



Short communication

Poly(tetrafluoroethylene) reinforced sulfonated poly(ether ether ketone) membranes for vanadium redox flow battery application

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ABSTRACT

Poly(tetrafluoroethylene) reinforced sulfonated poly(ether ether ketone) (SPEEK/PTFE) composite membranes are prepared for vanadium redox flow battery (VRB) application. Results show that SPEEK/PTFE composite membranes have lower water uptake and swelling ratio than that of SPEEK membranes due to the PTFE reinforcement. As a result, the composite membranes show higher elongation ratio and better mechanical stability than SPEEK membranes. VRB single cell tests are also carried out to further evaluate their performance. The batteries assembled with SPEEK/PTFE membranes exhibit higher columbic efficiency (CE) and energy efficiency (EE) than that of SPEEK membranes. Furthermore, the composite membranes show much better stability than pristine SPEEK, confirming that PTFE can effectively reinforce membranes to improve their chemical and mechanical stability under VRB operating condition.

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1. Introduction

Vanadium redox flow battery (VRB) proposed by Skyllaskazacos et al. has attracted wide attention due to its long cycle life, fast response, flexible design and high reliability [1,2]. Normally a VRB single cell includes two electrolyte tanks with $\text{VO}_2^+/\text{VO}^{2+}$ and $\text{V}^{3+}/\text{V}^{2+}$ redox couples in sulfuric acid solution, two pumps and a battery cell [3–6]. The electrolyte solutions were cyclically pumped into VRB cell during charge and discharge. As a key component of VRB, an ion exchange membrane is employed to separate the positive and negative electrolytes while still allowing the transport of the ions to complete current circuit. Thus an ideal ion exchange membrane of VRB should possess good ion conductivity, low permeability for vanadium ions, high mechanical property, good chemical stability and low cost. Nafion is the most commonly used membrane in VRB due to its high proton conductivity, good mechanical and chemical stability. However, the extremely high cost and low ion selectivity (high vanadium crossover) of Nafion membrane have limited their further commercialization [7–10]. Thus alternative membranes for VRB are being researched in these years [11–15].

Recently, sulfonated aromatic polymers, like sulfonated poly(arylene ether ketone) and poly(arylene ether sulfone) have received considerable attention due to their low cost, simplicity

in synthesis and processing [16–19]. Even this kind of polymer membranes have already been investigated in fuel cell field, their application in VRBs has just started [20–23]. Recently Mai et al. from our group have reported the application of sulfonated poly(tetramethyldiphenyl ether ether ketone) membranes in VRB. The membranes show much higher ion selectivity and a better performance than Nafion at the same operating condition [15]. However, the chemical stability and the life time of these membranes still need to be further improved. Especially for the membranes with high degree of sulfonation (DS), their high swelling, which induced by high content of ion exchange groups would lower their chemical and mechanical stability. Moreover, the high swelling could affect the ion selectivity of membranes and further lower their battery performance [20,24,25].

Porous PTFE reinforcement technique is considered as one of the most effective and facile methods to suppress membrane swelling and further improve membrane stability. The rigid structure of PTFE matrix can limit the swelling of polyelectrolyte, while the high mechanical strength of the matrix offers the possibility of fabricating very thin composite to reduce the resistance of membranes. PTFE reinforced membranes have already been researched in fuel cells applications to reduce the methanol crossover [26–28]. However, up to now, few reports are concerned on their application in VRB. Considering the swelling suppressing effect of porous PTFE, reinforcement with PTFE could be an efficient way to improve the ion selectivity, mechanical and chemical stability of sulfonated PEEK membranes with high DS and subsequently increase their life time and performance. In this paper, PTFE reinforced SPEEK membranes were prepared and first investigated in VRB application. The

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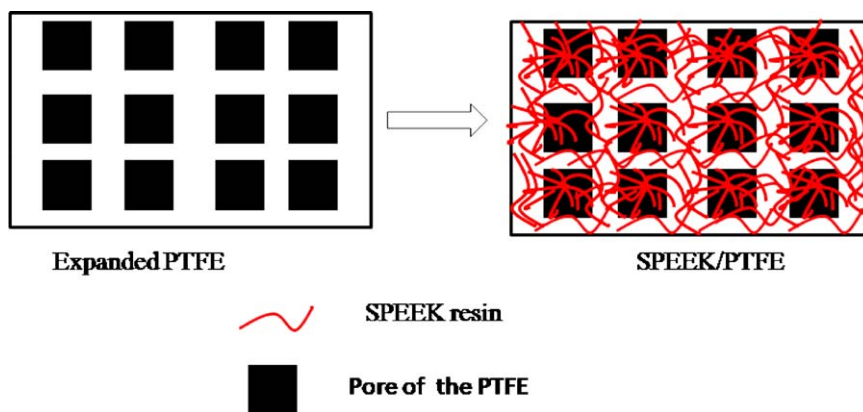


Fig. 1. Schematic diagram of preparation of SPEEK/PTFE.

VRB single cell performance and other relevant properties of these membranes were studied in detail.

2. Experimental

2.1. Materials

SPEEK was prepared by direct sulfonation of PEEK (VICTREX®) with sulfuric acid at 70 °C for 1 h as described elsewhere [29]. The degree of sulfonation (the number of SO₃H groups per repeating unit), as obtained by ¹H NMR is 0.73 [29]. Porous PTFE membranes with pore size distribution of 0.3–0.5 μm and porosity >90% were bought from Dagong New Mater. Co, Shanghai, China.

2.2. Preparation of SPEEK and SPEEK/PTFE membranes

Composite membranes with different thickness were prepared by solution casting on expanded PTFE film. Before casting, the PTFE was first treated with ethanol to improve its compatibility with SPEEK polymer. SPEEK was first dissolved in N,N-dimethylacetamide (DMAC) and then the solution was cast onto the PTFE film, which was extended on a stainless steel frame. The composite membranes were peeled off after evaporation at 70 °C for 12 h. The thickness of the membrane could be adjusted by changing the amounts of the SPEEK solution. The schematic diagram of preparation is shown in Fig. 1.

The pure SPEEK membranes were prepared by normal solution casting method. A SPEEK/DMAC solution was cast onto a glass plate and dried at 70 °C for 12 h. The membranes were peeled off from the substrate and immersed in 3 M H₂SO₄ overnight to transfer into acidic form. SPxx and Sxx were referred to as SPEEK/PTFE composite membrane and pristine SPEEK membrane with thickness of xx μm in the figures and tables, respectively.

2.3. Characterization of membranes

2.3.1. Fourier transform infrared (FTIR) and scanning electronic microscopy (SEM) measurements

FTIR spectra of the prepared membranes were measured by JASCO FTIR 4100 spectrometer. Each spectrum was recorded at the average rate of 48 scans with a resolution of 4 cm⁻¹ collected from 400 to 4000 cm⁻¹ in reflection mode.

The surface morphology of the prepared membranes was characterized by SEM (JEOL 6360LV, Japan). All the samples were gold coated before measurement.

2.3.2. Mechanical property

The stress–strain behavior of the membranes was measured on a tension tester AG-2000A (Shimadzu) at room temperature. Membrane samples (dry state) were tested by using a programmed elongation rate of 50 mm min⁻¹. For each test, at least three measurements were taken and average value was calculated.

2.3.3. Water uptake and swelling ratio

The dried membranes were first immersed into water for 24 h to saturate it with water. After quickly wiping out the surface water of the membranes by tissue, the weight and length of these membranes were measured. The water uptake and swelling ratio were calculated by the following equation:

$$\text{Water uptake (\%)} = \frac{W_w - W_d}{W_d} \times 100$$

$$\text{Swelling ratio (\%)} = \frac{L_w - L_d}{L_d} \times 100$$

where W_w and W_d are the weight of the membranes in wet and dry state, respectively. And L_w and L_d are the length of membrane in wet and dry state, respectively.

2.3.4. Area resistance

The area resistance of the membranes was tested by the method as described in previous study [30]. A diffusion cell, which separated by a membrane was used for measurement, each cell was filled with 0.5 M H₂SO₄. The electric resistance was measured by electrochemical impedance spectroscopy (EIS) over a frequency range from 1 kHz to 1 MHz. The effective area of the membrane was 3 cm² and the area resistance was calculated by Eq. (1):

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

The r_1 and r_2 represent the electric resistances of cell with and without a membrane. All the membranes were soaked in 0.5 M H₂SO₄ solution for 3 days before measurement.

2.3.5. VRB single 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. The solutions of 1.5 M V²⁺/V³⁺ and VO²⁺/VO₂⁺ in 3.0 M H₂SO₄ were served as negative and positive electrolytes, respectively. The volume of electrolyte solution on each side of the cell was 30 ml and the active area of cell was 9 cm². The charge–discharge cycling tests were carried out by LAND CT2001A with a constant current density of 80 mA cm⁻². The upper charge voltage and the lower discharge voltage were 1.65 V and 0.8 V, respectively.

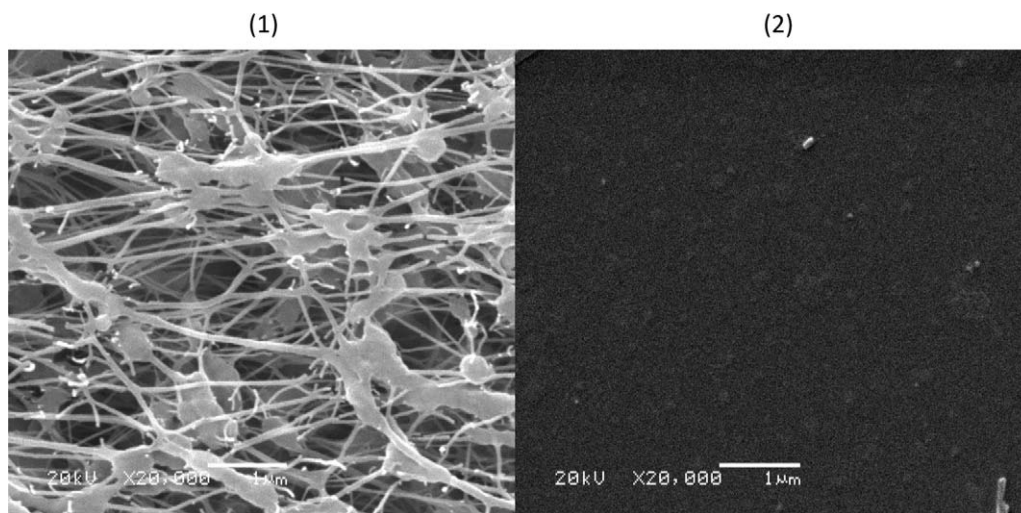


Fig. 2. SEM images of membranes surface: (1) PTFE membrane (2) SPEEK/PTFE membrane.

3. Result and discussion

3.1. SEM and FTIR

SEM was used to investigate the morphology of PTFE and its reinforced membranes. Fig. 2 shows the surface structures of expanded porous PTFE and SPEEK/PTFE membranes. The highly porous structure of the expanded PTFE membrane was fully impregnated by the SPEEK resin. The pores of PTFE were fully blocked and SPEEK is uniformly distributed in the composite membranes. The composite membranes show quite smooth surface. The result indicates the good compatibility between alcohol-treated PTFE and SPEEK resin.

FTIR was carried out to further confirm the membrane structure. Fig. 3 shows the ATR (attenuated total reflectance) spectra of pristine SPEEK, PTFE and SPEEK/PTFE composite membranes. SPEEK/PTFE membranes show similar character peaks with pristine SPEEK. Compared with pure PTFE membrane, the additional absorption band of SPEEK/PTFE membrane at 1080 cm^{-1} , which corresponds to symmetric $\text{O}=\text{S}=\text{O}$ stretching, indicates the successful impregnation of SPEEK resin in PTFE matrix [31].

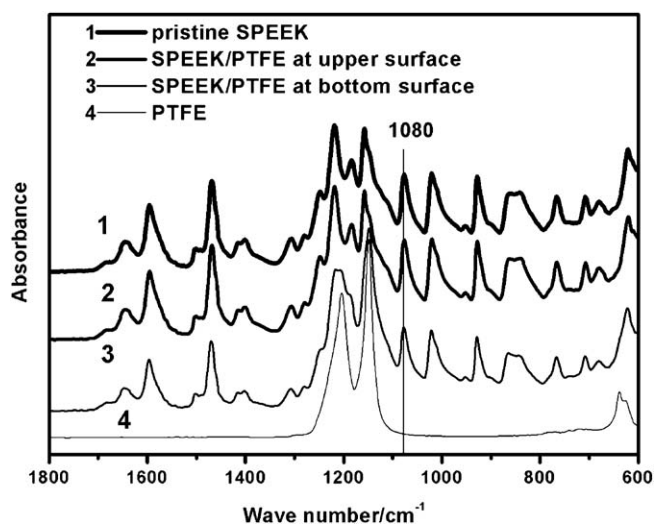


Fig. 3. ATR-FTIR spectra of surface of pristine SPEEK, SPEEK/PTFE and PTFE membranes.

3.2. Water uptake, swelling ratio and mechanical stability

For SPEEK membrane, higher water uptake will lead to lower ion selectivity. As demonstrated in previous study, SPEEK membranes with high sulfonated degree show quite high swelling ratio in water, which further leads to their low selectivity and chemical stability [32]. As can be seen in Fig. 4, the water uptake and swelling ratio of SPEEK/PTFE composite membrane are lower than those of pristine SPEEK membrane. As expected, that porous PTFE can efficiently suppress the swelling of SPEEK, due to its highly hydrophobic nature as well as its high mechanical stability. In this system, SPEEK was filled in the pores and on the surface of porous PTFE. Similar with other reports in fuel cells, the swelling of SPEEK can be efficiently suppressed since the SPEEK resin was confined in the pores of PTFE [33,34]. For SPEEK/PTFE membrane, thinner membranes show lower swelling ratio or higher dimensional stability due to the lower SPEEK content compare with that of thicker composite membranes. For example, the SP 40 membrane has swelling ratio of 1.0% while SP 60 has that of 3.7%.

The swelling behavior of membrane could be closely related to its mechanical stability. As shown in Table 1, the pristine SPEEK and SPEEK/PTFE membranes show similar tensile strength, which is around 40 MPa. Compare to pristine SPEEK, the SPEEK/PTFE

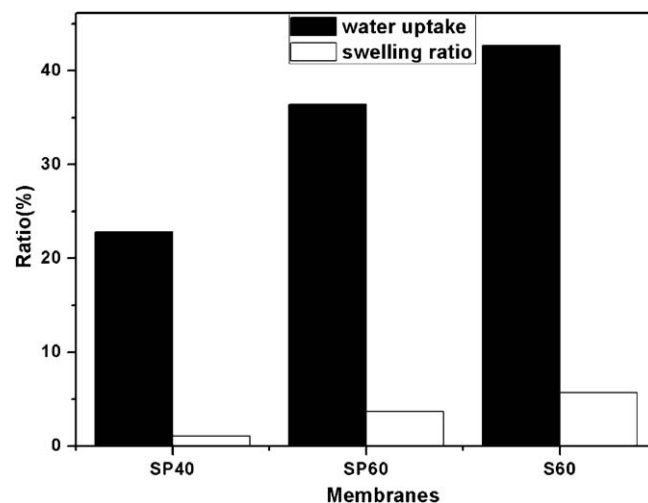


Fig. 4. Water uptake and swelling ratio of SPEEK/PTFE and SPEEK membranes.

Table 1
Mechanical property and area resistance of SPEEK/PTFE and SPEEK membranes.

Membrane	Tensile strength (MPa)	Break elongation (%)	Area resistance ($\Omega \text{ cm}^2$)
SP60	39.47	36.89	0.57
S60	39.16	17.45	0.43

composite membranes have much higher break elongation ratio, showing that the reinforced effect of PTFE could actually improve the mechanical stability of composite membranes. It is considered that the adsorption and diffusion of water molecules in SPEEK membranes mainly take place in the hydrophilic region, induced by sulfonic acid groups, while the fully hydrophobic PTFE networks provides the membranes mechanical stability. As expected, the porous PTFE can really suppress the swelling of SPEEK resins in the pores and further improve its mechanical stability. All these results are well in agreement with the swelling behavior of the membranes [33,34].

3.3. Single cell performance

Fig. 5 presents the single cell performance of VRB assembled by pristine SPEEK and SPEEK/PTFE composite membranes with the same thickness. As expected, the SPEEK/PTFE composite membranes show higher (columbic energy) CE than pristine SPEEK at the same current density, due to its low crossover of vanadium ions, which induced by low swelling of SPEEK/PTFE membranes. The SPEEK and SPEEK/PTFE membranes show similar (voltage energy) VE suggesting the similar resistance of these two membranes which is consistent with the area resistance value in Table 1. This might be due to the good compatibility between PTFE and SPEEK, which retain high proton conductivity. As an indicator of energy loss during charge–discharge process, energy efficiency (EE) is the key parameter to evaluate an energy storage system. In this system, SPEEK/PTFE membrane shows higher EE than pure SPEEK membranes indicating better performance.

Compared with the commercial Nafion 115 membrane ($EE = 82 \pm 1\%$, $VE = 86.7 \pm 1\%$), the SPEEK/PTFE composite membranes show higher EE and VE ($EE = 83.7 \pm 1\%$, $VE = 89.6 \pm 1\%$).

Self-discharge test method was carried out to investigate the transferring of the vanadium ions across the membranes. As presented in Fig. 6, the OCV (open circuit voltage) of the VRB cell with SPEEK/PTFE and SPEEK membranes retains above 1.30 V for about 27 h and 14 h respectively then gradually drops, afterwards,

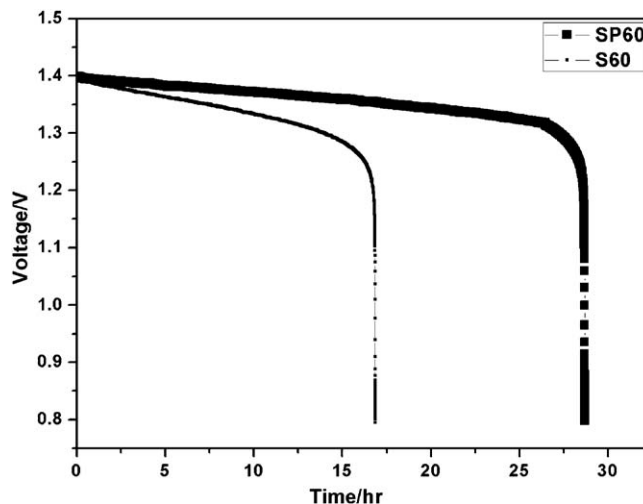


Fig. 6. Self-discharge test of SPEEK/PTFE and SPEEK membranes.

suddenly drops to 0.8 V due to the exhaustion of VO^{2+} in anode electrolyte [35]. The PTFE reinforced membranes maintain much longer time than the cell assembled with pristine SPEEK. The much slower OCV decay rate of the cell with SPEEK/PTFE membranes clearly indicates that the swelling suppressing effect of PTFE can effectively reduce the permeation of vanadium ions.

3.4. Stability test

To investigate the stability of membranes, lifetime tests were carried out via VRB single cell assembled with pristine SPEEK and SPEEK/PTFE composite membranes. Fig. 7 shows that the CE of the battery assembled with SPEEK/PTFE composite membranes is almost unchanged after running for more than 700 cycles, while the CE of the battery assembled with pristine SPEEK membrane suddenly decreased after running only about 27 cycles. The large difference in stability might be due to two reasons. Firstly, the reinforce effect of PTFE suppresses the swelling of membrane in vanadium solution and decreases the water uptake, enhancing the mechanical stability of the composite membranes. Furthermore, as material of high chemical and mechanical stability, PTFE itself could withstand the erosion and oxidation caused by vanadium solution. Thus, The PTFE reinforcement can greatly improve the chemical

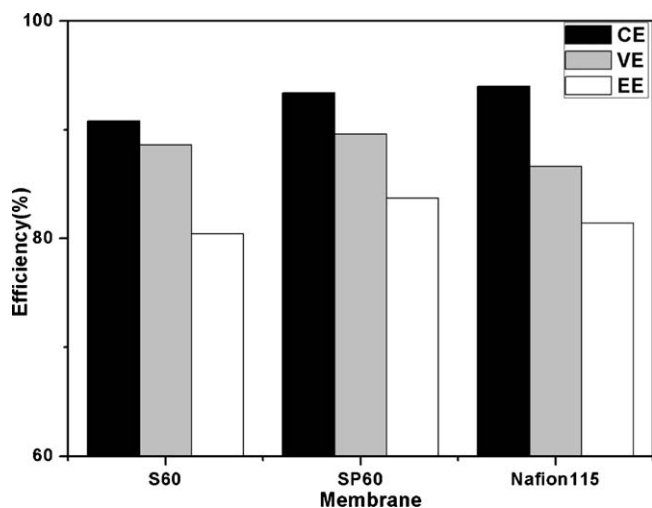


Fig. 5. VRB single cell performance of SPEEK, SPEEK/PTFE and Nafion 115 membranes.

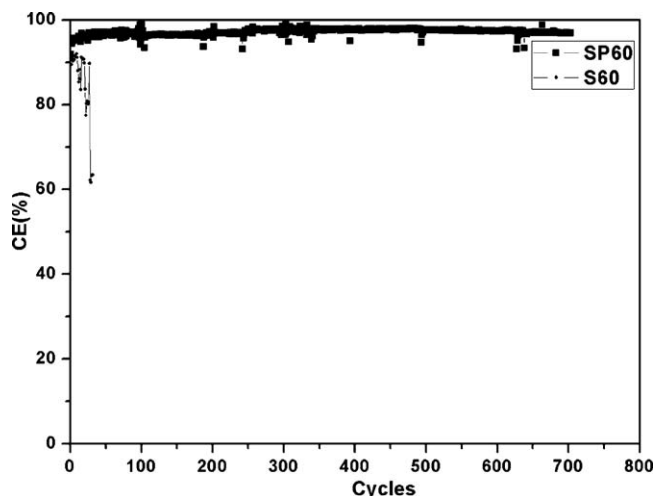


Fig. 7. Stability test of SPEEK/PTFE and SPEEK membranes.

stability of SPEEK membranes; further increase their life in VRB applications.

4. Conclusions

PTFE reinforced SPEEK composite membranes were fabricated to improve their chemical stability and ion selectivity in VRB applications. Compared to pristine SPEEK membranes, the composite membranes have the lower swelling ratio and higher mechanical stability due to the PTFE reinforcement. As expected, the SPEEK/PTFE membranes show much higher CE and EE than that for SPEEK membranes. In addition, the composite membranes exhibited much better stability than pristine SPEEK under VRB operating conditions. This paper provides a universal and effective way to prolong the life time of sulfonated aromatic polymer ion exchange membranes for VRB application.

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References

- [1] M. Sklaskazacos, R.G. Robins, All-Vanadium Redox Battery, US Pat. 4,786,567 (1986).
- [2] M. Sklaskazacos, F. Grossmith, *Journal of the Electrochemical Society* 134 (1987) 2950–2953.
- [3] C. Fabjan, J. Garcke, B. Harrer, L. Jorissen, C. Kolbeck, F. Philipp, G. Tomazic, F. Wagner, *Electrochimica Acta* 47 (2001) 825–831.
- [4] K.L. Huang, X.G. Li, S.Q. Liu, N. Tan, L.Q. Chen, *Renewable Energy* 33 (2008) 186–192.
- [5] C. Ponce de León, A. Frías-Ferrer, J. González-García, D.A. Szánto, F.C. Walsh, *Journal of Power Sources* 160 (2006) 716–732.
- [6] P. Zhao, H.M. Zhang, H.T. Zhou, J. Chen, S.J. Gao, B.L. Yi, *Journal of Power Sources* 162 (2006) 1416–1420.
- [7] Q.T. Luo, H.M. Zhang, J. Chen, P. Qian, Y.F. Zhai, *Journal of Membrane Science* 311 (2008) 98–103.
- [8] X.G. Teng, Y.T. Zhao, J.Y. Xi, Z.H. Wu, X.P. Qiu, L.Q. Chen, *Journal of Power Sources* 189 (2009) 1240–1246.
- [9] J. Zeng, C.P. Jiang, Y.H. Wang, J.W. Chen, S.F. Zhu, B.J. Zhao, R.L. Wang, *Electrochemistry Communications* 10 (2008) 372–375.
- [10] J.G. Xi, Z.G. Wu, X.G. Teng, Y.T. Zhao, L.Q. Chen, X.P. Qiu, *Journal of Materials Chemistry* 18 (2008) 1232.
- [11] T. Mohammadi, M. Sklaskazacos, *Journal of Membrane Science* 98 (1995) 77–87.
- [12] T. Mohammadi, M. Sklaskazacos, *Journal of Power Sources* 56 (1995) 91–96.
- [13] D.B. Xing, S.H. Zhang, C.X. Yin, B.G. Zhang, X.G. Jian, *Journal of Membrane Science* 354 (2010) 68–73.
- [14] X.F. Li, H.M. Zhang, Z.S. Mai, H.Z. Zhang, I. Vankelecom, *Energy and Environmental Science* 4 (2011) 1147.
- [15] Z.S. Mai, H.M. Zhang, X.F. Li, C. Bi, H. Dai, *Journal of Power Sources* 196 (2011) 482–487.
- [16] B.C. Johnson, I. Yilgör, C. Tran, M. Iqbal, J.P. Wightman, D.R. Lloyd, J.E. McGrath, *Journal of Polymer Science: Polymer Chemistry Edition* 22 (1984) 721–737.
- [17] R. Nolte, K. Ledjef, M. Bauer, R. Mülhaupt, *Journal of Membrane Science* 83 (1993) 211–220.
- [18] L. Leung, C. Bailly, J.F. Ogara, D.J. Williams, F.E. Karasz, W.J. Macknight, *Polymer Communications* 28 (1987) 20–21.
- [19] F. Helmer-Metzmann, F. Osan, *Polymer Electrolyte Membrane, and Process for the Production Thereof*, US Pat. 5,438,082 (1993).
- [20] S.M.J. Zaidi, S.D. Mikhailenko, G.P. Robertson, M.D. Guiver, S. Kaliaguine, *Journal of Membrane Science* 173 (2000) 17–34.
- [21] Y.S. Kim, F. Wang, M. Hickner, S. McCartney, Y.T. Hong, W. Harrison, T.A. Zawodzinski, J.E. McGrath, *Journal of Polymer Science Part B: Polymer Physics* 41 (2003) 2816–2828.
- [22] Y.S. Kim, B. Einsla, M. Sankir, W. Harrison, B.S. Pivovar, *Polymer* 47 (2006) 4026–4035.
- [23] C. Bi, H.M. Zhang, Y. Zhang, S.H. Xiao, *Journal of Power Sources* 194 (2009) 838–842.
- [24] J.A. Kerres, *Journal of Membrane Science* 185 (2001) 3–27.
- [25] C. Karthikeyan, S. Nunes, L. Prado, M. Ponce, H. Silva, B. Ruffmann, K. Schulte, *Journal of Membrane Science* 254 (2005) 139–146.
- [26] X.B. Zhu, H.M. Zhang, Y.M. Liang, Y. Zhang, Q.T. Luo, C. Bi, B.L. Yi, *Journal of Materials Chemistry* 17 (2007) 386.
- [27] J. Shin, B. Chang, J. Kim, S. Lee, D. Suh, *Journal of Membrane Science* 251 (2005) 247–254.
- [28] H.L. Lin, T.L. Yu, W.K. Chang, C.P. Cheng, C.R. Hu, G.B. Jung, *Journal of Power Sources* 164 (2007) 481–487.
- [29] P.X. Xing, G.P. Robertson, M.D. Guiver, S.D. Mikhailenko, K. Wang, S. Kaliaguine, *Journal of Membrane Science* 229 (2004) 95–106.
- [30] G.J. Hwang, H. Ohya, *Journal of Membrane Science* 120 (1996) 55–67.
- [31] S.G. Feng, Y.M. Shang, Y.W. Wang, G.S. Liu, X.F. Xie, W.Q. Dong, J.M. Xu, V.K. Mathur, *Journal of Membrane Science* 352 (2010) 14–21.
- [32] K. Jochen A, *Journal of Membrane Science* 185 (2001) 3–27.
- [33] T. Nguyen, X. Wang, *Journal of Power Sources* 195 (2010) 1024–1030.
- [34] T. Yamaguchi, F. Miyata, S. Nakao, *Journal of Membrane Science* 214 (2003) 283–292.
- [35] C.X. Sun, J. Chen, H.M. Zhang, X. Han, Q.T. Luo, *Journal of Power Sources* 195 (2010) 890–897.