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Modification and evaluation of membranes for vanadium redox battery applications

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Abstract

Several commercial ion exchange membranes were evaluated for application in the vanadium redox battery. The polyether membrane, DF120 cationic exchange membrane, showed the highest permeability to vanadium ions and the worst chemical stability in V(V) solution, while the divinylbenzene membrane, JAM anionic exchange membrane, showed the lowest permeability to vanadium ions and the best chemical stability in V(V) solution. In order to impart some cationic exchange capacity to the JAM anionic exchange membrane, sodium 4-styrenesulfonate was used to modify the anionic membrane by *in situ* polymerization. Measurements by infrared spectroscopy (IR) and cationic ion exchange capacity (IEC) verified that the modification procedure imparts cationic exchange capability to the membrane. Incorporation of cationic exchange groups to the anionic exchange membrane further results in a reduction in permeability to vanadium ions. The current and energy efficiencies averaged over 8 charge/discharge cycles of the cell with the treated JAM membrane were higher than that with the untreated JAM membrane. The current and energy efficiencies of the cell with the treated JAM membrane did not change over several charge/discharge cycles, which indicates good chemical stability of the treated membrane in the vanadium redox cell. The average efficiencies of the cell with the treated JAM membrane are higher than that with Nafion 117 over 8 charge/discharge cycles.

1. Introduction

The vanadium redox battery (VRB) is a new kind of electrochemical energy storage battery. It employs V(II)/V(III) and V(IV)/V(V) redox couples in the negative and positive half-cell electrolytes which are separated by a membrane [1]. The function of the membrane is not only to separate the electrolytes, but also to provide a conduction path between the two electrolytes. The logical choice of a membrane is therefore an ion exchange membrane, which may act simultaneously as an ionic conductor and a physical separator between the two electrolytes [2]. The ideal separator for the VRB should exhibit low permeation rates for vanadium active species to minimize self-discharge and to gain high current efficiency. It should also have a low area resistivity to minimize loss in voltage efficiency. Finally, the membrane should exhibit good chemical stability [3].

It was reported that the direct introduction of cationic exchange groups into the porous structure of the anionic separator should lead to the production of a cationic selective membrane having good performance [1]. A sulfonation treatment with concentrated sulfuric acid was applied to incorporate strong cationic exchange groups into the anionic membrane. However, this method led to deformation and severe deterioration of membrane substrate [4]. Mohammadi and Skyllas-Kazacos [1] used cationic poly-electrolyte, poly(sodium 4-styrenesulfonate) (PSSS) solution to soak New Selemion (type 2) and then neutralize anionic exchange groups at ambient temperature so as to reduce the anionic ion exchange capacity of the anionic membrane. But the reaction took a long time. In the present study, some types of commercial ion exchange membranes were evaluated for the vanadium redox battery. Anionic membrane, JAM-1-10 (JAM) was chosen as a base material for further modification due to its low permeability to vanadium ions and high chemical stability in the V(V) solution. JAM anionic exchange membrane was modified with sodium 4-styrenesulfonate (SSS) monomer by *in situ* polymerization. This method showed advantages of preventing the membrane substrate from deterioration during the process, and of shortening dramatically the reaction time of neutralization. SSS can polymerize in the membrane, and impart cationic selective capability to the anionic separator.

Table 1. Membrane characteristics

Ion exchange membrane	Ion-exchange capacity /mmol g^{-1} dry membrane	Area resistance /Ω cm^2	Manufacturer
DF120			Shandong Ocean Chemical Industry Scientific Research Institute (China)
Cationic DF120	$\geqslant 1.4$	$\leqslant 4.0$	
Anionic DF120	$\geqslant 1.6$	$\leqslant 4.0$	
JCM			Beijing Huanyu Lida Environment Protection Equipment Co., Ltd (China)
JCM-1-10	1.8–2.2	2–5	
JCM-1-15	1.8–2.2	3–6	
JAM			
JAM-1-10	1.6–2.0	3–6	
JAM-1-15	1.4–1.6	4–7	

2. Experimental

2.1. *Materials and reagents*

Three types of commercial homogenous ion exchange membranes, JAM, JCM with different cross-linking degree and DF120 were chosen for evaluation. The properties of these membranes are listed in Table 1. The 95.4% sodium 4-styrenesulfonate (China Zibo Xingzhilian Chemistry Co., Ltd) was used without further purification. Vanadyl sulfate was purchased from Shanghai Lvyuan Fine Chemicals Factory. The purity of the blue crystalline powder of the vanadium salt is 97.9%. Almost 0.32% is pentavalent vanadium and substances not precipitated by ammonia are 1.6%. All other chemicals used were analytical grade.

2.2. *Membrane preparation*

To incorporate strong cationic exchange groups (—SO_3^-, H^+) into the JAM anionic exchange membrane, a piece of JAM membrane was soaked for 24 h in a SSS solution with initiator at ambient temperature. The soaked membrane was then sealed between two glass plates, and heated at 60 °C for 6 h to obtain a JAM composite membrane. Following this, the composite membrane was soaked in distilled water and released from the glass plates.

2.3. *Membrane characterization*

The IEC and the area resistance of the membranes were evaluated by a method described previously [5].

The permeation of VO^{2+} ions across the membrane was determined as previously described [2, 5]. The equipment for the measurement of the permeation of VO^{2+} ions is shown in Figure l. One reservoir was filled with 2 mol l^{-1} H_2SO_4 solution and the other with a solution of VO^{2+} ions in 2 mol l^{-1} H_2SO_4 solution. Both solutions were 300 ml and circulated through the cell compartments which were separated by an ion exchange membrane with effective area of 6 cm^2 at ambient temperature. Samples of 25 ml were taken at regular intervals from the H_2SO_4 aqueous solution reservoir and analyzed to determine the vanadium ion content by the method of inductively coupled plasma emission spectrochemical analysis (ICP).

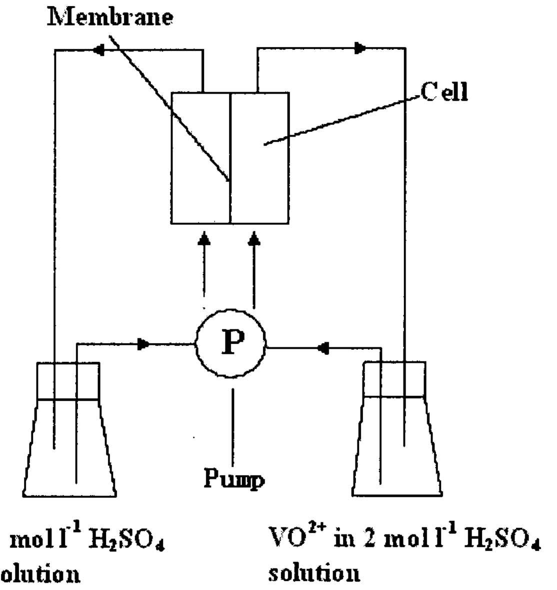

Fig. 1. Equipment used for measurement of vanadium ion permeability.

Membrane life was evaluated by the chemical degradation of the polymeric membrane material in VO_2^+ ion-containing solutions [6]. VO_2^+ solution was prepared according to [5]. A preweighed sample of each membrane was soaked in 50 ml of 0.1 mol l^{-1} $VO_2{}^+$ solution. Oxidation of the membrane by VO_2^+ ions leads to the formation of blue VO^{2+} species and the weight loss of membrane which can be used as indicators to evaluate the stability of a particular membrane. The concentration of VO_2^+ ions left in the solution was determined by potentiometric titration analysis [7]. A constant area membrane was used in each experiment. Each of the membranes was weighed after soaking in 0.1 mol l^{-1} VO_2^+ solution for 20 and 40 days.

The VRB used in the charge/discharge tests employed 1 mol l^{-1} solution of V(II)/V(III) and V(IV)/V(V) redox couples in 2 mol l^{-1} H_2SO_4 with a graphite plate and a dimensionally stable anode (DSA) as negative electrode and positive electrode, respectively. The membrane and electrode areas were all 15 cm^2. The positive and negative electrolytes were 35 and 45 ml, respectively. The cell was charged at 200 mA and discharged at 100 mA.

Morphological studies were undertaken with a XL-30FEG Philips scanning electron microscope (SEM). Samples were sputtered with a thin gold film before SEM observation. IR spectra were also obtained to verify whether cationic exchange groups were incorporated into the composite membrane after treatment by means of Magna-IR 560 Spectrometer (Nicolet) with the reflection technique.

3. Results and discussion

3.1. *Preparation of JAM composite membrane*

Figure 2 compares the IR spectra of the JAM anionic exchange membrane and the JAM composite membrane. The JAM composite membrane shows the particular bands of S=O within the 1250–1000 cm^{-1} region, indicating the introduction of sulfonic acid groups or cationic ion exchange capability into the JAM anionic exchange membrane. It also implies that SSS reacted with the anionic functional group of the JAM membrane and polymerized within the porous structure of the membrane

3.2. *Area resistance and IEC*

Table 2 shows the IEC and area resistance of the JAM composite membranes prepared with different concentration of SSS aqueous solutions. From Table 2, it is clear that cationic ion exchange capacity is introduced into the anionic exchange membrane after treatment, indicating that SSS permeates into the pores and reacts with anionic groups and polymerizes within the pores. The resulting polyelectrolyte material deposits in the membrane pores and may partially block the membrane pores, leading to a higher area resistance. For a SSS aqueous solution concentration of 2.0 g l^{-1}, the area resistance attains 11.9 Ω cm^2. The area resistance for the treated membrane is increased by 8.9 Ω cm^2 in comparison with that for the untreated membrane.

Table 2. Effect of the concentration of SSS on IEC and area resistance of the resulting composite membranes

Membrane	SSS concentration /g l^{-1}	Cationic IEC /mmol g^{-1}	Area resistance /Ω cm^2
JAM-1#	0	0	3.0
JAM-2#	0.5	1.79	3.2
JAM-3#	1.0	1.81	3.6
JAM-4#	2.0	1.78	11.9

3.3. *Permeation of vanadium ions*

Figures 3 and 4 shows the permeation of VO^{2+} ions through the membranes. The permeation of VO^{2+} ions through the DF120 cationic exchange membrane increased as the concentration of vanadium ions increased. It is clear that the concentration gradient of vanadium ions is one of the driving forces for the migration of vanadium ions through the membrane.

The permeation of 0.1 mol l^{-1} VO^{2+} ions in 2 mol l^{-1} H_2SO_4 solution through the two cationic and two anionic exchange membranes was determined at ambient temperature, as shown in Figure 4. The permeation of VO^{2+} ions through the membranes increases with time. The anionic membranes, JAM-1-10 and JAM -1-15, are also permeable to the vanadium ions, but with much lower permeability than the cationic membranes, which may be attributed to the Donnan exclusion effect [8]. It indicates that JAM-1-10 and JAM-1-15 will have a higher current efficiency in the VRB than the other

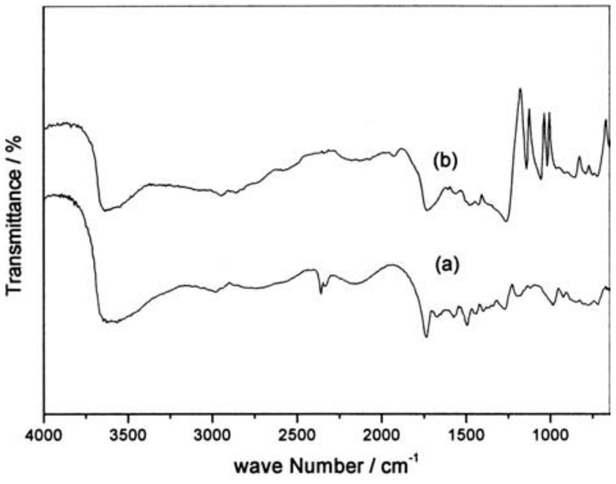

Fig. 2. IR spectra of the JAM anionic exchange membrane (a) and the JAM composite membrane (b).

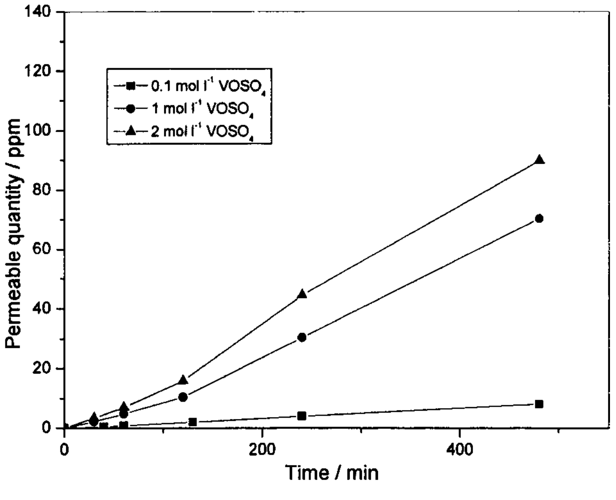

Fig. 3. Permeability of DF120 cationic exchange membrane for VO^{2+} ions in 2 mol l^{-1} H_2SO_4 solution.

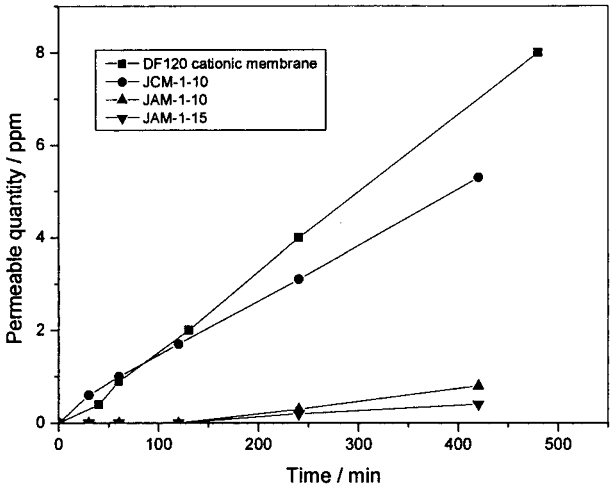

Fig. 4. Permeability of several ion exchange membranes for VO^{2+} ions in 2 mol l^{-1} H_2SO_4 solution.

membranes for their low permeation rates for vanadium ions. JAM-1-15 with higher crosslinking degree is less permeable than JAM-1-10, due to the smaller pore size of the high crosslinked membrane. DF120 cationic exchange membrane has the highest permeability.

The permeation of VO^{2+} ions through the modified membranes was measured. The two reservoirs of the measuring cell were respectively filled with 2 mol l^{-1} H_2SO_4 solution and 1 mol l^{-1} VO^{2+} solution in 2 mol l^{-1} H_2SO_4 of 100 ml, and circulated for 4 h. The results, as shown in Figure 5, show that the permeation of VO^{2+} ions through the composite membranes decreases rapidly with increasing concentration of SSS. The amount of VO^{2+} ions migrating through the untreated and the treated membranes modified with 2.0 g l^{-1} of SSS are 16 and 1 ppm, respectively. This may be ascribed to that the SSS polymerization occurring within the JAM anionic exchange membrane, causing the pores of the composite membrane to become partially blocked. However, a decrease in the permeability of the composite membrane is accompanied by an increase in the area resistance of the membrane. 0.5 and 1.0 g l^{-1} SSS can produce a cationic exchange composite membrane with acceptable permeability and area resistance.

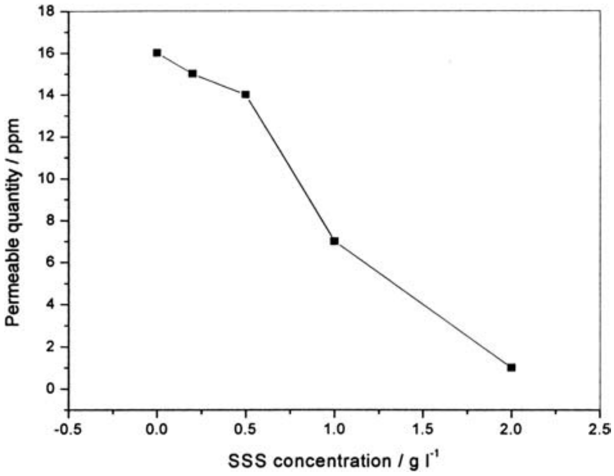

Fig. 5. Permeability of JAM composite membranes modified with different concentration of SSS for VO^{2+} ions in 2 mol l^{-1} H_2SO_4 solution.

3.4. *Membrane life*

A quantitative analysis for the formation of VO^{2+} species and the weight loss of the membranes is presented in Tables 3 and 4. As expected, weight loss is observed for some membranes after being exposed to the oxidizing VO_2^+ solution. The DF120 cationic membrane was soaked in 50 ml of the VO_2^+ solution for 20 days; all of the VO_2^+ ions in the solution were reduced to VO^{2+} ions and its weight loss was 0.4 g. JAM-1-10 and JAM-1-15 membranes showed zero weight loss after 20 days, in agreement with the very low conversion of VO_2^+ to VO^{2+} (10% and 0, respectively). It can also be seen that the anionic DF120 membrane exhibited less weight loss after immersion in the VO_2^+ solution for 40 days than for 20 days. It could be that hydrophilicity of the oxidized membrane increased and remarkable amounts of vanadium ions were absorbed in the membrane, which resulted in an increase in weight of the oxidized membrane [9].

Figure 6 gives the surface morphologies of the membranes before and after soaking in a solution of 1.0 mol l^{-1} VO_2^+ ions in 2 mol l^{-1} H_2SO_4 for 2 months. In general, the photographs show that soaking in the VO_2^+ solution led to a change in the surface morphology of the JCM cationic membrane. The thin layer on the surface of the original JCM membrane (Figure 6(a)) seems to be removed after soaking (Figure 6(b)). This implies that some sort of destruction of the membrane surface by VO_2^+ solution occurred. The destruction of the DF120 membrane is severer than that of the JCM membrane (Figure 6(c) and (d)). However, as seen in Figure 6(e) and (f), the surface of the JAM anionic membrane shows little change after soaking, indicating good stability of the membrane in the 1.0 mol l^{-1} VO_2^+ solution.

3.5. *Membrane performance in charge/discharge cycle test*

The JAM composite membrane prepared with 1.0 g l^{-1} SSS was chosen for charge and discharge cycle test. The efficiencies of the cell employing JAM composite membrane versus cycle number are shown in Figure 7. The untreated JAM membrane and Nafion 117 are tested in the same way for comparison. The current and energy efficiencies of the cell with the treated JAM membrane remained fairly constant with slight fluctuations during cycling. This indicates that the treated JAM membrane is chemically stable in the cell. The current and energy efficiencies averaged over 8 cycles with the treated JAM membrane were higher than for the cell with the untreated JAM membrane, as shown in Figure 8. The vanadium cell used in this test showed very low current

Table 3. Chemical stability evaluation of some membranes after soaking in 0.1 mol l^{-1} V(V) solution for 20 days

Membrane	Initial weight /g	Final weight /g	Weight loss /%	Reduction of V(V) to V(IV) /%
Cationic DF 120	1.8	1.4	22.2	100
Anionic DF 120	3.1	3.0	3.2	60
JCM-1-10	1.6	1.6	0	60
JCM-1-15	1.5	1.4	6.7	40
JAM-1-10	1.4	1.4	0	10
JAM-1-15	1.4	1.4	0	0

Table 4. Chemical stability evaluation of some membranes after soaking in 0.1 mol l^{-1} V(V) solution for 40 days

Membrane	Initial weight /g	Final Weight /g	Weight loss /%
Cationic DF 120	0.6	0.4	33.3
Anionic DF120	1.0	1.0	0
JCM-1-10	0.5	0.5	0
JCM-1-15	0.5	0.4	20
JAM-1-10	0.5	0.5	0
JAM-1-15	0.5	0.5	0

and energy efficiencies, so Nafion 117 was obtained to compare properties of the treated JAM in the cell. It can be seen that the average efficiencies for the JAM composite membrane are higher than that for Nafion 117 over 8 charge/discharge cycles.

4. Conclusions

This study of some commercially available membranes shows that, except for JAM anionic exchange membranes, other membranes, DF120 cationic and anionic exchange membranes, JCM cationic exchange membrane, are unsuitable for the vanadium redox battery due to their high permeation of vanadium ions and poor chemical stability in the V(V) solutions. A novel cationic exchange membrane was prepared by incorporation of

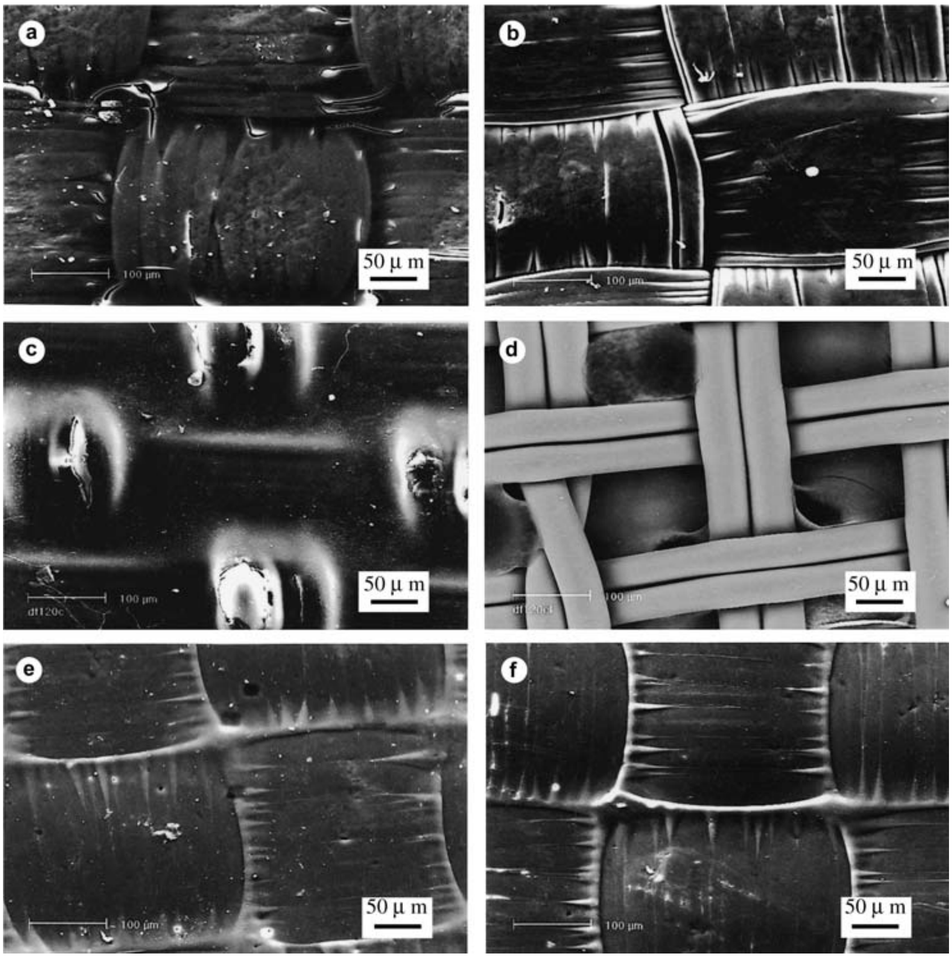

Fig. 6. SEM micrographs of untreated membranes: (a) JCM, (c) Cationic DF120, (e) JAM and treated membranes: (b) JCM, (d) Cationic DF120, (f) JAM after 2 months soaking in 1.0 mol l^{-1} VO_2^+ solution.

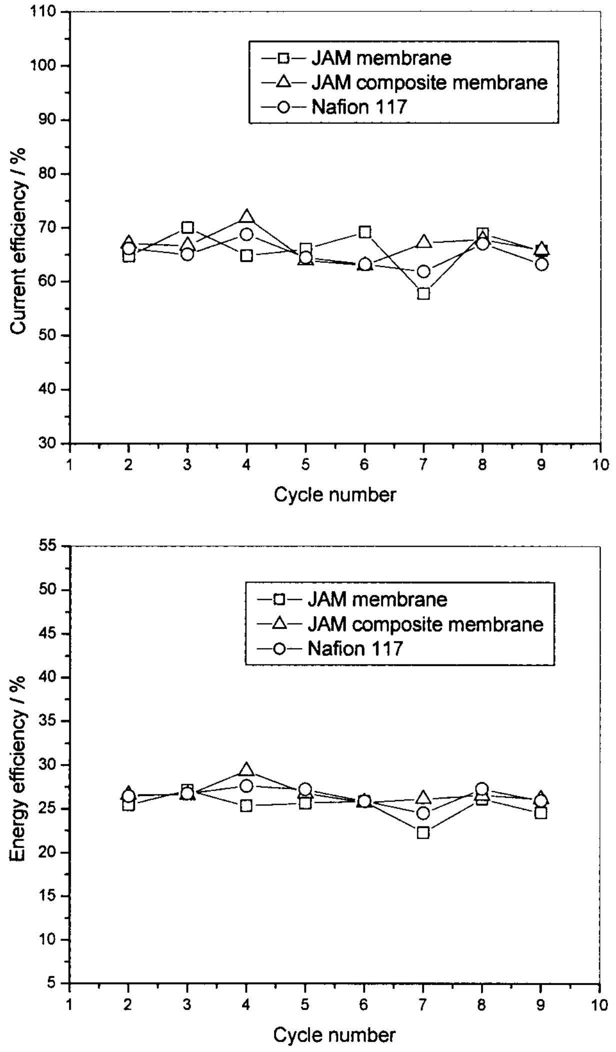

Fig. 7. Cell efficiencies for JAM membrane, JAM composite membrane and Nafion 117 in VRB charge/discharge cycling test.

poly (sodium 4-styrenesulfonate) into the JAM anionic exchange membrane by *in situ* polymerization. Some significant cationic exchange capability was imparted to the composite membrane. The composite membrane prepared by this method also showed lower permeability to vanadium ions and higher average current and energy efficiencies for the VRB in comparison with the untreated membrane. The vanadium redox cell with the JAM composite membrane has a better performance than that with Nafion 117.

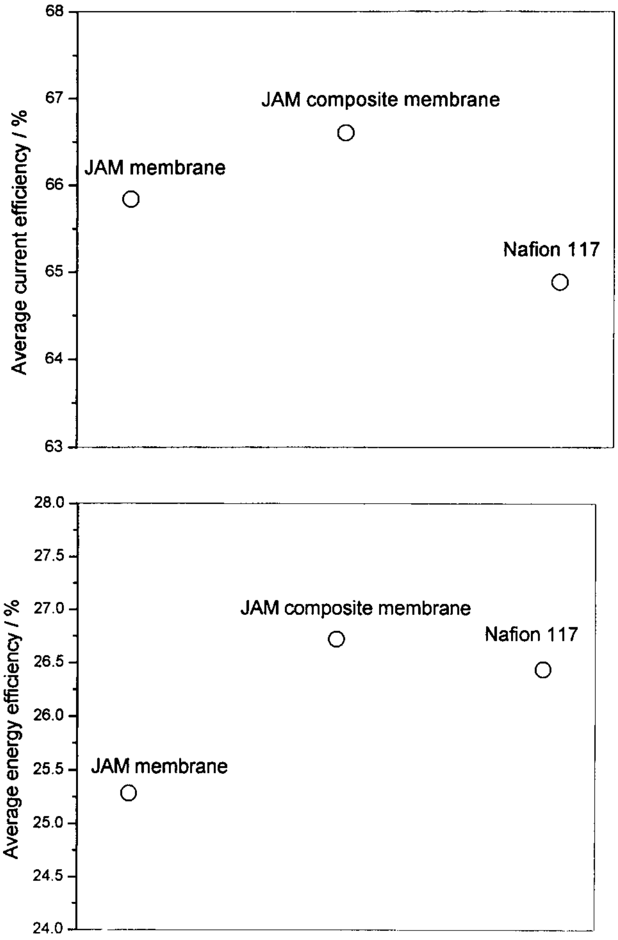

Fig. 8. Average cell efficiencies for JAM membrane, JAM composite membrane and Nafion 117 over 8 charge/discharge cycles.

References

1. T. Mohammadi and M. Skyllas-Kazacos, *J. Power Sources* **63** (1996) 179.
2. D.G. Oei, *J. Appl. Electrochem.* **15** (1985) 231.
3. G.J. Hwang and H. Ohya, *J. Membr. Sci.* **132** (1997) 55.
4. T. Mohammadi and M. Skyllas-Kazacos, *J. Membr. Sci.* **107** (1995) 35.
5. G.J. Hwang and H. Ohya, *J Membr. Sci.* **120** (1996) 55.
6. T. Mohammadi and M. Skyllas-Kazacos, *J. Appl. Electrochem.* **27** (1997) 153.
7. B. Tian, C.W. Yan, Q. Qu, H. Li and F.H. Wang, *Battery Bimonthly* **33** (2003) 261.
8. T. Mohammadi and M. Skyllas-Kazacos, *J. Membr. Sci.* **98** (1995) 77.
9. E. Wiedemann, A. Heintz and R.N. Lichtenthaler, *J. Membr. Sci.* **141** (1998) 207.