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Sulfonated poly(phthalazinone ether sulfone) membrane as a separator of vanadium redox flow battery

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Abstract To develop a novel and low-cost membrane as a separator of vanadium redox flow battery, sulfonated poly (phthalazinone ether sulfone) (SPPES) was prepared by sulfonating PPES with fuming sulfuric acid. By testing the sulfonation degree, intrinsic viscosity, and solubility of SPPES, the results showed that sulfonated polymers had higher intrinsic viscosities and excellent solubility in most polar solvents. IR analysis revealed that the –SO₃H group was successfully attached to SPPES backbone. DSC and TG results showed that SPPES exhibited higher T_g than that of PPES, and T_d at the first weight loss of SPPES was about 300 °C. The SPPES membrane (SP-02) showed a dramatic reduction in crossover of vanadium ions across the membrane compared with that of the Nafion membrane. Cell tests identified that VRB with the SPPES membrane exhibited a lower self-discharge rate, higher coulombic efficiency (92.82%), and higher energy efficiency (67.58%) compared with the Nafion system. Furthermore, cycling tests indicated that the single cell with SPPES membrane exhibited a stable performance during 100 cycles.

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Introduction

Vanadium redox flow battery (VRFB) is a promising electrochemical device for convenient and efficient power conservation due to its outstanding properties such as long life, high reliability, clean, low cost, high efficiency, and large scale [1–4]. Ionic exchange membrane (IEM) is a key component in VRB, which functions as a solid electrolyte for transferring ions, such as proton in the case of the cationic ion exchange membrane, to complete the current circuit as well as for separating the positive and negative electrolytes to prevent cross mixing of each other. As a separator, IEM should own such properties as high proton conductivity, low permeability of vanadium ions, good chemical stability, and low price [5, 6]. Although the present commercially used perfluorosulfonic polymers such as Du Pont Nafion® membranes assure excellent proton conductivity, oxidative resistance, and chemical stability in VRB [5, 7], large-scale application is limited by their high cost. The Nafion membranes also suffer from other drawbacks of high vanadium ions permeability [6] and severe water transfer [8], which can lead to the decrease of coulombic efficiency (CE) and energy efficiency of VRB system. These limitations have stimulated many efforts in the development of alternative membrane materials [9].

So far, aromatic polymers, such as poly(arylene ether ketone) [10], poly(arylene ether sulfone) [11], polyimide [12], and other special aromatic polymer [13] are well accepted as high performance for their good thermal and mechanical stability and can be used as a base polymer for ionic exchange membrane. Ionic exchange groups such as sulfonic acid group, carbonic acid group, phosphoric acid group, and quaternary

ammonium group can be attached to these polymers, which can provide their membranes with good ionic conductivity and make them able to be applied in the proton exchange membrane fuel cell and VRFB. Sulfonated aromatic polymers such as SPEEK, SPES, and SPESK can be obtained either using sulfonated monomers in direct synthesis or a variety of methods for post-sulfonation. Chen DY, et al. developed a novel sulfonated poly(fluorenyl ether ketone) membrane [14] and its composite membranes [15] for VRFB by aromatic nucleophilic polycondensation. However, sulfonation of monomers not only reduced their reactivity in the nucleophilic polycondensation but also increased the membrane cost compared with the post-sulfonation of their polymers. Chen DY, et al. develop a novel sulfonated aromatic polymers (poly(arylene ether sulfone) [16] and sulfonated poly(fluorenyl ether ketone) [17]) via step polymerization followed by post-sulfonation using chlorosulfonic acid for VRFB application. They found the sulfonation degree can be readily controlled by adjusting the ratio of the polymers to chlorosulfonic acid. The coulombic efficiencies of the single VRFB with these sulfonated aromatic polymer membranes are higher than that with Nafion membrane, due to their lower vanadium ions permeability.

Compared with other poly(arylene ether sulfone), a new high-performance polymer poly(phthalazinone ether sulfone) (PPES) has more excellent chemical and thermal stability, and higher mechanical strength and glass transition temperature (295 °C) [18, 19]. So its modification (sulfonation) [19] and applications of its membrane in nanofiltration and ultrafiltration [18, 20, 21] have been widely emphasized.

In this paper, the post-sulfonation with fuming sulfuric acid was applied to modification of PPES to obtain a low-cost cation ion exchange membrane for VRFB. The influence of sulfonating conditions on the sulfonated degree (SD), intrinsic viscosity, and solubility was investigated. Differential scanning calorimetry (DSC) and TG technologies were used to characterize the thermal properties of the sulfonated polymers. The membrane of SPPES was compared with Nafion membrane on the primary properties such as ion exchange capacity (IEC), water and electrolyte uptake, *swelling ratio*, permeability of vanadium ions, proton conductivity, and mechanical properties. The performance of VRFB with the SPPES membrane was evaluated in terms of the open-circuit voltage (OCV), charge–discharge curves, and coulombic, voltage and energy efficiencies compared with those of VRFB with Nafion membrane.

Experimental

Materials

PPES resin powder ($[\eta]$=0.67 dL/g in NMP at 30 °C) was supplied by Dalin Polymer New Material Company. Inherent viscosity ($[\eta]$) of PPES can reflect the molecular weight which determines its processability and application. The PPES powder with a high inherent viscosity (>0.5 dL/g) was adopted because it possessed an excellent film-forming property. Fuming sulfuric acid (27–33%) and concentrated sulfuric acid (95–98%) (analytical grade) were purchased from Huizhou Bestgrand St.An Chemicals Co., Ltd., China. Nafion 117 membrane was purchased from DuPont. Before used, Nafion 117 membrane (denoted as Nafion membrane) was treated according to [22], and stored in deionized water. VOSO$_4$·nH$_2$O was prepared in our laboratory. Electrolyte solution (1.5 M V^{3+}/V^{4+} (mol/mol=1:1) in 3.0 M H$_2$SO$_4$) was supplied by V-power New Power Co., Ltd., China. All other chemical agents (analytical grade) were commercially available and used without further purification.

Sulfonation of PPES

Sulfonation of PPES was carried out in the laboratory according to [19]. In a typical procedure, 5 g of dried PPES powder was gradually put into a 250-mL three-neck bottle filled with 40 mL solvent (96–98% sulfuric acid) to form a homogeneous liquid at room temperature and then 40 mL fuming sulfuric acid (27–33% SO$_3$) was slowly added to start sulfonation. The reaction system was fixed at 40 °C for a determined time under continuous mechanical stirring. SPPES with different SD would be obtained by changing the sulfonation time. After a determined reaction time, the reaction mixture was poured into 400 mL crushed ice water to precipitate the SPPES and filtrated to obtain a crude SPPES product. The crude product was washed with deionized water until neutral and dried for 24 h at 120 °C in a vacuum oven to obtain the resulting SPPES polymer.

Preparation of the membrane SPPES

Membranes were prepared by dissolving the SPPES in DMAc (10 wt.%), casting the solutions on a glass plate, drying and curing the membranes at 60 °C for 12 h, 80 °C for 6 h, and 120 °C for 4 h, respectively. Then, the cooled membranes were immersed in deionized water and peeled off from the glass plate. Finally, the membranes were kept in deionized water.

Polymer analysis and measurements

Inherent viscosities ($[\eta]$) were determined using an Ubbelohde viscometer for DMAc solutions of polymer with a concentration of 0.5 g/L at 30 °C. The IEC of the SPPES resin or its membrane is calculated by following equation described by Kazacos [23].

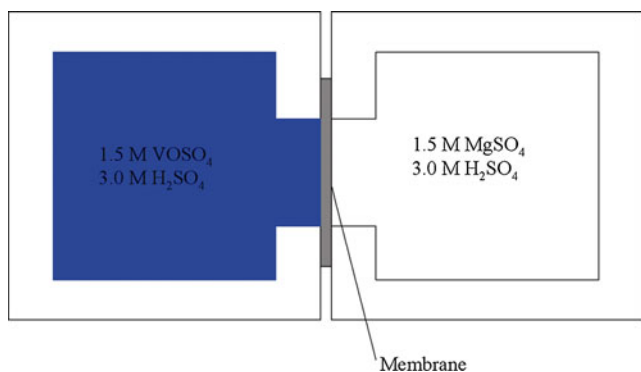$$IEC = \frac{M_{0,\mathrm{NaOH}} - M_{E,\mathrm{NaOH}}}{W_d} \tag{1}$$

Fig. 1 Equipment for the measurement of permeability of VO^{2+}

where $M_{0,NaOH}$ is the moles of NaOH in the flask at the beginning of titration, $M_{E,NaOH}$ is the moles of residual NaOH after the SPEES equilibrated within it for 48 h, and W_d is the weight of the SPEES (in grams). SD of the polymer can be calculated according to the following equation [17]:

$$SD = \frac{452\,IEC}{(1000 - 80\,IEC)} \qquad (2)$$

where IEC is the ion exchange capacity of the polymer sample (in millimoles per gram), 452 is the molar mass of the repeat unit on the PPES backbone chain, 80 is the molar mass of –SO_3H group.

IR spectra were measured on a Thermo Fisher Nicolet Avater 370 FT-IR spectrophotometer with film samples in air. Dynamic thermogravimetric analysis (TGA) was performed on NetZSch (German) TGA 209F1 system under nitrogen atmosphere. Polymer samples were preheated to 150 °C at 10 °C/min, held isothermally for 60 min, equilibrated at 80 °C, and then heated to 700 °C at 10 °C/min. DSC was conducted on a NetZSch (German) DSC 200F3 system under nitrogen calibrated with indium and zinc standards. Initial sample weight was set as 1–2 mg for each operation. The samples were scanned twice at a heating rate of 10 °C/min from ambient temperature to 300 °C. The first scan was served to remove water and the T_g was measured in the second scan.

Primary properties of the membranes

The water uptake is another important property of ion exchange membranes. Water uptake was calculated according to the following equation [15]:

$$Water\ uptake(\%) = \frac{W_w - W_d}{W_d} \times 100\% \qquad (3)$$
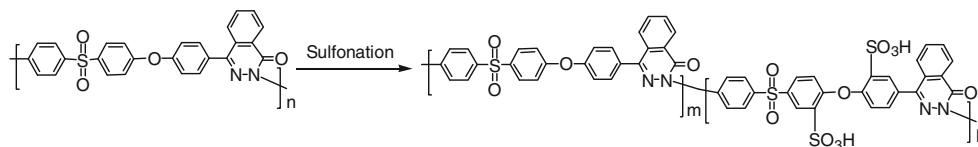
where W_w and W_d are the weight of the wet and dry membrane, respectively. Electrolyte uptake was calculated as follows [24]:

$$Elecrolyte\ uptake(\%) = \frac{W_1 - W_0}{W_0} \times 100\% \qquad (4)$$

where W_1 and W_0 are the weight of the membrane saturated by a 1.5 M $VOSO_4$/3 M H_2SO_4 solution and dry membrane, respectively.

The area resistance (AR) of membranes was measured according to [25]. The membranes were soaked in a solution of 1.5 M $VOSO_4$/3.0 M H_2SO_4 for 24 h. A conductivity cell was separated into two compartments filled with 1.5 M $VOSO_4$/3.0 M H_2SO_4. Two platinum electrodes with an area of 1×1 cm were held at a fixed distance apart and a constant depth of immersion. The effective area of membrane (S) was 1.0 cm^2. The area resistances of the cell with membrane r_1 (in ohms) and without membrane r_2 (in ohms) were measured by electrochemical impedance spectroscopy (EIS) over a frequency range of 100 kHz to 100 mHz using a PARAST electrochemistry workstation (AMETEK, Inc., USA) at room temperature. In this work, r_1 and r_2 values were obtained by interpolating the impedance data to the real axis on the high-frequency side (49,535~39,194 Hz), respectively. AR (in ohms per square centimeter) was calculated as follows:

$$AR = (r_1 - r_2)S \qquad (5)$$

The proton conductivity (σ) of the membranes was calculated as follows [26]:

$$\sigma = \frac{d}{AR} \qquad (6)$$

where d and AR were the thickness and area resistance, respectively. The swelling ratio was calculated from membranes 7–10 cm long as follows:

$$Swelling\ ratio = \frac{l_{wet} - l_{dry}}{l_{dry}} \times 100\% \qquad (7)$$

where l_{wet} and l_{dry} were the length of the membrane in wet and dry states, respectively.

The mechanical properties (tensile strength and elongation) of the membranes were determined by a WDW-100 Electromechanical Universal Test Machine (Jinan, China). The tensile properties were determined at 25±2 °C and 65% relative humidity. The samples were cut into dumbbell shape with the middle width of 2 mm. The crosshead speed was set at a

Scheme 1 Sulfonation pathway for PPES

Table 1 Effect of reaction condition on DS and intrinsic viscosity of SPPES

Polymer/oleum (g/mL)	Time (h)	Temperature (°C)	Solvent (ml)	SD	$[\eta]^a$ (dL/g)
5/40	4	60	40 mL CHCl$_3$	0.68	1.59
5/40	2	60	40 mL 98% sulfuric acid	0.76	1.67
5/40	4	60	40 mL 98% sulfuric acid	0.87	1.73
5/40	4	80	40 mL 98% sulfuric acid	0.90	1.66
5/40	2	40	40 mL 98% sulfuric acid	0.46	1.65
5/40	4	40	40 mL 98% sulfuric acid	0.75	1.88
5/40	6	40	40 mL 98% sulfuric acid	0.85	1.87
5/40	8	40	40 mL 98% sulfuric acid	0.90	1.82
5/40	12	40	40 mL 98% sulfuric acid	0.91	1.80

[a] Determination conditions: SPPES 0.5 g/L in DMAc, 30 °C

constant of 2 mm/min. For each material being tested, three measurements were taken and the average value was recorded.

Permeability of vanadium ions through the membrane

The permeability of vanadium ions through the membrane sample was investigated using the equipment as shown in Fig. 1 [27, 28]. The left reservoir was filled with 1.5 M VOSO$_4$ in 3.0 M H$_2$SO$_4$ solution and the right one was filled with 1.5 M MgSO$_4$ in 3.0 M H$_2$SO$_4$ solution, respectively. MgSO$_4$ was used to balance the ionic strength and reduce the osmotic pressure. The area of the membrane exposed to the solution was 8.1 cm^2 and the volume of solutions in both sides was 25 mL. The two solutions were continuously stirred during measurements at room temperature. Samples of solution from the right reservoir were taken at a regular time interval and analyzed for vanadium ions concentration by a UV–vis spectrometer.

The vanadium ion permeability (P) is calculated by the following equation [29, 30]:

$$V_R \frac{dc_R(t)}{dt} = A \frac{P}{L}[c_L - c_R(t)] \tag{8}$$

where c_L is the vanadium ion concentration in the left reservoir, and $c_R(t)$ refers to the vanadium ion concentration

in the right reservoir as a function of time. A and L are the area and thickness of the membrane, respectively. P is the permeability of the vanadium ions, and V_R is the volume of right reservoir. It is supposed that the change of vanadium ion concentration in the left reservoir can always be negligible and a pseudo-steady-state condition is used inside the membrane.

VRFB single cell tests

A VRFB single cell was fabricated by sandwiching the membrane between two pieces of 5 cm thickness carbon felt (Shenhe Carbon Fiber Materials Co., Ltd.) with effective reaction area of 9 cm^2, which was served as the electrodes, and conductive plastic were used as the current collectors. Two 40 mL solutions of 1.5 M V^{3+}/V^{4+} (mol/mol=1:1) in 3.0 M H$_2$SO$_4$ serving as negative and positive electrolytes, respectively, were cyclically pumped into the corresponding half-cell. The single cell was charged and discharged by a CT2001C-10V/2A battery test system (Wuhan Land Co., Ltd.) with a constant current density of 40 mA/cm^2. To avoid the corrosion of the carbon felt electrodes and conductive plastic, the upper limit of charge voltage was 1.7 V and the lower limit of discharge voltage was 0.7 V.

Table 2 Solubilities of SPPES

Sample	SD	Methanol	Toluene	Acetone	THF	Chloroform	NMP	DMAc	DMSO	DMF
PPES	−	−	−	−	−	+	+	−	−	−
SP-01	0.46	−	−	−	−	−	+	+	+	+
SP-02	0.75	−	−	−	−	−	+	+	+	+
SP-03	0.85	−	−	−	−	−	+	+	+	+
SP-04	0.90	−	−	−	−	−	+	+	+	+
SP-05	0.91	−	−	−	−	−	+	+	+	+

+ soluble, +− soluble when heating, − insoluble, sw swell

Results and discussion

Sulfonation reaction

The sulfonation pathway of PPES is shown in Scheme 1. As expected, sulfonation occurred around the electro-donating ether linkage. In general, the sulfonation of the polymers can be conducted with several sulfonating agents such as concentrated sulfuric acid, fuming sulfuric acid, chlorosulfonic acid, and acetyl sulfate, and so on, depending on the polymer reactivity. For PPES, concentrated sulfuric acid cannot sulfonate it due to its strong electron-withdrawing sulfone group per repeat unit which reduced the reactivity of the electron-donating ether linkage of the polymer. Gao Y et al. [19, 31] found that almost no sulfonation of poly(phthalazinones) (PPs) with 95–98% concentrated sulfuric acid took place at 60 °C, even after a long reaction time. Due to lower cost than chlorosulfonic acid, fuming sulfuric acid (oleum) was used as a sulfonating agent for preparation of SPPES. As shown in Table 1, the SD and intrinsic viscosity of SPPES in the chloroform solvent are lower than those in the concentrated sulfuric acid solvent, and in the experiments, we found that there was a small amount of PPES in the resulting SPPES powder which indicated the sulfonation of PPES in the chloroform solvent was non-uniform due to the fact that the chloroform is a good solvent for PPES but not for SPPES. With temperature from 40 to 60 °C, SD can be remarkably improved but the intrinsic viscosity cannot, which may be attributed to the fact that the harsh condition of sulfonation can partly degrade the polymer so as to decrease its molecular weight. With the temperature at 40 °C, the increase in the SD of PPES is fast with the time first and then slow from 6 h; the intrinsic viscosity was increased to 1.88 and then decreased slightly. The result can be ascribed to that the concentration of oleum was gradually decreased with the sulfonation prolonging, and in a long time, oleum may partly cause degradation of SPPES.

Solubility

Solubilities of SPPES are listed in Table 2. It shows that the sulfonation changed the solubilities of polymer. The PPES is dissolved in the chloroform while all SPPES samples are insoluble in it. PPES is insoluble in the polar solvents such as DMAc, DMSO, and DMF while the SPPES samples with various SD are soluble in them. The difference of solubility between PPES and SPPES is due to polarity of the polymers and intermolecular forces relating to hydrogen bond before and after sulfonation of the PPES.
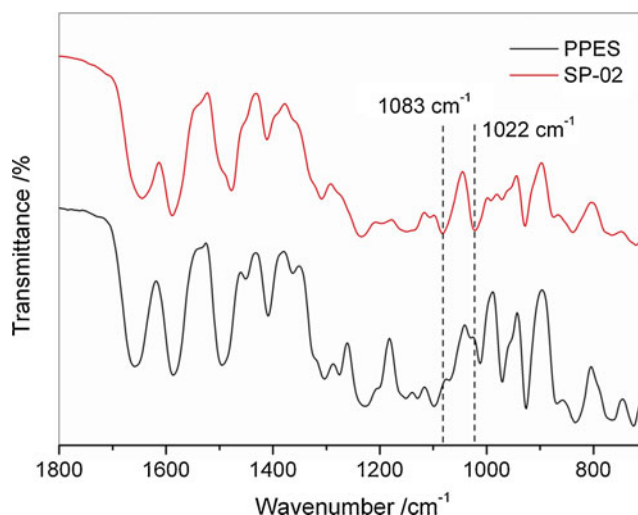

Fig. 2　IR spectra of PPES and SP-02 samples

IR

The IR spectroscopy can be used to confirm the pendant –SO_3H group attached to the polymer backbone. Figure 2 shows the IR spectra of the PPES and SP-02. Comparing these spectra, it is obvious that the SP-02 sample adsorption bands at 1,022 and 1,083 cm^{-1} are characteristics of the aromatic SO_3H symmetric and asymmetric stretching vibrations, respectively. This is confirmed that the sulfonic acid groups were successfully introduced to the resulting polymer main chain.

Thermal property

The thermal stabilities of the PPES and SP-02 were determined by TGA and DSC (Fig. 3). As for PPES, only 5% weight loss temperature is nearly 500 °C which shows that PPES possesses good thermal stability. For its sulfonated
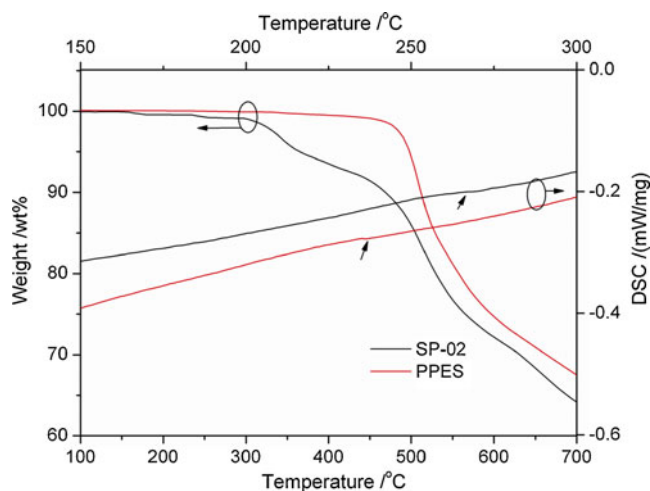

Fig. 3　DSC and TG curves of PPES and SP-02 samples

**Table 3** Water uptake, swelling ratio, and mechanical properties of SPPES

Sample	IEC/ (mmol/g)	Uptake/%		Swelling ratio/%		Mechanical properties[a]	
		Water	Electrolyte	Water	Electrolyte	Tensile strength/ MPa	Elongation/ %
SP-02	1.42	17.42	9.53	16.71	0.91	45.06	15.52
Nafion	0.92	22.57	20.37	28.96	2.15	20.77	107.01

[a] Measured in wet state

product (SP-02 sample), there are two transitions of weight loss. The first one occurred at 300 °C, which could be attributed to the decomposition of the –SO₃H group. The second thermal loss at 500 °C was owing to the degradation of the main chain of SPPES which shows sulfonation has not degraded the backbone of the parent PPEK. It can be seen from Fig. 3 that T_g values of PPES and SP-02 are 235 and 267 °C, respectively. The higher T_g of SP-02 than that of PPES is attributed to the introduction of –SO₃H group to the polymer backbones leading to the increased intermolecular interactions for SP-02 sample. The DSC curves of PPES and SP-02 also show that both polymers are amorphous [13].

Primary properties of the membrane

IEC, water and electrolyte uptake, swelling ratio and mechanical properties of SP-02, and Nafion membrane samples were determined and summarized in Table 3. IEC is an important property for ionic exchange membrane. The IEC of the SPPES sample (SP-02) is higher than that of Nafion membrane, which indicates the numbers of –SO₃H group per gram in the SPPES membrane are more than those in Nafion membrane. However, the water and electrolyte uptakes and swelling ratio in water, and electrolyte solution of the SPPES sample (SP-02) are less than those of Nafion
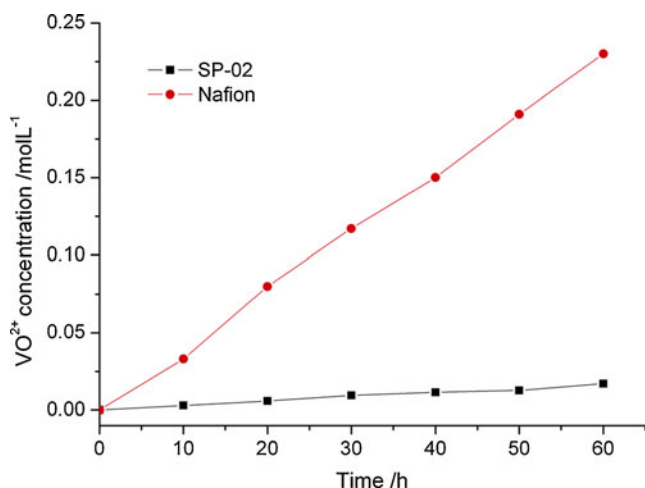
Fig. 4 Change of concentration of VO^{2+} with time in the right reservoir of the cell with SP-02 and Nafion membranes

membrane. These differences were ascribed to their difference in microstructures. The less pronounced hydrophobic/hydrophilic separation of SPPES membrane compared to Nafion membrane corresponds to narrower, less connected hydrophilic channels and to larger separations between the less acidic sulfonic acid functional groups [32, 33]. The tensile strength of SP-02 is much more than Nafion membrane, while elongation of SP-02 is much less than that of Nafion membrane, which is due to the rigidity of backbone and lower swelling ratio of SPPES compared with Nafion membrane.

Permeability of vanadium ions and proton conductivity

Diffusion of vanadium ions across the IEM is disadvantageous to VRFB because it will lead to self-discharge of the battery and lower the coulombic efficiency. The change of concentration of VO^{2+} (vs. time) is presented in Fig. 4. It is obvious that the concentration of VO^{2+} through the SP-02 membrane is remarkably lower than that of VO^{2+} through Nafion membrane. The vanadium ion permeability (P) was calculated according to Eq. 8 and listed in Table 4. It is found that P decreased to 1.24×10^{-7} cm²/min for SP-02 membrane from 22.63×10^{-7} cm²/min for Nafion membrane. The decrease of P could be attributed to their different microstructures. Compared with Nafion membrane, membrane SP-02 has smaller hydrophilic/hydrophobic separation corresponding to highly dispersed sulfonic groups and the high rigidity of the SPPES backbone to which the SO₃H groups are attached also prevent the neighboring dispersed –SO₃H groups from aggregating to bigger clusters. Thus, the water-filled channels in SPPES membrane are narrow and branched with more dead-end pockets compared with those in Nafion membrane [32, 34]. This is

Table 4 Proton conductivity and permeability of vanadium ions

Membrane	Thickness[a]/ cm	AR/Ω cm²	σ/mS cm⁻¹	P/(10⁻⁷ cm²/min)
SP-02	0.026	1.39	18.71	1.24
Nafion	0.030	1.04	28.85	22.63

[a] Measured in wet state

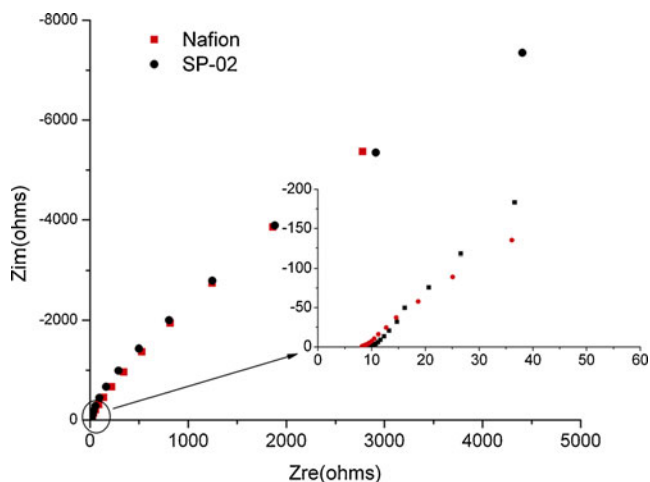**Fig. 5** The typical ac impedance plots of the conductivity cell with SP-02 and Nafion membranes in 1.5 M VOSO$_4$/3.0 M H$_2$SO$_4$ solution

Fig. 7 Charge and discharge curves at 40 mA/cm^2

perhaps the reason for the reduction of vanadium permeability in SPPES membranes.

In order to compare AR and σ between SP-02 and Nafion membranes, EIS was employed. Their typical ac impedance plots are shown in Fig. 5. In the complex plane plots for the two membranes, the absence of a well-defined semicircle at high frequencies reflecting the charge-transfer process is noted due to the rapid charge-transfer reaction kinetics on platinum electrodes in the VOSO$_4$/H$_2$SO$_4$ solution; however, a linear section indicating the diffusion process is observed at low frequencies. So the impedance due to mass-transport impedance becomes progressively more dominant. Enlarging the plots at high frequencies in Fig. 5, it is found that the Zre value for SP-02 membrane is larger than that for Nafion membrane. From the interception at Zre axis where −Zim= 0, the cell resistance can be obtained. According to the Eqs. 4 and 6, AR and σ for the membrane are obtained respectively and listed in Table 4. From Table 4, it can be seen that σ of SP-
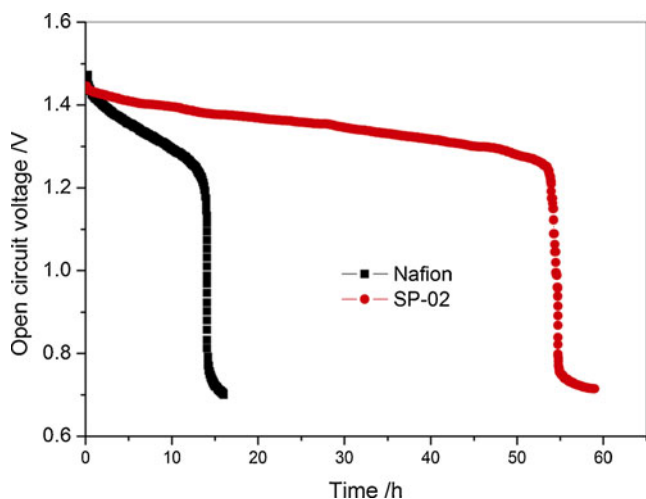
02 is less than that of Nafion membrane. Proton conduction in polymer electrolyte membranes is an intimate function of equivalent weight (EW), water content (relative humidity (RH)), crystallinity (cluster structure involving hydrophilic and hydrophobic components) [35]. Although the IEC of SP-02 is higher than that of Nafion membrane, the water uptake of SP-02 is lower than that of Nafion membrane due to their different microstructures. These factors are responsible for its lower proton conductivity.

Performance of VRFB single cell

The OCV value of the cell can reveal the self-discharge degree of a VRFB and indicate the vanadium blockage performance of the membrane. Figure 6 displays the OCV of the VRB with SP-02 and Nafion membranes charged to a 75% state of charge. It can be seen that the OCV value with the two membranes decreases gradually with the time at first and then drops sharply. As for the VRB with SP-02 membrane, the time for OCV value remaining beyond 1.2 V is nearly 55 h, while for the VRB with Nafion membrane, the value is only about 14 h. The self-discharge of VRB is mainly attributed to the crossover of vanadium ions through the membrane. This indicates that the self-discharge of VRFB has been reduced remarkably by using the SPPES membrane.

The charge–discharge curves of VRFB with SP-02 and Nafion membranes at a current of 40 mA/cm^2 are presented in Fig. 7. It can be seen that the charge capacity and voltage of a single cell with Nafion membrane are higher than those

Fig. 6 OCV of VRFB with Nafion and SP-02 membranes

Table 5 VRFB single cell performance of SP-02 and Nafion membranes

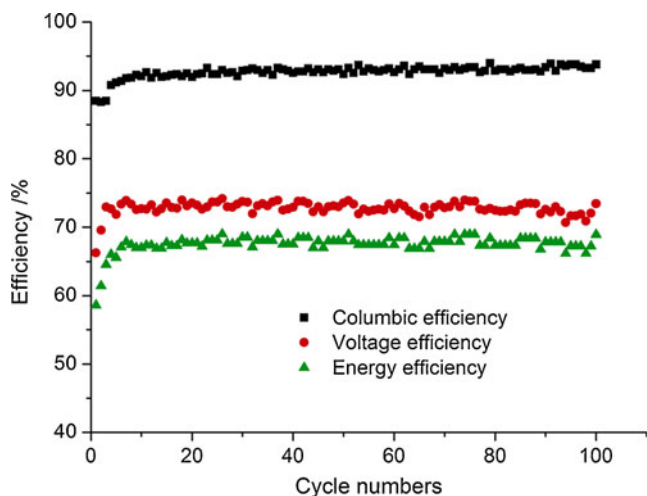| Membrane	CE/%	VE/%	EE/%
SP-02	92.82	72.81	67.58
Nafion	90.91	74.06	67.32

Fig. 8 Charge–discharge cycling performance (40 mA/cm^2) of the cell with SP-02

with SP-02 membrane; meanwhile, the discharge voltage of the single cell with Nafion membrane is higher than that with SP-02 membrane. This is assigned to the lager IR drop caused by the higher AR of the SP-02 membrane compared with that of Nafion membrane. However, the discharge capacity of a single cell with SP-02 membrane is very near to Nafion membrane, which is attributed to the lower self-discharge of the cell with SP-02 membrane resulted from the reduction of permeation of vanadium ions across it.

The results of average coulombic efficiency (CE), average voltage efficiency (VE), and average energy efficiency (EE) of the VRFB with SP-02 and Nafion membranes at a current density of 40 mA/cm^2 are listed in Table 5. As shown in Table 5, the VRB employing SP-02 membrane presents a CE of 92.82%, being higher than the value of 90.91% for VRFB employing Nafion membrane. This is in good agreement with the fact that the high crossover of vanadium ions through the membrane results in a large loss of electrochemical energy [34]. The VE of the VRFB single cell with SP-02 and Nafion membrane was 72.81% and 74.06%, respectively. The lower VE obtained with SP-02 membrane is due to its higher AR and lower σ. As an indicator of energy loss in charge–discharge process, EE is a key parameter to evaluate an energy storage system. Compared with EE value of 67.32% for Nafion membrane, EE of VRFB for SP-02 membrane was 67.58%, which indicates that the VRFB performance can be improved by the SPPES membrane separator.

The cycle performance of VRFB single cell with SP-02 membrane was shown in Fig. 8. As presented, the CE, VE, and EE of the single cell with SP-02 show no efficiency decline after 100 cycles, suggesting the membrane chemically endurable to survive the harsh testing condition.

Conclusions

To develop a novel and low-cost membrane as a separator of vanadium redox flow battery (VRFB), sulfonated poly (phthalazinone ether sulfone) (SPPES) with various sulfonation degree was prepared by sulfonation of PPES using fuming sulfuric acid and concentrated sulfuric acid by controlling the sulfonaton time. Intrinsic viscosity and solubility of SPPES verified that sulfonation changed PPES polarity resulting in the increased intrinsic viscosity and excellent solubility in most polar solvents. IR spectra revealed that the SO$_3$H group was successfully attached to SPPES polymer main chain, which led to the presence of a T_d of its first weight loss at 300 °C and a higher T_g. IEC of SPPES membrane (SP-02) was higher than that of Nafion membrane, while the water and electrolyte uptakes and the proton conductivity of the former were lower than those of the latter, which is due to the difference in their microstructures. The permeation of vanadium ions across the membrane was reduced significantly by using SPPES membrane. VRFB single cell with the SPPES membrane exhibited a higher CE (92.82%) and EE (67.58%) compared with that of Nafion system. In 100 charge–discharge cycles, the VRB single cell with SPPES membrane showed a stable performance.

References

1. Sum E, Rychcik M, Skyllas-kazacos M (1985) Investigation of the V(V)/V(IV) system for use in the positive half-cell of a redox battery. J Power Sources 16(2):85–95
2. Sum E, Skyllas-Kazacos M (1985) A study of the V(II)/V(III) redox couple for redox flow cell applications. J Power Sources 15(2–3):179–190
3. Skyllas-Kazacos M, Grossmith F (1987) Efficient vanadium redox flow cell. J Electrochem Soc 134(12):2950–2953
4. Skyllas-Kazacos M, Rychcik M, Robins RG, Fane AG, Green MA (1986) New all-vanadium redox flow cell. J Electrochem Soc 133 (5):1057–1058
5. Mohammadi T, Skyllas-Kazacos M (1995) Preparation of sulfonated composite membrane for vanadium redox flow battery applications. J Membr Sci 107(1–2):35–45
6. Hwang G-J, Ohya H (1997) Crosslinking of anion exchange membrane by accelerated electron radiation as a separator for the all-vanadium redox flow battery. J Membr Sci 132(1):55–61
7. Skyllas-Kazacos M, Kasherman D, Hong DR, Kazacos M (1991) Characteristics and performance of 1 kW UNSW vanadium redox battery. J Power Sources 35(4):399–404
8. Mohammadi T, Chieng SC, Skyllas Kazacos M (1997) Water transport study across commercial ion exchange membranes in the vanadium redox flow battery. J Membr Sci 133(2):151–159

9. Gu S, He G, Wu X, Li C, Liu H, Lin C, Li X (2006) Synthesis and characteristics of sulfonated poly(phthalazinone ether sulfone ketone) (SPPESK) for direct methanol fuel cell (DMFC). J Membr Sci 281(1–2):121–129

10. Gardner KH, Hsiao BS, Faron KL (1994) Polymorphism in poly (aryl ether ketone)s. Polymer 35(11):2290–2295

11. Rose JB (1974) Preparation and properties of poly(arylene ether sulphones). Polymer 15(7):456–465

12. Xiao Y, Low BT, Hosseini SS, Chung TS, Paul DR (2009) The strategies of molecular architecture and modification of polyimide-based membranes for CO2 removal from natural gas—a review. Prog Polym Sci 34(6):561–580

13. Wang N, Huang K, Wang L (2011) Synthesis and characterization of poly(arylene ether ketone)s containing triazole units through click chemistry. Polym Bull 67(8):1569–1581

14. Chen D, Wang S, Xiao M, Meng Y (2010) Preparation and properties of sulfonated poly(fluorenyl ether ketone) membrane for vanadium redox flow battery application. J Power Sources 195(7):2089–2095

15. Chen D, Wang S, Xiao M, Han D, Meng Y (2010) Sulfonated poly (fluorenyl ether ketone) membrane with embedded silica rich layer and enhanced proton selectivity for vanadium redox flow battery. J Power Sources 195(22):7701–7708

16. Chen D, Wang S, Xiao M, Meng Y (2010) Synthesis and properties of novel sulfonated poly(arylene ether sulfone) ionomers for vanadium redox flow battery. Energy Conversion Manag 51 (12):2816–2824

17. Chen D, Wang S, Xiao M, Meng Y (2010) Synthesis and characterization of novel sulfonated poly(arylene thioether) ionomers for vanadium redox flow battery applications. Energy Environ Sci 3 (5):622–628

18. Jian XG, Meng YZ, Zheng HB, Allan SH (1993) Poly(phthalazinone ether sulfone)s and their preparation method. Chinese Patent 93109180.2

19. Gao Y, Robertson GP, Guiver MD, Jian X, Mikhailenko SD, Wang K, Kaliaguine S (2003) Sulfonation of poly(phthalazinones) with fuming sulfuric acid mixtures for proton exchange membrane materials. J Membr Sci 227(1–2):39–50

20. Jian XG, Zhang HH, Yang Dl, Wang JY, Liu C, Han RL (2009) Ultrafiltration membranes of poly(phthalazinone ether sulfone)s and their preparation method. Chinese Patent 200910220545.2

21. Jian XG, Zhan SH, Yang Dl, Wang jY, Liu C (2009) Ultrafiltration membranes of sulfonated poly(phthalazinone ether sulfone)s and their preparation method. Chinese Patent 200910220544.8

22. Damay F, Klein LC (2003) Transport properties of Nafion(TM) composite membranes for proton-exchange membranes fuel cells. Solid State Ionics 162–163:261–267

23. Sukkar T, Skyllas-Kazacos M (2004) Membrane stability studies for vanadium redox cell applications. J Appl Electrochem 34:137–145

24. Mai Z, Zhang H, Li X, Bi C, Dai H (2011) Sulfonated poly (tetramethydiphenyl ether ether ketone) membranes for vanadium redox flow battery application. J Power Sources 196(1):482–487

25. Hwang G-J, Ohya H (1996) Preparation of cation exchange membrane as a separator for the all-vanadium redox flow battery. J Membr Sci 120(1):55–67

26. Sang S, Wu Q, Huang K (2007) Preparation of zirconium phosphate (ZrP)/Nafion1135 composite membrane and H^+/VO^{2+} transfer property investigation. J Membr Sci 305(1–2):118–124

27. Xi J, Wu Z, Teng X, Zhao Y, Chen L, Qiu X (2008) Self-assembled polyelectrolyte multilayer modified Nafion membrane with suppressed vanadium ion crossover for vanadium redox flow batteries. J Mater Chem 18(11):1232–1238

28. Qiu JY, Zhao L, Zhai ML, Ni JF, Zhou HH, Peng J, Li JQ, Wei GS (2008) Pre-irradiation grafting of styrene and maleic anhydride onto PVDF membrane and subsequent sulfonation for application in vanadium redox batteries. J Power Sources 177(2):617–623

29. Xi JY, Wu ZH, Qiu XP, Chen LQ (2007) Nafion/SiO2 hybrid membrane for vanadium redox flow battery. J Power Sources 166(2):531–536

30. Qiu J, Zhang J, Chen J, Peng J, Xu L, Zhai M, Li J, Wei G (2009) Amphoteric ion exchange membrane synthesized by radiation-induced graft copolymerization of styrene and dimethylaminoethyl methacrylate into PVDF film for vanadium redox flow battery applications. J Membr Sci 334(1–2):9–15

31. Gao Y, Robertson GP, Guiver MD, Jian X (2003) Synthesis and characterization of sulfonated poly(phthalazinone ether ketone) for proton exchange membrane materials. J Polymer Sci Polymer Chem 41(4):497–507

32. Kreuer KD (2001) On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells. J Membr Sci 185(1):29–39

33. Yang B, Manthiram A (2006) Comparison of the small angle X-ray scattering study of sulfonated poly(etheretherketone) and Nafion membranes for direct methanol fuel cells. J Power Sources 153 (1):29–35

34. Luo QT, Zhang HM, Chen J, You DJ, Sun CX, Zhang Y (2008) Preparation and characterization of Nafion/SPEEK layered composite membrane and its application in vanadium redox flow battery. J Membr Sci 325(2):553–558

35. Ma C, Zhang L, Mukerjee S, Ofer D, Nair B (2003) An investigation of proton conduction in select PEM's and reaction layer interfaces-designed for elevated temperature operation. J Membr Sci 219(1–2):123–136