



Sulfonated poly(tetramethyldiphenyl ether ether ketone) membranes for vanadium redox flow battery application

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ABSTRACT

Sulfonated poly(tetramethyldiphenyl ether ether ketone) (SPEEK) with various degree of sulfonation is prepared and first used as ion exchange membrane for vanadium redox flow battery (VRB) application. The vanadium ion permeability of SPEEK40 membrane is one order of magnitude lower than that of Nafion 115 membrane. The low cost SPEEK membranes exhibit a better performance than Nafion at the same operating condition. VRB single cells with SPEEK membranes show very high energy efficiency (>84%), comparable to that of the Nafion, but at much higher columbic efficiency (>97%). In the self-discharge test, the duration of the cell with the SPEEK membrane is two times longer than that with Nafion 115. The membrane keeps a stable performance after 80-cycles charge–discharge test.

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1. Introduction

Vanadium redox flow battery (VRB), originally proposed by Skollaskazacos et al., has been receiving considerable attention in the last few years due to its technical benefits [1–3]. These benefits include the flexibility in design, the facility to regenerate the electrolyte solution and the reliability for large-scale energy storage, among several others. The structure of VRB single cell as illustrated by many researchers [4–7], consists of two electrolyte tanks with $\text{VO}_2^+/\text{VO}^{2+}$ and $\text{V}^{3+}/\text{V}^{2+}$ electrolyte solution, two pumps and battery cell. As the key component of VRB, ion exchange membranes (IEMs) are employed to separate the positive and negative electrolyte and complete the current circuit by transferring ions. The ideal ion exchange membrane should possess good ion conductivity, i.e. low area resistance, and high chemical and mechanical stability. The membranes traditionally used in VRB are perfluorosulfonic polymers such as Dupont Nafion[®]. Although they show both high proton conductivity and chemical stability, the extremely high cost and low ion selectivity of these membranes (high vanadium crossover) have limited their further commercialization [8–11]. Hence alternative ion exchange membrane materials are being sought.

Various types of commercial membranes, such as cationic Selemion CMV, anionic Selemion AMV, DMV, and microporous Daramic, have been investigated in VRB application. However, most of them were proved unsuitable due to the following reasons

[9,12,13]: porous membranes lack ionic permselectivity and are incapable of preventing the cross mixing of vanadium ions. Anion exchange membranes can hardly achieve a high ion conductivity considering the intrinsic thermodynamic properties of anion transportation in the membranes, even though they effectively lowered vanadium permeation rates. Furthermore, the oxidation decomposition of polymer chains by pentavalent vanadium ions (VO_2^+) severely shortened the lifetime of nearly all types of membranes in VRB system.

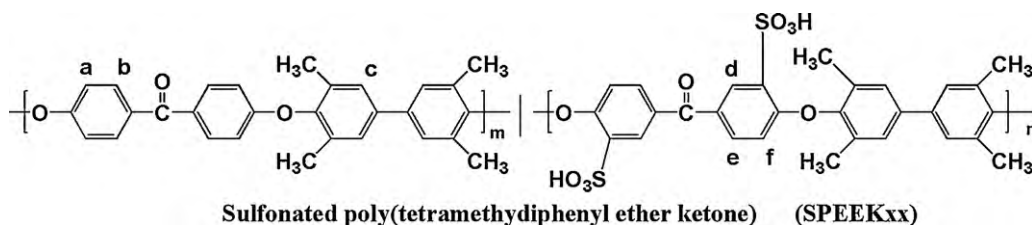
Aromatic polymers, such as poly(arylene ether ketone), poly(arylene ether sulfone) and polyimide, are well-known for their good thermal and mechanical stability. Attaching ion conductive groups to these polymers can provide the membranes with good proton conductivity, which has been extensively exploited for use in fuel cells and gas separation. Nevertheless, it is rarely reported to utilize sulfonated aromatic polymers in VRB systems. Luo et al. prepared a composite membrane for VRB, by chemically crosslinking a Nafion shielding layer onto the post-sulfonated poly(arylene ether ketone) membrane [14]. Chen et al. reported a sulfonated poly(arylene ether ketone) membrane containing fluorenyl groups via direct synthesis of sulfonated monomer [15].

In this work, a series of sulfonated poly(tetramethyldiphenyl ether ether ketone) membranes with different degree of sulfonation (DS) were prepared and characterized. Rigid biphenyl groups were introduced in the PEEK backbone to increase the membranes chemical and mechanical stability. VRB single cell performances of these membranes were first investigated and compared with Nafion 115. Furthermore, a charge–discharge test was conducted for 80 cycles to estimate the stability of the SPEEK membrane in VRB operation.

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Scheme 1. Polymerization of sulfonated poly(tetramethyldiphenyl ether ether ketone), $xx = 100n/(m + n)$.

2. Experimental

2.1. Polymer synthesis

SPEEK polymers with different degree of sulfonation were prepared by direct aromatic nucleophilic substitution step polymerization. Detailed synthesis procedures and characterization of these copolymers were reported previously [16,17]. The structure of polymers is shown in Scheme 1. The sulfonated degree was determined by ^1H NMR [18,19].

2.2. Membrane preparation

The SPEEK membranes were prepared by solution casting method. SPEEK polymer was dissolved in N-methyl-2-pyrrolidone (NMP) to form 10 wt.% solution. The solution was casted onto a glass plate and dried at 80°C for 12 h. The membrane was peeled off from the substrate and immersed in 1 M H_2SO_4 overnight to obtain a membrane in acidic form.

2.3. Membrane characterization

2.3.1. NMR

^1H NMR was used to determine the chemical composition of the polymers. BRUKER DRX400 was used to determine ^1H NMR with DMSO as solvent and tetramethylsilane as internal standard.

2.3.2. Area resistance

The area resistances of the membranes were measured by the method described elsewhere [12]. A conductivity cell was separated into two compartments filled with 1.5 M VOSO_4 and 3 M H_2SO_4 solution. The effective area of the cell (S) was 15 cm^2 . r_1 and r_2 , which represent the electric resistances of the cell with and without a membrane respectively were measured by electrochemical impedance spectroscopy (EIS) over a frequency range from 100 kHz to 100 mHz. The area resistance r was calculated by Eq. (1):

$$r = (r_1 - r_2)S \quad (1)$$

All the membranes were soaked in 1.5 M VOSO_4 and 3 M H_2SO_4 solution for 3 days before measurement.

2.3.3. Ion exchange capacity (IEC)

IEC was determined by the conventional titration method [16]. Membrane with fixed weight was immersed in 1 M NaCl solution for 24 h to liberate all fixed H^+ ions of the membrane into the solution. Afterwards, the H^+ concentration in the solution was titrated with 0.01 M NaOH. Finally IEC can be calculated by Eq. (2):

$$\text{IEC} = \frac{\Delta V_{\text{NaOH}} C_{\text{NaOH}}}{W_d} \quad (2)$$

where ΔV_{NaOH} is the consumed volume of NaOH solution, C_{NaOH} is the concentration of NaOH solution and W_d is the dried weight of the membrane.

2.3.4. Electrolyte uptake

The dried membrane was immersed in 1.5 M VOSO_4 and 3 M H_2SO_4 solution for 2 days in order to saturate it with solution. After quickly wiping out the surface solution of the membrane by tissue, the weight of the saturated membrane was measured. The vanadium solution uptake is defined as the weight ratio of the absorbed vanadium solution to the dry membrane, as shown in Eq. (3):

$$\text{vanadium solution uptake (\%)} = \frac{W_s - W_d}{W_d} \times 100 \quad (3)$$

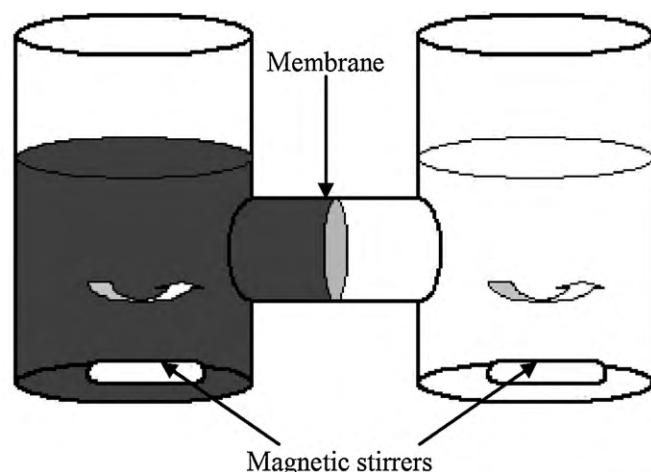
where W_s and W_d are the weight of saturated and dry membrane, respectively.

2.3.5. Vanadium permeability

The permeability of VO^{2+} through the membrane was determined according to literature [8]. The diffusion cells are shown in Scheme 2. The left cell was filled with 150 ml 1.5 M VOSO_4 in 3 M H_2SO_4 solution, while the right one was filled with 150 ml 1.5 M MgSO_4 in 3 M H_2SO_4 solution to equalize the ionic strengths and to minimize the osmotic pressure effects. Magnetic stirrers were used in both cells to avoid the concentration polarization. The effective area of the membrane, i.e. the area exposed to the solution was 10.2 cm^2 . Samples from the right cell were collected at regular time interval. The concentration of VO^{2+} in sample solution was measured by using a UV-vis spectrometer.

Given that the change of VO^{2+} concentration in the left reservoir is very low, the relationship between VO^{2+} concentration in the right reservoir and time could be described by Fick's diffusion law as Eq. (4):

$$V_B \frac{dC_B(t)}{dt} = A \frac{P}{L} (C_A - C_B(t)) \quad (4)$$



Scheme 2. Diffusion cell for measuring VO^{2+} permeability.

Table 1
Physicochemical properties of SPEEK and Nafion 115 membranes.

Membrane	Thickness (μm)	^a Calculated DS	IEC (mequiv. g^{-1})	Permeability of VO^{2+} ($\times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$)	Area resistance ($\Omega \text{ cm}^2$)	Electrolyte uptake (%)
SPEEK 40	90	0.73	1.45	0.36	1.22	26.7
SPEEK 50	85	0.93	1.69	–	1.10	31.8
SPEEK 60	90	1.10	2.07	2.12	1.23	25.3
Nafion 115	127	–	0.91	7.95	0.95	25.8

^a DS based on ^1H NMR integration calculation.

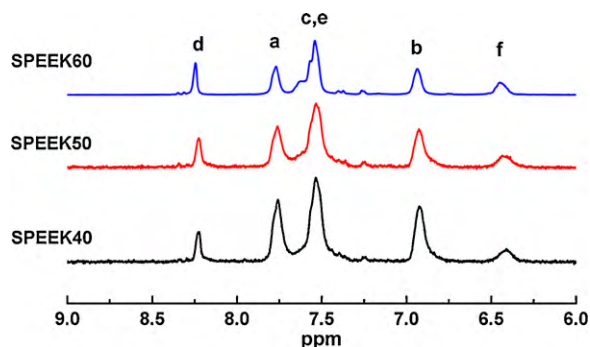


Fig. 1. ^1H NMR spectra of SPEEK in $\text{DMSO-}d_6$.

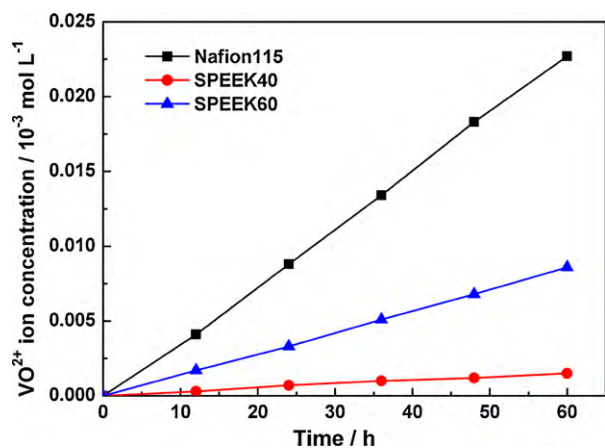


Fig. 2. VO^{2+} concentration in the right reservoir of the permeation measuring device with SPEEK and Nafion 115 membranes.

where V_B is the solution volume in the right reservoir, A and L are the effective area and thickness of the membrane, respectively, P is the permeability of VO^{2+} , C_A is VO^{2+} concentration in the left reservoir, C_B is VO^{2+} concentration in the right reservoir as a function of time t .

2.3.6. Scanning electronic microscopy (SEM)

SEM (JEOL 6360LV, Japan) was employed to observe the surface and cross-section morphology of the SPEEK40 membrane before and after 80 cycles test. The cross-section was obtained after breaking the membranes in liquid nitrogen.

2.3.6.1. VRB single cell performance. The VRB single cell was fabricated by sandwiching a membrane with two carbon felt electrodes, clamped by two graphite polar plates. All these components were fixed between two stainless plates. $1.5 \text{ M V}^{2+}/\text{V}^{3+}$ in $3.0 \text{ M H}_2\text{SO}_4$ solution and $1.5 \text{ M VO}^{2+}/\text{VO}_2^+$ in $3.0 \text{ M H}_2\text{SO}_4$ solution, serving as negative and positive electrolytes, respectively, were cyclically pumped into the corresponding half-cell. The active area of the cell was 6 cm^2 and the volume of electrolyte solution was 30 ml in each half-cell. Charge–discharge cycling tests were conducted by LAND CT2001A with a constant current density of 50 mA cm^2 . The maximum voltage of 1.65 V and minimum voltage of 0.8 V for charge and

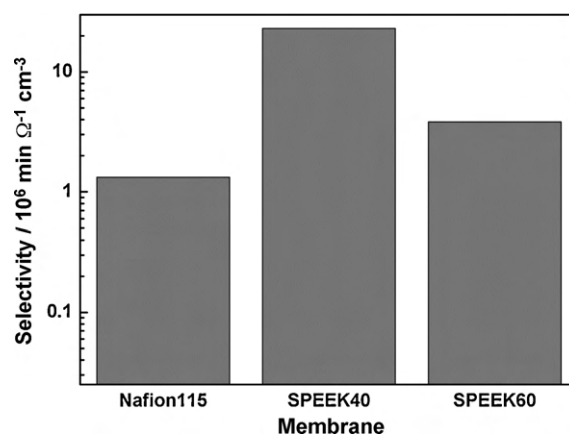


Fig. 3. Selectivity of SPEEK and Nafion 115 membranes between VO^{2+} and H^+ .

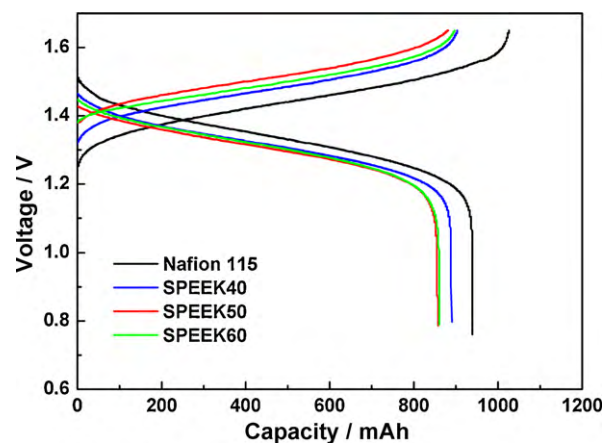


Fig. 4. Charge and discharge curves of SPEEK and Nafion 115 membranes in VRB operation (50 mA cm^2).

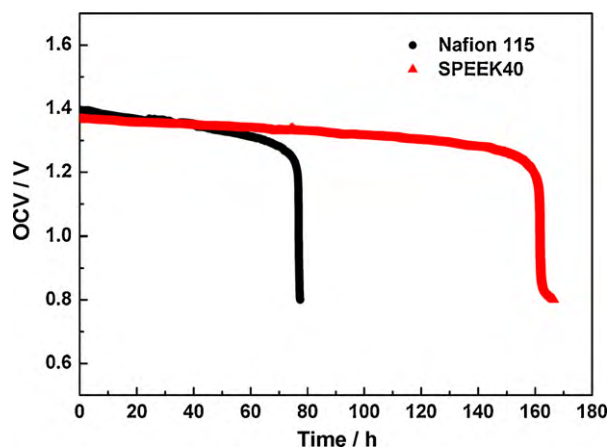


Fig. 5. OCV decay of the VRB cell with SPEEK 40 and Nafion 115 membrane.

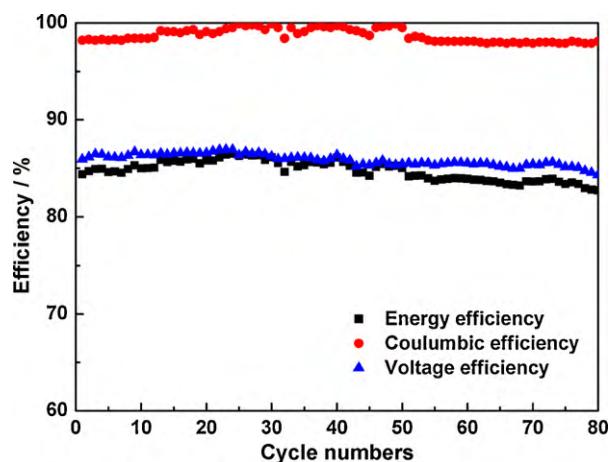


Fig. 6. Charge–discharge cycling performance (60 mA cm^{-2}) of the cell with SPEEK 40.

discharge were employed to avoid the corrosion of carbon felts and graphite plates.

3. Results and discussion

3.1. Polymer preparation and characterization

Fig. 1 represents the ^1H NMR spectra of SPEEK, confirming the composition of the polymer. Peaks between 6.0 and 8.5 ppm corresponded to the chemical shifts of protons attaching to the aromatic rings, as denoted in Scheme 2. Furthermore, the DS can be calculated from the proton integration:

$$\text{DS} = \frac{12}{(\sum A_H/A_{H_d}) + 1} \quad (5)$$

where $\sum A_H$ is the integration area of all proton peaks, $\sum A_{H_d}$ is the integration area of H_d peak.

The calculated DS in Table 1 is well in agreement with the expected design.

3.2. IEC, electrolyte uptake and area resistance

As DS increases, a regular rise of IEC can be observed from Table 1. The results show that area resistances of different SPEEK membranes varied only in a narrow range from 1.10 to $1.23 \Omega \text{ cm}^2$, in spite of distinct differences in IEC. As demonstrated in previous studies [9,13], the conductivity of a membrane could be remarkably enhanced by SO_4^{2-} or HSO_4^- ions in the pores of membrane which were introduced by the electrolyte solution. In other words, these “free acid”, along with fixed sulfonic acid group $-\text{SO}_3\text{H}$, affect the area resistance of a membrane. As listed in Table 1, the similar electrolyte uptakes suggest that these membranes absorbed similar amount of “free acid” and thus explain their approximate area resistance.

Table 2

VRB single cell performances of SPEEK and Nafion 115 membranes.

Membrane	Coulombic efficiency (%)	Voltage efficiency (%)	Energy efficiency (%)
SPEEK 40	98.5	88.8	87.5
SPEEK 50	97.3	86.3	84.0
SPEEK 60	96.1	87.6	84.2
Nafion 115	91.7	92.3	84.7

3.3. Vanadium permeability

A linear relation between time and the concentration of VO^{2+} in the right cell was clearly demonstrated in Fig. 2. Comparison of SPEEK40 and SPEEK60 reveals that the permeability rises with IEC due to a well known fact that the increment and enrichment of $-\text{SO}_3\text{H}$ groups in the membrane would provide larger and more continuous transport channel for cations [20].

However, Nafion 115, with lower IEC, displays the steepest slope and its VO^{2+} permeability is $7.95 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$, which is the highest of the three. It could be attributed to the fact that the ion conductivity is determined not only by IEC but also the microstructure of the membrane [21]. It is believed that the flexible ionic side chain and perfluorinated backbone lead to networks of ionic channels through Nafion membrane, while continuous ionic clusters in rigid aromatic polymers, such as SPEEK, could hardly occur [22]. As a result, ionic cluster region formed in SPEEK is smaller than that in Nafion, reducing the permeation rate of vanadium ions.

The SPEEK40 possesses comparable area resistances to Nafion 115. Meanwhile, its VO^{2+} permeability is one order of magnitude lower than that of Nafion 115. In general, the selectivity of SPEEK40 is distinctly superior to Nafion 115 in VRB system, as shown in Fig. 3. Accordingly, a balance between ion conductance and vanadium permeation could be hopefully achieved in a VRB cell fabricated with SPEEK membranes.

3.4. Single cell performance

Table 2 shows the VRB single cell performance by using SPEEK as membranes. Obviously, the VRB cells with SPEEK exhibit higher coulombic efficiency (CE) than that of Nafion 115 membrane at similar energy efficiency.

CE is the ratio of a cell's discharge capacity (Q_{dis}) divided by its charge capacity (Q_{ch}), described as Eq. (5). In the constant current (I_{con}) charge–discharge mode, Eq. (6) is satisfied and CE can be presented as the discharge time (t_{dis}) divided by charge time (t_{ch}).

$$\text{CE} = \frac{Q_{dis}}{Q_{ch}} \times 100\% \quad (6)$$

$$\text{CE} = \frac{I_{con} t_{dis}}{I_{con} t_{ch}} \times 100\% = \frac{t_{dis}}{t_{ch}} \times 100\% \quad (7)$$

The higher coulombic efficiency, indicating lower capacity loss, is mainly due to the lower rate of cross-mixed vanadium ions. During discharge, electrochemical reduction and oxidation of vanadium ions occur, as described in reactions (I) and (II). Once vanadium ions cross-mixed, the non-electrochemical side reactions (reactions (III)–(V)) [23], would happen and further reduce the quantity of the active species for reactions (I) and (II). SPEEK membranes have reasonably higher CE, due to the lower permeation of vanadium ions.



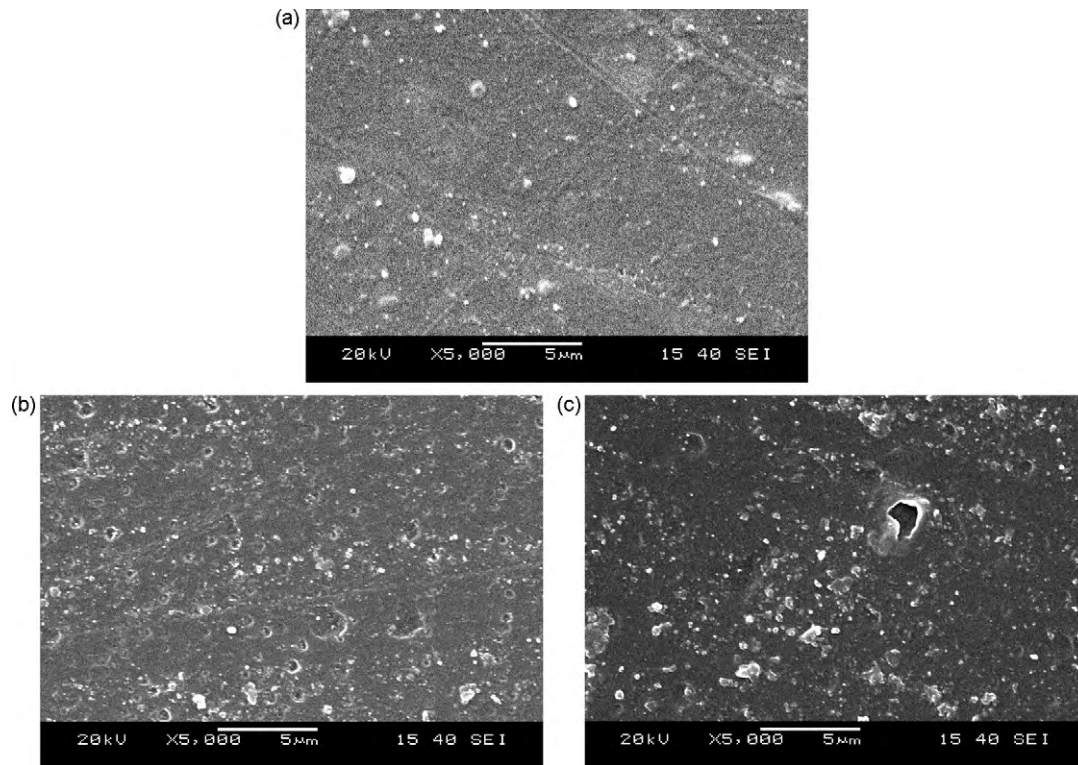


Fig. 7. SEM micrographs of membrane surface: (a) initial; (b) after 80 charge–discharge cycles (facing positive half cell); (c) after 80 charge–discharge cycles (facing negative half cell).

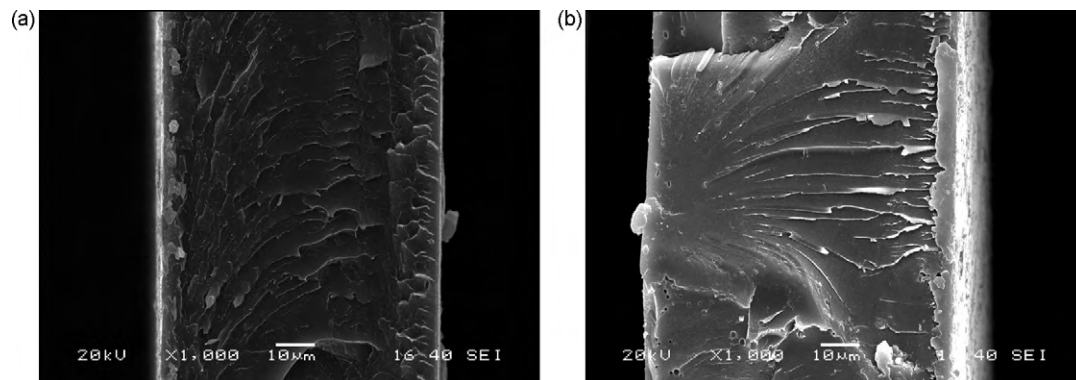


Fig. 8. SEM micrographs of membrane cross-section: (a) initial; (b) after 80 charge–discharge cycles.



Voltage efficiency (VE) is defined as the ratio of a cell's mean discharge voltage (V_{dis}) divided by its mean charge voltage (V_{ch}), presented in Eq. (7). Discharge voltage and charge voltage are both determined by the thermodynamic reduction potential of the redox couples in each half cell and the overpotential of the cell. In VRB system, the ohmic overpotential is partly attributed to the membrane resistance. Therefore, higher membrane resistance will lead to higher charge voltage and lower discharge voltage, which is clearly shown in Fig. 4. Accordingly, all the cells with SPEEK membranes exhibit VE lower than 89%, while VE of the cell with Nafion 115 is 92.3% (Table 2). These results are well-matched with the higher area resistance of SPEEK membranes mentioned in Table 1.

$$\text{VE} = \frac{V_{dis}}{V_{ch}} \times 100\% \quad (8)$$

VRB cells with SPEEK membranes and Nafion 115 membrane exhibit similar energy efficiency (EE), which is higher than 84%. EE

is calculated from VE and CE, as described in Eq. (8). As an indicator of energy loss in charge–discharge process, energy efficiency (EE) is the key parameter to evaluate an energy storage system. The similar EE of SPEEK membranes with Nafion 115 indicates the similar VRB performance by using SPEEK instead of Nafion 117. However, much higher CE of SPEEK efficiently avoids the vanadium cross-mixed problem of Nafion 117.

$$\text{EE} = \text{CE} \times \text{VE} \quad (9)$$

Self-discharge test was conducted to investigate the transfer of vanadium ions across SPEEK40 and Nafion membrane. In this test, $1.5 \text{ M V}^{2+}/\text{V}^{3+}$ in $3.0 \text{ M H}_2\text{SO}_4$ solution and $1.5 \text{ M VO}^{2+}/\text{VO}_2^+$ in $3.0 \text{ M H}_2\text{SO}_4$ solution were cyclically pumped into negative and positive half cell, respectively. Self-discharge began at the state of charge (SOC) of 50%, i.e. the capacity of 600 mAh. The procedure stopped when the open circuit voltage (OCV) was lower than 0.8 V. As demonstrated in Fig. 5, the OCV of the VRB cell with SPEEK40 membrane maintains above 1.3 V for about 140 h, then gradually

decreased. After 160 h, the OCV quickly dropped from 1.2 V to 0.8 V. The entire self-discharge procedure of this VRB cell lasts for about 170 h, while the OCV of the cell with Nafion 115 decreases to 0.8 V in less than 80 h. The much slower OCV decay rate of the cell with SPEEK40 clearly indicates that the SPEEK membranes effectively reduce the permeation of vanadium ions.

3.5. Stability tests

To further investigate the oxidation stability of SPEEK membrane in VRB, the single VRB cell with SPEEK run continuously more than 80 cycles at a current density of 60 mA cm^{-2} . The VRB cell showed stable performance during 80 cycles. The CE remained above 98%, indicating a low permeation rate of vanadium ions. The VE is around 85%, suggesting the membrane was chemically endurable to survive the test and provided stable conductive channels (Fig. 6).

SEM was carried out on the membranes before and after VRB test to further investigate the membrane stability. In Fig. 7(a), a dense and flat surface of initial membrane can be observed. In comparison, Fig. 7(b) shows the membrane surface facing the positive half cell, which was covered with dents and lumps. The similar morphology is recorded in Fig. 7(c), in which the membrane surface facing the negative half cell is shown. The reason of these morphology changes is possibly due to the direct contact between the membrane and carbon felts, rough fibers of the compressed carbon felts could leave the membrane with rougher surface. However, two surfaces of the membrane were contacted by electrolyte with different constituent. VO_2^+ ions, as a strong oxidant, substantially exist in positive electrolyte. The adsorption and diffusion of VO_2^+ ions on the membrane surface may cause some degradation to the polymer. Considering that the surface in (c) is contacted by negative electrolyte ($\text{V}^{3+}/\text{V}^{2+}$), oxidation decomposition would probably not take place. In this system, no obvious changes after 80 cycles test were found from both sides, indicating the good stability of SPEEK membranes during VRB operation.

To further confirm the chemical stability of the membranes, the cross-section of the initial membrane and tested membrane were recorded and shown in Fig. 8(a) and (b). The initial membrane possesses a dense and uniform internal structure, with the thickness of about $90 \mu\text{m}$. After test, an integrated internal structure is still maintained and the reduction of thickness can hardly be observed. The comparison between the two cross-section images supports the stability of the membrane during 80 charge–discharge cycles.

Because the stability of a membrane in VRB system is a complex issue involving mechanical damage and chemical degradation, it is unlikely to infer the entire lifespan of the SPEEK membrane merely based on an 80-cycles test. Cycling test for a longer term is proposed in our next paper to obtain an experimental result. Still more effort will be performed to further increase the chemical stability of these membranes by thermal and irradiation crosslinking in future. Moreover, the mechanism of oxidation decomposition caused by pentavalent vanadium ions has not yet been exactly

understood. Further effort is needed to realize the degradation mechanism.

4. Conclusions

In this work, low cost ion exchange membrane was prepared from in-house-made sulfonated poly(tetramethy ether ether ketone) with various degree of sulfonation. Physicochemical properties were characterized, showing that SPEEK membranes possess much higher selectivity in VRB system than Nafion 115. It is probably owing to less connected ionic cluster region in SPEEK membrane [24], which reduces the permeation rate of vanadium ions. In VRB single cell test, the SPEEK membranes exhibited comparative, even superior performances compared with Nafion 115. In the 80-cycles charge–discharge test, the SPEEK40 membrane exhibited stable performance and its internal structure remained dense. Further study will be focused on the long-term cycling test and degradation mechanism to confirm and elongate its lifespan.

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References

- [1] M. Skyllaskazacos, F. Grossmith, J. Electrochem. Soc. 134 (1987) 2950–2953.
- [2] E. Sum, M. Rychcik, M. Skyllaskazacos, J. Power Sources 16 (1985) 85–95.
- [3] E. Sum, M. Skyllaskazacos, J. Power Sources 15 (1985) 179–190.
- [4] C.P. de Leon, A. Frias-Ferrer, J. Gonzalez-Garcia, D.A. Szanto, F.C. Walsh, J. Power Sources 160 (2006) 716–732.
- [5] C. Fabjan, J. Garche, B. Harrer, L. Jorissen, C. Kolbeck, F. Philipp, G. Tomazic, F. Wagner, Electrochim. Acta 47 (2001) 825–831.
- [6] L. Joerissen, J. Garche, C. Fabjan, G. Tomazic, J. Power Sources 127 (2004) 98–104.
- [7] P. Zhao, H.M. Zhang, H.T. Zhou, J. Chen, S.J. Gao, B.L. Yi, J. Power Sources 162 (2006) 1416–1420.
- [8] Q. Luo, H. Zhang, J. Chen, P. Qian, Y. Zhai, J. Membr. Sci. 311 (2008) 98–103.
- [9] T. Mohammadi, M.S. Kazacos, J. Appl. Electrochem. 27 (1997) 153–160.
- [10] X.G. Teng, Y.T. Zhao, J.Y. Xi, Z.H. Wu, X.P. Qiu, L.Q. Chen, J. Power Sources 189 (2009) 1240–1246.
- [11] J.Y. Xi, Z.H. Wu, X.P. Qiu, L.Q. Chen, J. Power Sources 166 (2007) 531–536.
- [12] G.J. Hwang, H. Ohya, J. Membr. Sci. 120 (1996) 55–67.
- [13] T. Sukkar, M. Skyllas-Kazacos, J. Appl. Electrochem. 34 (2004) 137–145.
- [14] Q.T. Luo, H.M. Zhang, J. Chen, D.J. You, C.X. Sun, Y. Zhang, J. Membr. Sci. 325 (2008) 553–558.
- [15] D.Y. Chen, S.J. Wang, M. Xiao, Y.Z. Meng, J. Power Sources 195 (2010) 2089–2095.
- [16] X.F. Li, Z. Wang, H. Lu, C.J. Zhao, H. Na, C. Zhao, J. Membr. Sci. 254 (2005) 147–155.
- [17] X.F. Li, C.P. Liu, H. Lu, C.J. Zhao, Z. Wang, W. Xing, H. Na, J. Membr. Sci. 255 (2005) 149–155.
- [18] G.P. Robertson, S.D. Mikhailenko, K. Wang, P. Xing, M.D. Guiver, S. Kaliaguine, J. Membr. Sci. 219 (2003) 113–121.
- [19] S.M.J. Zaidi, S.D. Mikhailenko, G.P. Robertson, M.D. Guiver, S. Kaliaguine, J. Membr. Sci. 173 (2000) 17–34.
- [20] X.F. Li, G. Zhang, D. Xu, C.J. Zhao, H. Na, J. Power Sources 165 (2007) 701–707.
- [21] T.B. Norsten, M.D. Guiver, J. Murphy, T. Astill, T. Navessin, S. Holdcroft, B.L. Frankamp, V.M. Rotello, J.F. Ding, Adv. Funct. Mater. 16 (2006) 1814–1822.
- [22] M.A. Hickner, H. Ghassemi, Y.S. Kim, B.R. Einsla, J.E. McGrath, Chem. Rev. 104 (2004) 4587–4611.
- [23] C. Sun, J. Chen, H. Zhang, X. Han, Q. Luo, J. Power Sources 195 (2010) 890–897.
- [24] K.D. Kreuer, J. Membr. Sci. 185 (2001) 29–39.