMP} > \text{PS/DMF}$ . The permeability ( $P$ ) of four membranes is calculated according to eq. (3) and demonstrated in Figure 4(b). The  $P$  values of SPEEK, PS/DMAc, PS/NMP, and PS/DMF are  $5.13 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$ ,  $4.06 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$ ,  $2.33 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$ , and  $1.69 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$ , respectively. This result reveals that the ability to block the transform of  $\text{VO}^{2+}$  for three kinds of PS membranes is superior to that of pristine SPEEK. The reason should be that the PTFE substrate acts as a vanadium ion block layer and makes them hard to crossover. Furthermore, the different



**Figure 3.** SAXS patterns of SPEEK and PS membranes casted with different solvents.

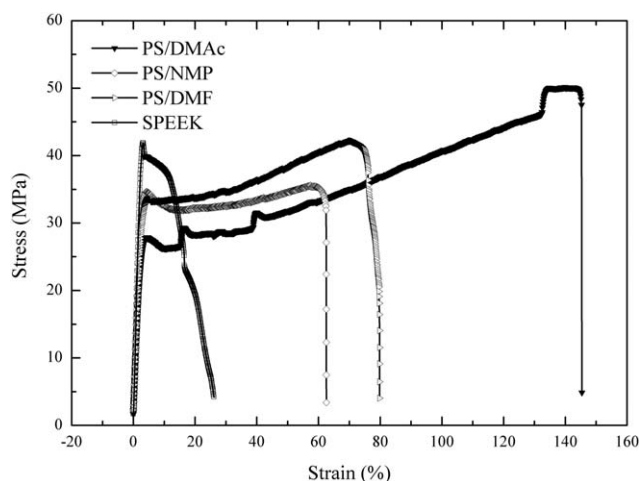


**Figure 4.** Change of  $\text{VO}_2^+$  concentration with (a) time and (b) permeability of SPEEK and three PS membranes.

permeability of PS membranes should be because of their different microstructure as proved by SAXS test.

### Mechanical Properties

Stress–strain curves of SPEEK and PS membranes are displayed in Figure 5. For SPEEK membrane, with the increase of elongation, the tensile strength reaches up to about 40 MPa and then drops suddenly. The result shows that the SPEEK has high intensity but low ductility. However, for PS membranes, they have shown different stress–strain behavior compared with that of SPEEK membrane. After being blended with PTFE, the ductility of all the PS membranes has been greatly enhanced. Especially for PS/DMAc membrane, its elongation rate is 145%, which is about 5.6 times of SPEEK. For the pristine SPEEK membrane, H-bonding effect between the sulfonic acid groups is closely related to its mechanical properties,<sup>26</sup> but for PS membranes, the interaction between PTFE and SPEEK may also affect the mechanical properties of the PS membranes. Because of the difference of solubility parameter of DMAc, NMP, and DMF, the bonding force between PTFE and SPEEK may be changed during solvent evaporation process and thus caused the different mechanical properties of three kinds of PS membranes.



**Figure 5.** Stress–strain curves of SPEEK and three PS membranes.

**Table II.** Weight Loss and Permeability Change of the PS Membranes after Being Saturated in  $1.5 \text{ mol L}^{-1} \text{ V(V)}$  Solution for 3 Weeks

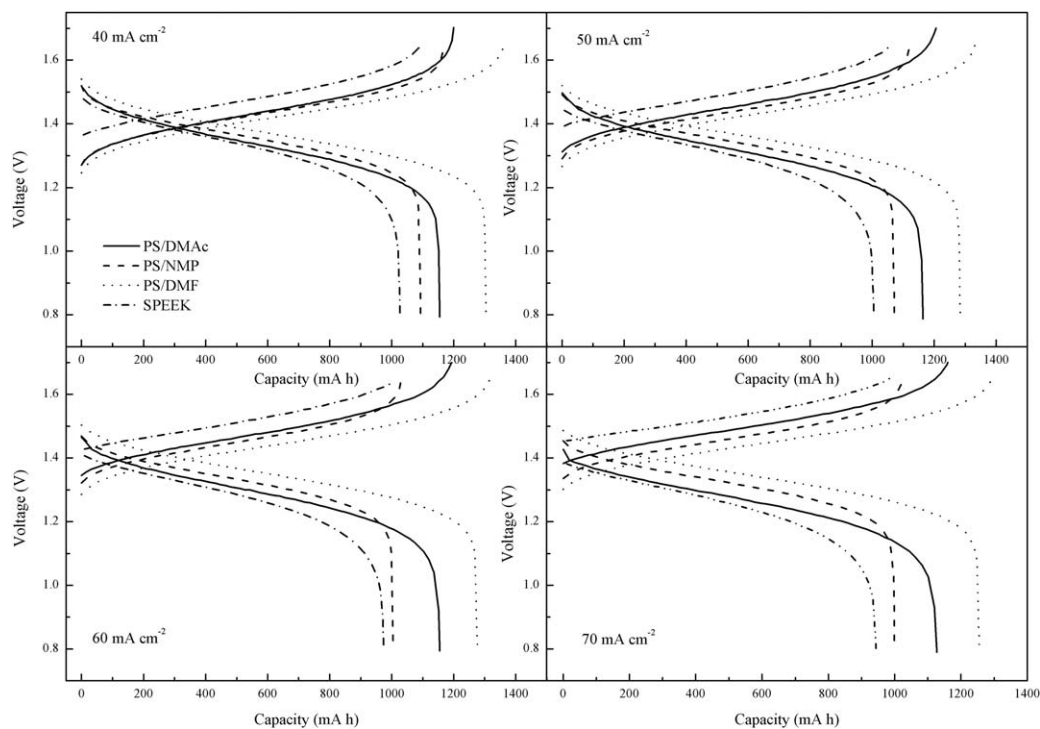
Membrane	Weight loss (%)	Permeability ( $\times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$ )	
		0 day	21 days
PS/DMF	1.6	1.7	1.8
PS/DMAc	1.8	4.1	4.2
PS/NMP	2.1	2.3	2.8

### Chemical Stability

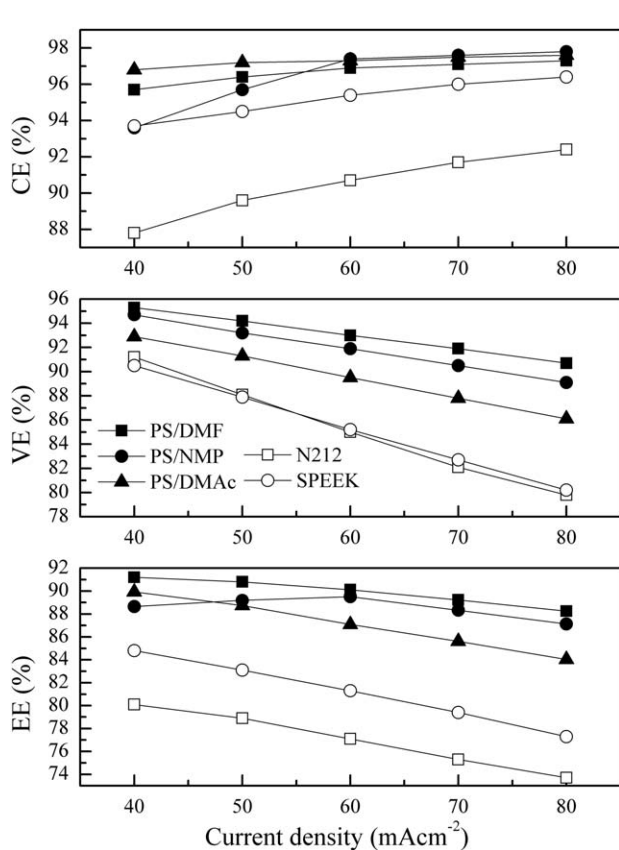
The weight loss and vanadium permeability change of PS membranes are illustrated in Table II. It shows that all the membranes have slight weight loss after being immersed in  $1.5 \text{ mol L}^{-1} \text{ VO}_2^+$  solution for 3 weeks, which is because of the degradation of membrane backbone since the  $-\text{SO}_3\text{H}$  group is stable.<sup>9</sup> It can also be found that although the weight loss of PS/NMP membrane is over 2%, the weight loss of PS/DMAc and PS/DMF are both less than 2%, which is similar to that of recast Nafion membrane.<sup>27</sup> This result suggests that PS membranes are very stable even exposed to the highly oxidizing  $\text{VO}_2^+$  solution. Furthermore, the permeability values of all the PS membranes slightly increase after 21 days immersion, the reason should be because of the slight destruction of SPEEK backbone since PTFE is rather stable in most situations.

### Single Cell Performance

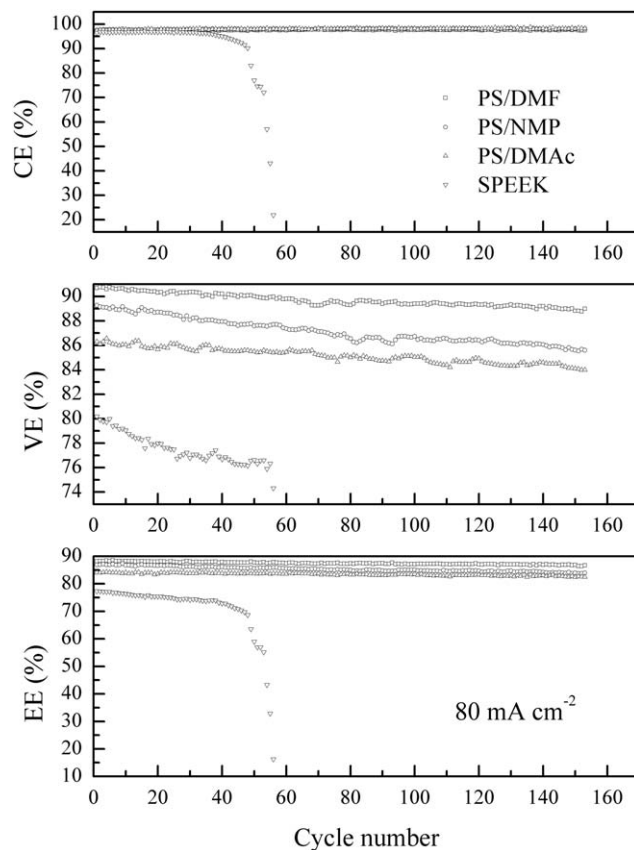
Charge–discharge curves of the VRBs with SPEEK, PS/DMF, PS/DMAc, and PS/NMP at current density of  $40\text{--}70 \text{ mA cm}^{-2}$  are presented in Figure 6. It can be seen that the charge–discharge curves are all very smooth and the difference between charge voltage and discharge voltage are all very small. And the charge–discharge capacities of all the PS membranes are higher than that of pristine SPEEK membrane. The results validate the fact that the as-prepared PS hybrid membranes are promising candidates for VRB application. However, it can also be seen that the charge/discharge capacity are different for three PS membranes. Generally, the single cell performance is related to the inner resistance, vanadium ion permeability, cycle time, and so on. Detailed cell performance between  $40$  and  $80 \text{ mA cm}^{-2}$  and their comparison with Nafion 212 and pristine SPEEK membrane are presented in Figure 7. It is obvious that both the CE and VE of the VRBs with PS membranes are much higher than that of Nafion 212 and pristine SPEEK membrane. The highest CE of Nafion 212 and SPEEK membrane is 92.4% and 96.4% at  $80 \text{ mA cm}^{-2}$ , respectively. However, for PS/DMF membrane, it is 97.8% at the same current density. As for VE is concerned, the highest VE of Nafion 212 and SPEEK membrane is only 91.2% and 90.5% at  $40 \text{ mA cm}^{-2}$ , respectively. While for PS/DMF membrane, it is 95.3% at the same current density. Consequently, the highest EE of Nafion 212 and SPEEK membrane is only 80.1% and 84.8% at  $40 \text{ mA cm}^{-2}$ , respectively, but for PS/DMF membrane, it is 91.2% at the same current density. Although the PS membranes are thinner than that of Nafion 212 membrane, their vanadium permeability is still lower than that of Nafion 212 membrane.<sup>15</sup> Consequently, both higher CE and VE are obtained compared with Nafion 212



**Figure 6.** Charge–discharge curves of SPEEK and different PS membranes at current density of 40–70 mA cm<sup>-2</sup>.

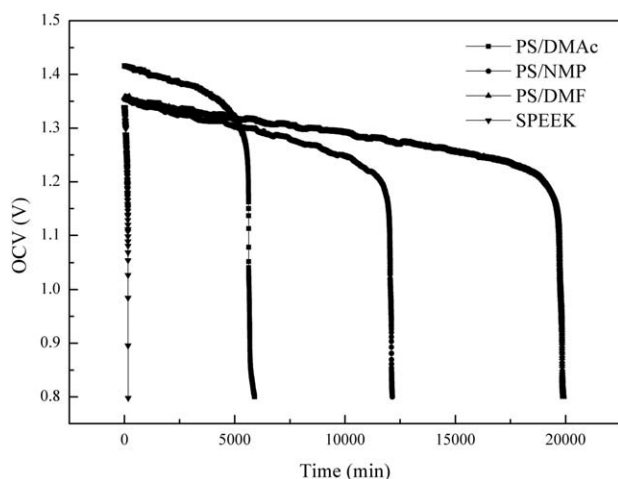


**Figure 7.** Comparison of CE, VE, and EE of Nafion 212, SPEEK and three PS membranes at current density of 40–80 mA cm<sup>-2</sup>.



**Figure 8.** Cycle performance of the three PS membranes at current density of 80 mA cm<sup>-2</sup>.





**Figure 9.** Change of the OCV with time for SPEEK and three PS membranes.

membrane. Furthermore, among the three PS membranes, the comprehensive cell performance of PS/DMF is better than that of PS/NMP and PS/DMAc, the reason should be due to the different ionic cluster size of PS membranes caused by different polymer solvent interaction during membrane casting process as SAXS test proved.

The cycle performance of the pristine SPEEK and PS membranes charge–discharged at  $80 \text{ mA cm}^{-2}$  is displayed in Figure 8. As can be seen, despite a very slight decay in VEs, the CEs and EEs for all the VRBs have shown no decay and kept constant over 150 times charge–discharge test. But for SPEEK membrane, the CE of the battery suddenly decreases after only 45 times charge–discharge test. This result proves that all the PS membranes have superior chemical stability to that of pristine SPEEK membrane. The reason is mainly because of PTFE can greatly improve the chemical stability of SPEEK membranes because of its reinforcement ability.<sup>22</sup> Furthermore, the VRB with PS/DMF membrane have exhibited the best performance during long cycle test because of its highest VE among three PS membranes.

In order to investigate the “on-line” vanadium permeability, self-discharge of the VRBs with pristine SPEEK and three membranes are further conducted and illustrated in Figure 9. It can be seen that all the PS membranes have exhibited lower self-discharge rate than that of pristine SPEEK membrane. For SPEEK membrane, it can only keep the OCV beyond 0.8 V for about 170 min, but even the PS/DMAc membrane can keep the OCV beyond 0.8 V for more than 5,000 min, For PS/DMF membrane, the time that OCV beyond 0.8 V can reach up to 20,000 min. The sequence of the self-discharge rate is SPEEK > PS/DMAc > PS/NMP > PS/DMF, which is in accordance with the  $\text{VO}^{2+}$  permeability of the membranes discussed above. This result further proves that PS membranes, especially PS/DMF membrane is very suitable for VRB application.

## CONCLUSIONS

In this article, a series of  $40 \text{ }\mu\text{m}$  polytetrafluoroethylene/sulfonated poly(ether ether ketone) membrane (PS membrane) with

solvent of NMP, DMAc, and DMF were prepared by solution casting method. Studies show that the casting solvents could influence the physico-chemical properties of the PS membrane. SAXS analysis reveals that the microstructure of the PS membrane is different from each other. The water uptake, proton conductivity, vanadium ion permeability, and mechanical behavior of different PS membranes are diverse, too. VRB single cell tests show that the cell performance of all the PS membrane is much better than commercial Nafion 212 and pristine SPEEK membranes. Furthermore, the PS membrane is much cheaper and thinner than that of Nafion 212 membrane. At current density of  $40\text{--}80 \text{ mA cm}^{-2}$ , the highest energy efficiency of PS/DMF membrane can even reach up to 91.2%, which is 11.1% higher than that of Nafion 212 membrane. Furthermore, cycle test proves that all the PS membranes are much stable than that of pristine SPEEK membrane. Especially for PS/DMF membrane, its comprehensive performances prove that it is one of the promising candidates for VRB application.

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