

Development of Pore-filled Ion-exchange Membranes for Efficient All Vanadium Redox Flow Batteries

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Abstract : Thin pore-filled cation and anion-exchange membranes (PFCEM and PFAEMs, $t_m = 25\text{--}30\text{ }\mu\text{m}$) were prepared using a porous polymeric substrate for efficient all-vanadium redox flow battery (VRB). The electrochemical and charge-discharge performances of the membranes have been systematically investigated and compared with those of commercially available ion-exchange membranes. The pore-filled membranes were shown to have higher permselectivity as well as lower electrical resistances than those of the commercial membranes. In addition, the VRBs employing the pore-filled membranes exhibited the respectable charge-discharge performances, showing the energy efficiencies (EE) of 82.4% and 84.9% for the PFCEM and PFAEM, respectively (*cf.* $EE = 87.2\%$ for Nafion 1135). The results demonstrated that the pore-filled ion-exchange membranes could be successfully used in VRBs as an efficient separator by replacing expensive Nafion membrane.

Keywords : Pore-filled, Cation and anion-exchange membranes, All-vanadium redox flow battery, Charge-discharge performances

1. Introduction

Recently, large-scale energy storage systems have been attracting great attention because they are one of the essential components of the smart grid for a stable electricity supply. Especially, redox flow battery (RFB) is known as one of very promising large-scale energy storage batteries.¹⁻³⁾ The main feature of this system is the use of active electrode materials dissolved in a solution, and therefore it can offer several advantages such as very fast electrode reaction, unlimited system design for high power and capacity, instant and fast recharging by replacing the spent electrolytes and so on.¹⁻³⁾ There are a variety of redox couples which can be used in flow batteries, and, for example, all-vanadium redox flow battery (VRB), which is the most widely used, is a type of rechargeable flow battery that employs vanadium ions in different oxidation states as the active electrode materials.¹⁻⁵⁾ Since a membrane is one of

the most important components dominating the charge-discharge performances in a RFB system, the development of highly efficient membranes is very essential for successful application of RFBs.^{2,4)} In a RFB system, both cation- and anion-exchange membranes can be used for the separation between anolyte and catholyte. Especially, cation-exchange membranes with high proton permeability such as Nafion have been most widely utilized in VRB systems.⁶⁾ Meanwhile, since the cation-exchange membranes intrinsically cannot prevent the crossover of cationic redox species through the membrane and the use of highly expensive membranes such as Nafion causes the increase in the system cost.^{4,7)} Recently, therefore, anion-exchange membranes are being investigated and developed for RFB applications due to their cost-effectiveness and relatively low crossover of active electrode materials.^{4,8-13)} As suggested by Vijayakumar *et al.*, moreover, the irreversible membrane fouling degrading the ion-exchange capacity is possibly originated from the charge interaction between positively charged redox materials and negatively charged sulfonic acid groups in cation-

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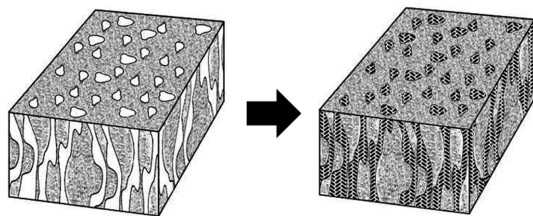


Fig. 1. The concept of pore-filled membranes.

exchange membranes.¹⁴⁾ In this respect, the use of anion-exchange membranes with positively charged groups seems to be more advantageous for long-term operation.

Among various types of ion-exchange membranes, a pore-filled membrane (PFM) is known to possess extraordinary properties such as high dimensional and chemical stabilities.^{15,16)} The PFMs composed of a chemically inert and mechanically tough porous substrate and a polymer with ion-exchange groups (*i.e.* ionomers) that fills the pores can provide both high ion conductivity and excellent mechanical properties. The concept of the PFM is shown in Fig. 1. In addition, undesirable excessive swelling of the membrane can be effectively prevented by the mechanically strong porous substrate. Recently, there have been several attempts with the pore-filled membrane in RFBs.¹⁷⁻²¹⁾

In this paper, we reported the development of pore-filled cation and anion-exchange membranes (PFCEMs and PFAEMs, respectively) with a thickness of about 25-30 μm for efficient VRB applications. In addition, their electrochemical properties and charge-discharge efficiencies were compared with those of the commercial membranes.

2. Experimental

2.1. Materials and membrane preparation

A commercial battery separator film (Hipore, $t_m = 25 \mu\text{m}$, Asahi Kasei E-materials Corp., Japan) having excellent mechanical properties (*i.e.* tensile strength = 152 MPa and elongation ratio at break = 68.2%) was employed as the substrate for preparing thin ion-exchange membranes. The physical characteristics of the porous substrate are summarized in Table 1. Styrene (Sty), vinylbenzyl chloride

Table 1. Characteristics of commercial porous substrate

Material	Thickness (μm)	Porosity, ε (%)	Tortuosity, τ (-)	Pore size ^{a)} (μm)
Polyethylene	25	48.5	4.74	ranged from 0.05 to 1

^{a)} estimated from the FE-SEM image ²²⁾

(VBC), and divinylbenzene (DVB) were employed as the base monomers and benzoyl peroxide (BPO) was utilized for an initiator. Monomer mixtures were prepared with Sty, VBC, DVB, and BPO and the mole ratios (Sty to VBC) were 1:0.8 and 1:0 for the PFAEM and PFCEM, respectively. A weight fraction of Sty and VBC mixture was 95% while that of DVB was 5%. In those mixtures, additional 2 wt.% of BPO based on the weight sum of monomers was further added as an initiator. All the chemicals were purchased from Aldrich (USA) and used as received without further purification. The porous substrate was immersed in monomer mixture for an hour, followed by a radical polymerization process conducted in a thermal oven at 80°C for 3 hr. The porous film filled with poly(Sty-DVB) polymer was treated in a strong acid solution (chlorosulfuric acid : sulfuric acid = 1:1 wt. ratio) at 30°C for 10 h to prepare the PFCEM. An amination process was also conducted by soaking the film filled with poly(Sty-VBC-DVB) copolymer in a 0.5 M trimethylamine (TMA) aqueous solution at 40°C for 5 h. Finally, the membranes were washed with deionized water and kept in a 0.5 M NaCl solution.

2.2. Membrane characterizations

Fourier transform infrared (FT-IR) spectrometry analysis was performed with a BIO-RAD FTS 3000 FT-IR spectrometer, equipped with a GRASEBY SPECAC diamond-attenuated total reflectance, and averaged 16 scans at 4 cm^{-1} of resolution. The water uptake (WU, %) of the membranes were measured by comparing the wet and dry weights and the ion-exchange capacity (IEC, meq./g dry membrane) was determined by a conventional titration method described elsewhere.²³⁾ The membrane conductivities were measured using lap-made 4-point probe cell connected to an impedance analyzer. A membrane electrical resistance (MER) was measured using the electrical impedance spectroscopy with a clip cell. The magnitude of impedance ($|Z|$)

and the phase angle of impedance (θ) of a membrane were measured and converted into MER ($\Omega \cdot \text{cm}^2$) value using the following equation:^{24,25)}

$$MER = (|Z|_{\text{sample}} \cdot \cos \theta_{\text{sample}} - |Z|_{\text{blank}} \cdot \cos \theta_{\text{blank}}) \times \text{area} \quad (1)$$

The apparent transport number of anion through the membranes was also determined by the conventional *emf* method using a two-compartment cell (each volume = 0.23 L) and a pair of Ag/AgCl electrodes.²⁴⁾ The current-voltage (*I-V*) curves for the membranes were obtained using the two-compartment cell equipped with a pair of Ag/AgCl reference electrodes and the voltage was swept from 0 to 5 V at a scan rate of 10 mV s⁻¹ during the measurement.²⁴⁾

2.3. RFB performance evaluation tests

As the redox active materials, 2 M V₂(OSO₄)₃ in 3 M H₂SO₄ (anolyte) and 2 M VOSO₄ in 3 M H₂SO₄ (catholyte) were employed to evaluate the charge-discharge characteristics of membranes. The galvanostatic charge-discharge tests using different membranes were performed using a battery cyler (WBCS3000S, Wonatech, Korea) in the potential range of 0.9-1.9 V at a current of 250 mA with a lab-made non-flowing cell (membrane effective area = 12.5 cm²) including a pair of carbon felt electrodes (GF20-3, Nippon Graphite, Japan).

3. Results and Discussion

The pictures of porous substrate and prepared pore-filled ion-exchange membrane (Fig. 2) revealed that an opaque porous substrate was changed into a transparent film after the pore-filling and successive polymerization of monomers. The FE-SEM images also clearly demonstrate that pores in the substrates are completely filled with polymers and there are no visible open pores in the membranes (data not shown).²²⁾

The structures of the quaternized poly(Sty-DVB-VBC) and sulfonated poly(Sty-DVB) are illustrated in Fig. 2. The syntheses of the ion-exchange polymers were confirmed from the FT-IR/ATR spectra shown in Fig. 3. The absorption bands assigned to the aromatic group were observed at 1600 and 1475 cm⁻¹, indicating that styrene and DVB were introduced to the membranes. In

the sulfonated membrane, the absorption bands assigned to sulfonic acid groups were observed at 1123 and 1002 cm⁻¹, and the spectra for S=O stretching vibration was also shown at 1370 and 1163 cm⁻¹. In the aminated membrane, the peaks assigned to quaternary ammonium group were observed at 980, 893, and 812 cm⁻¹.

The *I-V* characteristics of the commercial mem-

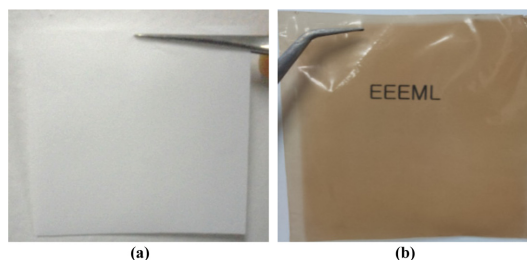


Fig. 2. Pictures of (a) porous substrate and (b) prepared pore-filled ion-exchange membrane (right).

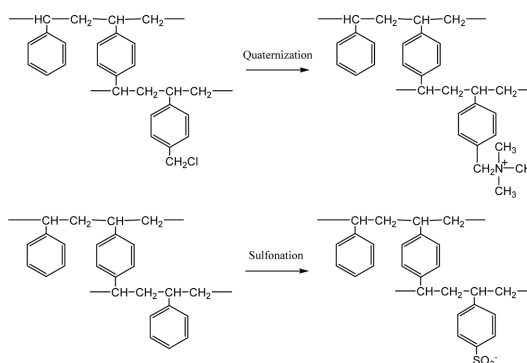


Fig. 3. Molecular structures of quaternized poly(Sty-DVB-VBC) and sulfonated poly(Sty-DVB).

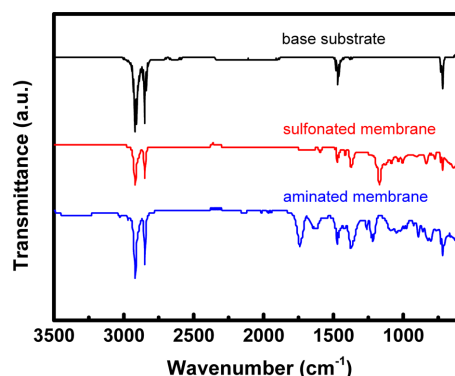


Fig. 4. FT-IR spectra of porous substrate and pore-filled ion-exchange membranes.

brane and prepared membranes are shown in Fig. 5. The typical three characteristic regions (*i.e.* the first region of approximately ohmic behavior, the second region showing a plateau, and the third region of a rapid current increase governed by electroconvec-

tion) were observed in all the curves, proving that the membranes function as an ion-selective barrier.^{26,27)} Moreover, the pore-filled membranes exhibited excellent *I-V* properties comparable with those of the commercial membranes.

The physical and electrochemical properties of the membranes are summarized in Table 2. The PFCEM and PFAEM showed higher levels of the WU and IEC compared with those of the commercial membranes. In addition, the electrical resistances of the pore-filled membranes were significantly lower than those of the commercial membranes mainly due to the reduced membrane thickness. The pore-filled membranes also exhibited high conductivities comparable with those of the commercial membranes. The transport numbers for counter ions of the pore-filled membranes were shown to be somewhat higher than those of the commercial membranes. In summary, the prepared pore-filled membranes (both the PFCEM and PFAEM) exhibited excellent electrochemical properties for an efficient ion-exchange membrane.

The RFB experiments were conducted to investigate the effect of the membranes on the charge-discharge characteristics. Fig. 6 shows the charge-discharge curves of VRBs utilizing different cation and anion-exchange membranes, showing that the charge-discharge performances were largely dependent upon the membrane properties. The efficiencies in the charge-discharge tests are listed in Table 3. Nafion

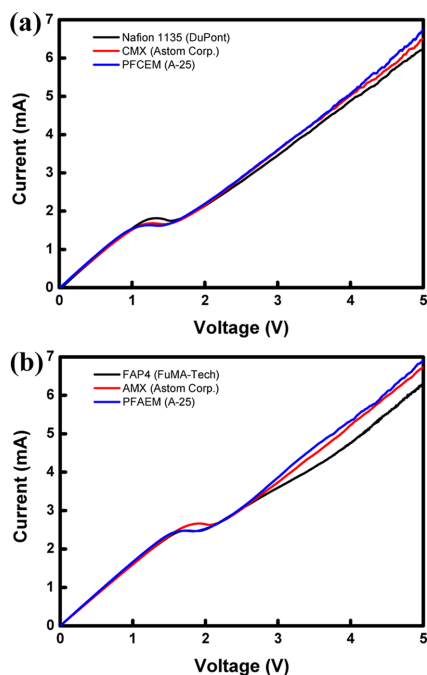


Fig. 5. *I-V* curves of (a) cation-exchange membranes and (b) anion-exchange membranes (measured in a 0.05 M NaCl solution).

Table 2. Physical and electrochemical characteristics of membranes

Membranes	WU ^{a)} (%)	IEC ^{b)} (meq./g)	Membrane thickness (μm)	Conductivity ^{c)} (mS/cm)	Electrical resistance ^{d)} ($\Omega\text{ cm}^2$)	Transport No. ^{e)} (-)
Nafion 1135 (DuPont)	19.5	0.91	95	9.31	1.02	0.962
CMX (Astom Corp.)	26.2	1.60	165	5.87	2.81	0.966
PFCEM	34.3	2.35	30	5.51	0.55	0.981
FAP4 (FuMA-Tech)	16.2	0.76	55	2.27	2.42	0.932
AMX (Astom Corp.)	21.1	1.40	135	3.40	3.97	0.970
PFAEM	55.7	1.79	25	5.19	0.48	0.975

^{a)} Water uptake (WU)

^{b)} Ion-exchange capacity (IEC)

^{c)} Membrane conductivity obtained by 2-point probe impedance measurement (in a 0.5 M NaCl aq. solution)

^{d)} Membrane area resistance measured using a clip cell connected to an impedance analyzer (in a 0.5 M NaCl aq. solution)

^{e)} Transport number for anion (Cl^-) measured by *emf* method (in a 0.5 M NaCl aq. solution)

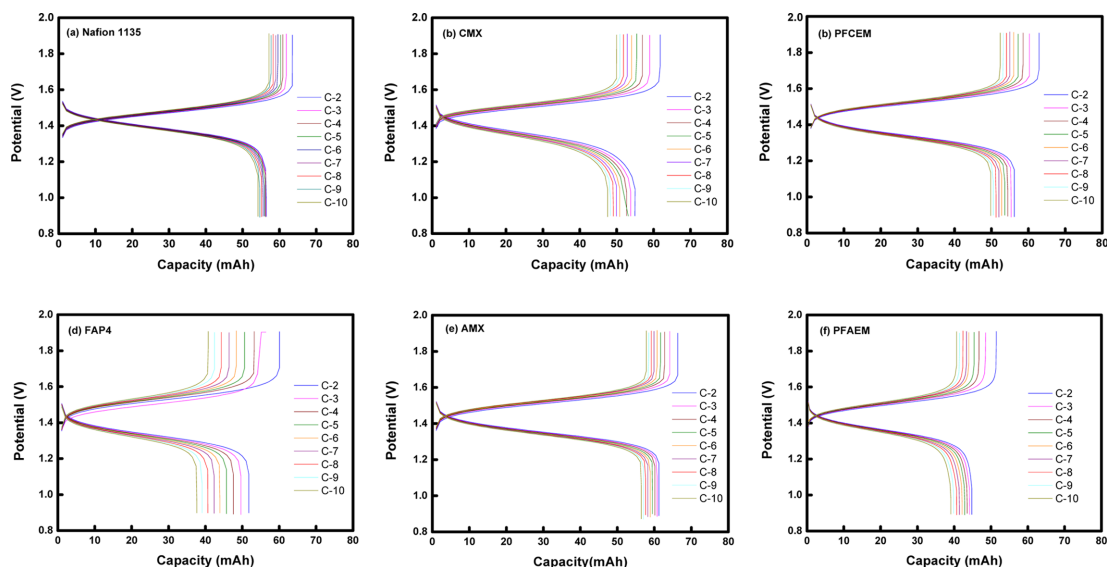


Fig. 6. Charge-discharge curves of VRBs utilizing different cation and anion-exchange membranes (current density = 20 mA cm^{-2}).

Table 3. Charge-discharge efficiencies of VRBs utilizing different cation- and anion-exchange membranes (calculated from the results of Fig. 6, based on the 10th cycle)

Membranes	Coulombic efficiency (CE) (%)	Voltage efficiency (VE) (%)	Energy efficiency (EE) (%)
Nafion 1135 (DuPont)	94.8	92.0	87.2
CMX (Astom Corp.)	95.2	86.7	82.5
PFCEM	95.1	86.7	82.4
FAP4 (FuMA-Tech)	92.4	86.0	79.5
AMX (Astom Corp.)	97.6	87.5	85.4
PFAEM	96.3	88.1	84.9

membrane exhibited the highest value of the energy efficiency among the tested membranes due to its extraordinary proton conductivity. Among the cation-exchange membranes, the PFCEM also showed high energy efficiency comparable with that of CMX membrane. In the case of anion-exchange membranes, the PFAEM and AMX exhibited the similar energy efficiencies with each other and the charge-discharge efficiencies were shown to be superior to those of the cation-exchange membranes except for Nafion. The

relatively low crossover of cationic redox materials in the anion-exchange membranes seems to enhance the coulombic efficiencies and contribute to the increase in the energy efficiencies. However, FAP4 with relatively low permselectivity (as transport number for counter ions) compared with those of the PFAEM and AMX (as shown in Table 2) resulted in the most degraded charge-discharge performance among the membranes. As shown in Fig. 6 and Table 3, the RFB equipped with FAP4 exhibited the lowest coulombic efficiency and the most significant capacity loss by increasing the cycle number possibly due to the significant crossover of redox materials through the membrane. In summary, the use of the pore-filled ion-exchange membranes resulted in excellent VRB performances. Especially, the performances of the PFAEM ($EE = 84.9\%$) were shown to be superior to those of the PFCEM ($EE = 82.4\%$) and comparable with those of Nafion membrane ($EE = 87.2\%$). More detailed studies on the crossover and fouling phenomena of the cation and anion-exchange membranes occurred during the long-term operation are still in progress.

4. Conclusions

In this work, thin pore-filled ion-exchange membranes ($t_m = 25\text{--}30 \mu\text{m}$) with notably low electrical

resistance and excellent permselectivity were successfully prepared using a commercial battery separator film as the substrates. The prepared membranes were shown to have excellent physical and electrochemical properties for an efficient ion-exchange membrane. Especially, both the PFCM and PFAEM showed the significantly low electrical resistances and high permselectivity compared to those of the commercial membranes. In addition, the results of VRB tests revealed that the use of the pore-filled ion-exchange membranes promises the high charge-discharge performances. Especially, the performances of the PFAEM ($EE = 85\%$) were almost comparable to those of Nafion membrane ($EE = 87\%$).

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References

1. M. Skyllas-Kazacos and F. Grossmith, 'Efficient vanadium redox flow cell' *J. Electrochem. Soc.*, **134**, 2950 (1987).
2. G. J. Hwang and H. Ohya, 'Preparation of cation exchange membrane as a separator for the all-vanadium redox flow battery' *J. Membr. Sci.*, **120**, 55 (1996).
3. W. Wang, Q. Luo, B. Li, X. Wei, L. Li, and Z. Yang, 'Recent progress in redox flow battery research and development' *Adv. Funct. Mater.*, **23**, 970 (2013).
4. G. J. Hwang and H. Ohya, 'Crosslinking of anion exchange membrane by accelerated electron radiation as a separator for the all-vanadium redox flow battery' *J. Membr. Sci.*, **132**, 55 (1997).
5. Z. Yang, J. Zhang, M. C. W. Kintner-Meyer, X. Lu, D. Choi, J. P. Lemmon, and J. Liu, 'Electrochemical energy storage for green grid' *Chemical reviews*, **111**, 3021 (2011).
6. M. Vijayakumar, B. Schwenzer, S. Kim, Z. Yang, S. Thevuthasan, J. Liu, G. L. Graff, and J. Hu, 'Investigation of local environments in Nafion-SiO₂ composite membranes used in vanadium redox flow batteries' *Solid State Nuclear Magnetic Resonance*, **42**, 71 (2012).
7. C. Sun, J. Chen, H. Zhang, X. Han, and Q. Luo, 'Investigations on transfer of water and vanadium ions across Nafion membrane in an operating vanadium redox flow battery' *J. Power Sources*, **195**, 890 (2010).
8. Y. Lorrain, G. Pourcelly, and C. Gavach, 'Influence of cations on the proton leakage through anion-exchange membranes' *J. Membr. Sci.*, **110**, 181 (1996).
9. T. Mohammadi and M. Skyllas-Kazacos, 'Use of polyelectrolyte for incorporation of ion-exchange groups in composite membranes for vanadium redox flow battery applications' *J. Power Sources*, **56**, 91 (1995).
10. T. Mohammadi, S. C. Chieng, and M. Skyllas Kazacos, 'Water transport study across commercial ion exchange membranes in the vanadium redox flow battery' *J. Membr. Sci.*, **133**, 151 (1997).
11. J. Qiu, M. Li, J. Ni, M. Zhai, J. Peng, L. Xu, H. Zhou, J. Li, and G. Wei, 'Preparation of ETFE-based anion exchange membrane to reduce permeability of vanadium ions in vanadium redox battery' *J. Membr. Sci.*, **297**, 174 (2007).
12. T. Sukkar and M. Skyllas-Kazacos, 'Modification of membranes using polyelectrolytes to improve water transfer properties in the vanadium redox battery' *J. Membr. Sci.*, **222**, 249 (2003).
13. D. Xing, S. Zhang, C. Yin, B. Zhang, and X. Jian, 'Effect of amination agent on the properties of quaternized poly(phthalazinone ether sulfone) anion exchange membrane for vanadium redox flow battery application' *J. Membr. Sci.*, **354**, 68 (2010).
14. M. Vijayakumar, M. S. Bhuvaneswari, P. Nachimuthu, B. Schwenzer, S. Kim, Z. Yang, J. Liu, G. L. Graff, S. Thevuthasan, and J. Hu, 'Spectroscopic investigations of the fouling process on Nafion membranes in vanadium redox flow batteries' *J. Membr. Sci.*, **366**, 325 (2011).
15. T. Yamaguchi, S. Nakao, and S. Kimura, 'Plasma-graft filling polymerization: preparation of a new type of pervaporation membrane for organic liquid mixtures' *Macromolecules*, **24**, 5522 (1991).
16. T. Yamaguchi, F. Miyata, and S. Nakao, 'Pore-filling type polymer electrolyte membranes for a direct methanol fuel cell' *J. Membr. Sci.*, **214**, 283 (2003).
17. S.-J. Seo, B.-C. Kim, K.-W. Sung, J. Shim, J.-D. Jeon, K.-H. Shin, S.-H. Shin, S.-H. Yun, J.-Y. Lee, and S.-H. Moon, 'Electrochemical properties of pore-filled anion exchange membranes and their ionic transport phenomena for vanadium redox flow battery applications' *J. Membr. Sci.*, **428**, 17 (2013).
18. W. Wei, H. Zhang, X. Li, Z. Mai, and H. Zhang, 'Poly(tetrafluoroethylene) reinforced sulfonated poly(ether ether ketone) membranes for vanadium redox flow battery application' *J. Power Sources*, **208**, 421 (2012).
19. X. Li, H. Zhang, Z. Mai, H. Zhang, and I. Vankelecom, 'Ion exchange membranes for vanadium redox flow battery (VRB) applications' *Energy Environ. Sci.*, **4**, 1147 (2011).
20. T. Sukkar and M. Skyllas-Kazacos, 'Modification of membranes using polyelectrolytes to improve water transfer properties in the vanadium redox battery' *J. Membr. Sci.*, **222**, 249 (2003).
21. T. Mohammadi and M. Skyllas-Kazacos, 'Modification of anion-exchange membranes for vanadium redox flow battery applications' *J. Power Sources*, **63**, 179 (1996).
22. D.-H. Kim, S.-J. Seo, M.-J. Lee, J.-S. Park, S.-H. Moon,

- Y. S. Kang, Y.-W. Choi, and M.-S. Kang, 'Pore-filled anion-exchange membranes for non-aqueous redox flow batteries with dual-metal-complex redox shuttles' *J. Membr. Sci.*, in revision (2014).
23. J. Ran, L. Wu, J. R. Varcoe, A. L. Ong, and S. D. Poynton, T. Xu, 'Development of imidazolium-type alkaline anion exchange membranes for fuel cell application' *J. Membr. Sci.*, **415-416**, 242 (2012).
24. M.-S. Kang, Y.-J. Choi, and S.-H. Moon, 'Water-swollen cation-exchange membranes prepared using poly(vinyl alcohol) (PVA)/poly(styrene sulfonic acid-co-maleic acid) (PSSA-MA)' *J. Membr. Sci.*, **207**, 157 (2002).
25. Y. Tanaka, Ion Exchange Membranes: Fundamentals and Application, Elsevier, Amsterdam, 2007.
26. M. Mulder, Basic Principles of Membrane Technology, Kluwer Academic, Dordrecht, 1996.
27. J. J. Krol, M. Wessling, and H. Strathmann, 'Concentration polarization with monopolar ion exchange membranes: current-voltage curves and water dissociation' *J. Membr. Sci.*, **162**, 145 (1999).