

# Use of polyelectrolyte for incorporation of ion-exchange groups in composite membranes for vanadium redox flow battery applications

T. Mohammadi, M. Skyllas-Kazacos \*

*School of Chemical Engineering and Industrial Chemistry, The University of New South Wales, Sydney, NSW 2052, Australia*

Received 27 March 1995; revised 29 May 1995; accepted 6 June 1995

## Abstract

Daramic (W.R. Grace, USA), which consists of ultra high molecular polyethylene, amorphous silica and mineral oil, is cross-linked with divinylbenzene (DVB) to obtain a composite microporous separator with modified properties. In the present study, poly(sodium 4-styrene-sulfonate) (PSSS) (Aldrich Chemical Company, Inc., USA, mol. wt.  $\sim 70\,000$ ) is used as a polyelectrolyte to impart cation-exchange capacity to the cross-linked Daramic. Incorporation of cation-exchange groups in this composite membrane results in a reduction in solvent transfer across the membrane when used in a vanadium redox cell. The ion-exchange capacity (IEC) of the new PSSS composite membrane is also evaluated. Due to the solubility of PSSS in water, the IEC of the membrane decreases initially when the membrane is soaked in water, but then stabilizes and remains unchanged after a few weeks. Water-transport measurements across the PSSS composite membrane show promising results compared with those across the untreated cross-linked Daramic separator. A detailed  $^{13}\text{C}$  nuclear magnetic resonance (NMR) and X-ray dispersive analysis has been carried out to confirm the incorporation of PSSS into the membrane.

*Keywords:* Daramic; Divinylbenzene; Polyelectrolyte; Poly(sodium 4-styrenesulfonate); Vanadium redox battery

## 1. Introduction

Membranes and separators are used widely in batteries and fuel cells, as well as in electrochemical processes in many industrial applications. More and more novel electrochemical processes, e.g., redox flow batteries, are being developed and require a membrane (or a separator) to play an integral function in the whole process. In the vanadium redox flow battery, the function of the membrane/separator is to prevent cross-mixing of the positive and negative electrolytes, but still to allow the transport of ions for completion of the circuit during the passage of current.

Evaluation of a number of commercial ion-exchange membranes for the vanadium redox battery (VRB) has shown that, except for a few which are generally perfluorinated but currently too expensive for commercial use, most are unsuitable due to their poor stability in the vanadium solutions [1]. Daramic, a microporous separator, was chosen on account of its low cost and its reasonable chemical stability in vanadium (V) solution. Daramic contains a special mineral oil as a stabilizer against oxidation. Unfortunately, because of its high permeability for vanadium solutions, very low coulombic efficiency is obtained by VRBs. As reported earlier [2],

however, cross-linking of DVB into the pores of Daramic gives an overall energy efficiency of 74% at a charge/discharge current density of  $40\text{ mA cm}^{-2}$ , compared with only 40% for the untreated Daramic.

During charge/discharge cycling of a VRB, as with other kinds of redox flow batteries, there is a preferential volumetric transfer of the solution across the membrane. For a cell that employs an anion-exchange membrane or a non-ionic membrane, it is observed that the net volumetric transfer is towards the negative half-cell, whereas for a cation-exchange membrane, the net volumetric transfer is towards the positive half-cell. This leads not only to a reduction in the cell capacity because of concentration of one side and depletion of the other, but also to possible flooding of the solution reservoir. Neither the commercial ion-exchange membranes nor the earlier cross-linked Daramic separators displayed acceptable volumetric solution transfer behaviour [1,3].

Sulfonation of the cross-linked Daramic separators (using concentrated sulfuric acid) has thus been investigated in order to impart some cation-exchange capacity and it is successful in reducing the amount of water transport across the membrane in a VRB [3]. While the sulfonated composite membrane exhibits properties that makes it suitable for use in VRBs, scale-up is both difficult and expensive due to the very corrosive nature of concentrated sulfuric acid. Incorporation

\* Corresponding author.

ration of cation-exchange groups using poly(sodium 4-styrenesulfonate) (PSSS) has thus been studied and the results presented here show that the method reduces the water transport across the membrane. Unlike the sulfonation process, however, the PSSS treatment step can be readily scaled up. In the present investigation, incorporation of PSSS into a cross-linked Daramic separator and characterization of the PSSS composite membrane will be discussed.

## 2. Experimental

### 2.1. Membrane preparation

The PSSS composite membranes were prepared by the following method. A piece of Daramic (size = 12 cm × 14 cm) was soaked for 24 h in a solution of PSSS (75 g of PSSS per 1 l of distilled water). The soaked Daramic was then transferred into a solution of 40 parts DVB to 60 parts ethanol (40:60) and soaked for 12 h. The soaked Daramic was transferred to a reactor in which distilled water and sodium persulfate were heated at 95 °C. Sodium persulfate was used as an initiator for polymerization of DVB. The temperature was increased to 98 °C in 10 min and the reaction then allowed to proceed for either 1 or 3 h.

### 2.2. Membrane characterization

The area resistance and the permeability of the membranes were evaluated by the methods described in Ref. [4]. For the permeability measurements, the diffusion coefficient of V(IV) ions across the membrane was determined. The membrane was exposed to a solution of 1 M VOSO<sub>4</sub> in 2 M H<sub>2</sub>SO<sub>4</sub> on one side, and a solution of 1 M MgSO<sub>4</sub> in 2 M H<sub>2</sub>SO<sub>4</sub> on the other side. MgSO<sub>4</sub> was used to equalize the ionic strengths of the two solutions and to minimize the osmotic pressure effects. For the area resistance measurements, the membrane was exposed to a solution of 2 M VOSO<sub>4</sub> in 3 M H<sub>2</sub>SO<sub>4</sub> on both sides. For each measurement, three samples were prepared, and the average values are presented; the typical scatter between samples is less than 10%.

The water transfer across the membranes was evaluated in a cell that consisted of two half-cells described in Ref. [5]. Each half-cell was constructed from a cylindrical Perspex block (volume = 45 ml) connected to a Perspex tube. The negative and positive half-cell electrolytes at 50% state-of-charge, 1 M V(II) + 1 M V(III) on one side and 1 M V(IV) + 1 M V(V) on the other side, were used to evaluate the water-transport behaviour of the composite membranes. The tube connected to each compartment had an internal diameter of 4.25 mm, so each 7.05 cm change in height for both sides can be considered as 1 ml solution transfer from one side to another. Generally, for cation-exchange membranes, the solution transfer in the vanadium redox cell is from the negative half-cell to the positive half-cell. The solution transfer for anion-exchange membranes and non-selective

membranes is, however, from the positive side to the negative side [1].

The ion-exchange capacity (IEC) of the membranes was evaluated by the method described in Ref. [6]. The membrane in the Na<sup>+</sup> form was soaked in 1 M HCl solution to effect conversion to the H<sup>+</sup> form membrane. The membrane was then immersed in a known volume of 0.05 M KOH solution for 48 h at room temperature. The amount of H<sup>+</sup> (in mmol) was determined by back titration with a 0.05 M HCl solution. The membrane was then washed with distilled water and dried under vacuum. The IEC was calculated as the ratio of the amount of H<sup>+</sup> to the weight of dried membrane. For each measurement, three samples were prepared, and the presented results are averages, the typical scatter between samples is less than 8%.

The vanadium redox flow cell used in the charge/discharge tests has been described in Ref. [7]. The cell employed 2 M solutions of V(II)/V(III) and V(IV)/V(V) redox couples in H<sub>2</sub>SO<sub>4</sub>, with graphite felt electrodes and graphite plates as the current collectors. The electrode and membrane areas were 25 and 30 cm<sup>2</sup>, respectively. The volume of the electrolytes was 65 ml for each half-cell. The cell was charged and discharged at a constant current density. The cell efficiencies and the cell resistance were determined by the methods described in Ref. [7].

Both nuclear magnetic resonance (NMR) and X-ray dispersion analysis were carried out to establish whether any PSSS was incorporated into the PSSS composite membrane. BRUKER MSL 300 NMR, JEOL JXA-840 scanning microanalyser and Link An 10000, EDAX (energy dispersive X-ray analyser) instruments were used.

## 3. Results and discussion

Since the PSSS solution can permeate into the pores of Daramic during soaking, the polyelectrolyte material should deposit into the pores of Daramic. On the other hand, due to its solubility in aqueous solutions, the PSSS would be expected to re-dissolve in the electrolyte solution, when the soaked Daramic is employed in the vanadium redox cell. Cross-linking with DVB, which has been found previously [2] to block partially the pores of Daramic, should be able to restrict the re-dissolution of incorporated PSSS when the membrane is employed in the cell.

The function of the solvent (i.e., ethanol) is to swell the pores of Daramic, so that DVB can permeate more easily into the pores. As a result, there should be a greater chance of polymerization of DVB into the pores as well as on the surface. Also, the solvent is the medium between the water-insoluble monomer, DVB, and distilled water. Free radicals generated from the water-soluble initiator, sodium persulfate, can transfer from water to the monomer through the solvent [2].

It was found previously [2] that increase in the reaction time for cross-linking of DVB lowered the permeation of

Table 1  
Effect of incorporation of PSSS and polymerization time on area resistance and diffusivity of resulting composite membranes

| Sample no. | Polymerization time (h) | PSSS concentration ( $\text{g l}^{-1}$ ) | Area resistance ( $\Omega \text{ cm}^2$ ) | Diffusivity $\times 10^4$ ( $\text{cm min}^{-1}$ ) |
|------------|-------------------------|--|---|--|
| 1          | 1                       | 75                                       | 1.09                                      | 4.48   |
| 2          | 3                       | 75                                       | 1.36                                      | 3.31   |
| 3          | 1                       | N/A <sup>a</sup>                         | 1.56                                      | 4.15   |
| 4          | 3                       | N/A <sup>a</sup>                         | 2.68                                      | 2.15   |

<sup>a</sup> Not soaked in the PSSS solution.

vanadium ions through the composite membrane, but raised the area resistance of the membrane. In other words, polymerization times as short as one 1 h can lead to the production of composite membranes with lower area resistance and higher, but still acceptable, diffusivity. Table 1 presents area resistance and diffusivity values for both PSSS composite membranes and cross-linked Daramic separators. The results show that incorporation of PSSS into the composite membrane leads to lower area resistance and higher diffusivity of the resulting membrane. This can be attributed to the presence of cation-exchange groups in the PSSS composite membrane.

As mentioned previously, cation-exchange membranes generally exhibit higher conductivity and vanadium-ion diffusivity compared with anion-exchange membranes when employed in a VRB. The former is due to the fact that for cation-exchange membranes, the current is carried exclusively by  $\text{H}^+$  ions, while the current is carried by both  $\text{H}^+$  and  $\text{SO}_4^{2-}$  ions for anion-exchange membranes. The lower resistivity of the cation-exchange membranes is thus due to the higher mobility of  $\text{H}^+$  ions compared with  $\text{SO}_4^{2-}$  ions. The lower diffusivity of the vanadium ions through the anion-exchange membranes can be attributed to the Donnan exclusion effect [1].

The PSSS composite membranes exhibited an IEC as high as 1.03 millimoles per gram of dried membrane ( $\text{mmol/dg}$ ), while those which had not been soaked in the PSSS solution did not show any IEC. The PSSS composite membranes were soaked in distilled water and their IEC was evaluated periodically to determine whether this would remain constant. The IEC values of the PSSS composite membranes which had been cross-linked for 3 h are presented in Table 2. The results show that the IEC decreases with time but reaches a steady-state value of 0.53  $\text{mmol/dg}$  after three weeks. The reduction of IEC from 1.03 to 0.53 can be attributed to the partial re-dissolution of the incorporated PSSS when the membrane is soaked in water.

Water-transport measurements of the composite membranes were also performed. The net transfer of water across the PSSS composite membranes was found to be less than that across samples that had not been soaked initially in the PSSS solution. It shows that the method is able to incorporate cation-exchange capability and to diminish to some extent the water transport in the VRB.

Earlier water-transport studies of a variety of commercial ion-exchange membranes and non-ionic separators in the vanadium redox cell have shown that the net water transport through anion-exchange membranes and non-ionic separators in the vanadium redox cell is from the positive half-cell to the negative half-cell, while for cation-exchange membranes, the direction of the water transport direction is opposite. This phenomenon is common to ion-exchange membranes and is due to the fact that the transfer of water across different membranes is the net effect of a number of processes, namely, the water transported by the ions moving under the concentration gradient, the water carried by the charge-carrying species, and the water transferred due to the osmotic pressure difference between the two solutions [3]. The contribution from each process varies for different membranes so that the net effect in each case produces different water transport properties.

Fig. 1 presents the results of water-transport measurements across the composite membranes. It shows that less water is transferred across the PSSS composite membrane than the cross-linked Daramic separator (Fig. 1, curves (1) and (4)). It can be concluded that the incorporation of PSSS into the composite membrane is able to minimize the water transfer through the membrane. The results (Fig. 1, curves (1) and

Table 2  
Ion-exchange capacity (IEC) of PSSS composite membrane (no. 2 in Table 1) before and after soaking in water

| PSSS composite membrane       | IEC ( $\text{mmol/dg}$ ) |
|-------------------------------|--------------------------|
| After preparation             | 1.03                     |
| One week after preparation    | 0.64                     |
| Three weeks after preparation | 0.53                     |
| Five weeks after preparation  | 0.51                     |

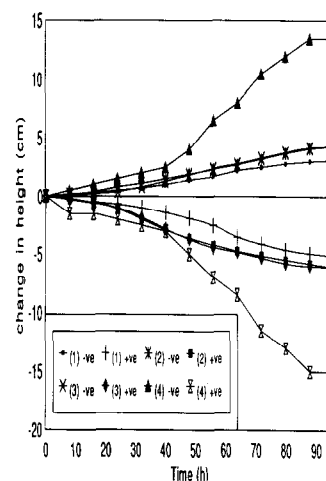


Fig. 1. Transport of water across PSSS composite membrane after: (1) preparation; (2) three weeks soaking in distilled water, and (3) five weeks soaking in distilled water (no. 2). Curve (4) is water transport across cross-linked Daramic separator (no. 4). Vanadium electrolytes of 50% initial state-of-charge. (-ve) = negative electrolyte level and (+ve) = positive electrolyte level.

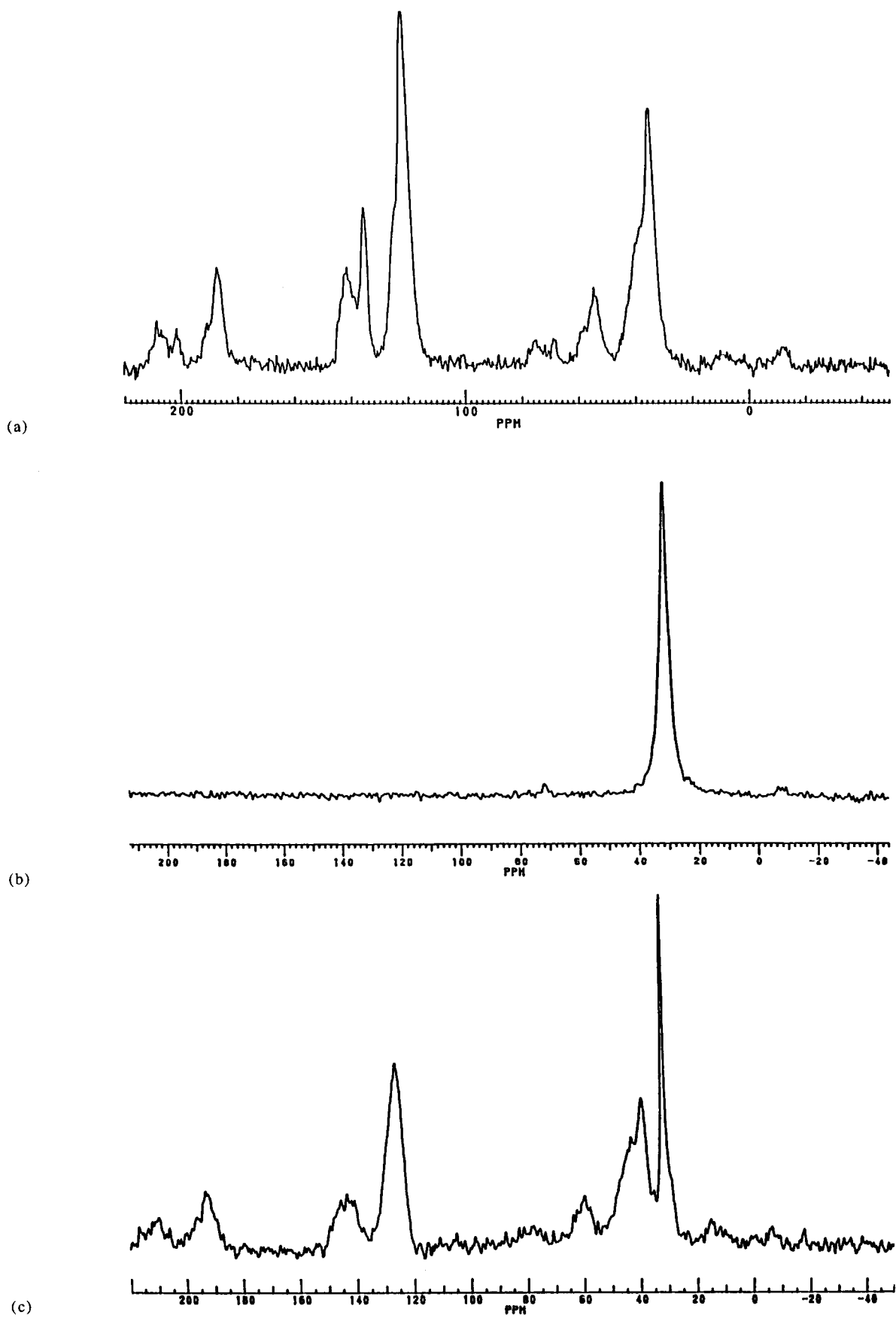


Fig. 2. <sup>13</sup>C NMR spectrum of (a) PSSS; (b) Daramic, and (c) PSSS composite membrane (no. 2).

(2)) also show that slightly more water is transferred across the membrane when the membrane is soaked in water. This is also due to the re-dissolution of the incorporated PSSS in water. The results (Fig. 1, curves (2) and (3)) reveal the same amount of water is transferred across the membranes that had been soaked in water for three weeks or more. Thus, it can be concluded that cross-linking of Daramic with DVB can restrict, to some extent, the re-dissolution of the incorporated PSSS in water.

Fig. 2(a), (b) and (c) presents the  $^{13}\text{C}$  NMR spectra of PSSS, Daramic and the PSSS composite membrane, respectively. In Fig. 2(a), the peaks of 36, 55, 122, 135, 143 and 188 ppm are predominant and can be attributed to various carbon atoms of PSSS, while the peak of the carbon atom in polyethylene (Daramic) is observed at 32 ppm in Fig. 2(b) [8]. As expected, a combination of this peak at 32 ppm and the peaks at 38, 57, 126, 143 and 191 ppm are also observed in Fig. 2(c), and this can be attributed to the presence of both carbon atoms of polyethylene and those of PSSS. The peak of 126 ppm, which is associated with a carbon atom in an aromatic ring in Fig. 2(c), may mark the presence of both DVB and PSSS in the PSSS composite membrane [2]. Accordingly, the NMR results confirm the presence of PSSS in the PSSS composite membrane.

Elemental analysis of Daramic and the PSSS composite membrane has been carried out to further investigate the presence of PSSS by determination of the sulfur content of the samples. The samples were coated with carbon before analysis. The PSSS composite membrane was studied after it had been soaked in distilled water for five weeks. Fig. 3(a) shows the elemental analysis of Daramic in which the presence of silica is predominantly observed. Fig. 3(b) gives the elemental analysis of the PSSS composite membrane. The presence of sulfur is evident and thus confirm the incorporation of PSSS into the PSSS composite membrane. A very small amount of sulfur which is also observed in Daramic (Fig. 3(a)) may be attributed to the contamination of Daramic before analysis.

The performance characteristics for Daramic and the PSSS composite membrane in the vanadium redox flow cell are presented in Table 3; a typical charge/discharge curve is presented in Fig. 4. The results for the cross-linked Daramic separator which had not been soaked initially in the PSSS solution are reported in Table 3 for comparison. The vanadium redox flow cell employing the PSSS composite membrane gave an overall energy efficiency of 77% over more than 100 cycles at a current density of  $40 \text{ mA cm}^{-2}$ , compared with only 40% for Daramic. By contrast, the cross-linked Daramic separator yielded an overall energy efficiency of 74%. As expected, due to its lower area resistance, the PSSS composite membrane delivered the higher voltage efficiency of 84.7% compared with the value of 78.6% for the cross-linked Daramic separator. Due to the greater permeation of vanadium ions through the PSSS composite membrane, however, a lower coulombic efficiency of 90.9%

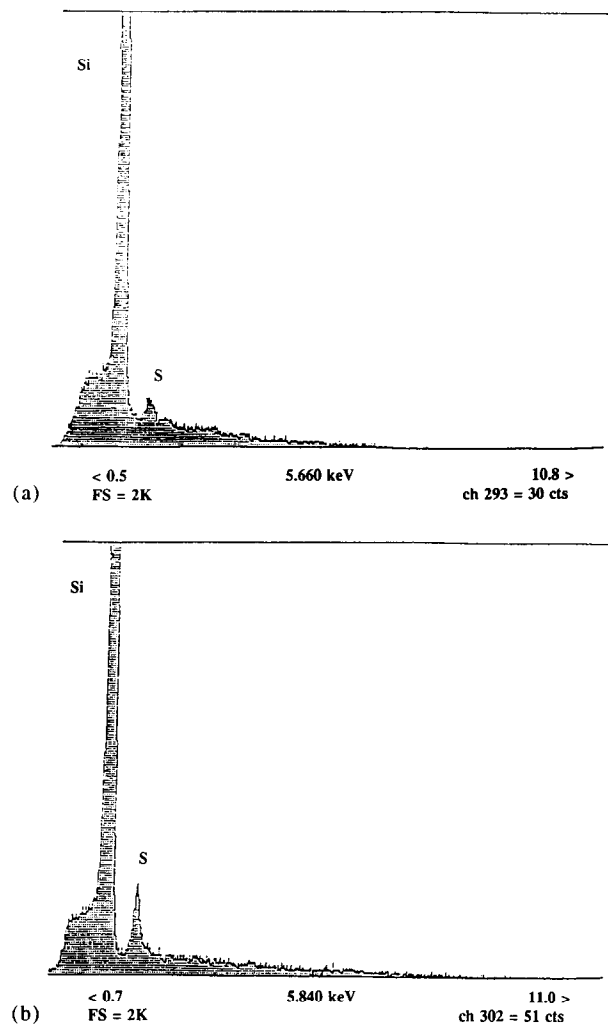


Fig. 3. X-ray dispersive analysis of (a) Daramic, and (b) PSSS composite membrane (no. 2). X-ray: 0–20 keV. Live = 100 s, preset: 100 s, remaining: 0 s. Real: 110 s; 9° dead.

was obtained compared with the value of 94.1% for the cross-linked Daramic separator.

The cell resistance, measured at 50% state-of-charge during charge/discharge cycling, was  $4.03 \Omega \text{ cm}^2$  on average for the PSSS composite membrane, compared with  $4.28 \Omega \text{ cm}^2$  for the cross-linked Daramic separator. The cell effi-

Table 3  
Cell performance characteristics of membranes before and after modification

| Parameter                | Daramic | Cross-linked Daramic separator (no. 4) | PSSS composite membrane (no. 2) |
|--------------------------|---------|--|---------------------------------|
| Coulombic efficiency (%) | 47      | 94.1                                   | 90.9                            |
| Voltage efficiency (%)   | 86      | 78.6                                   | 84.7                            |
| Energy efficiency (%)    | 40      | 74                                     | 77                              |

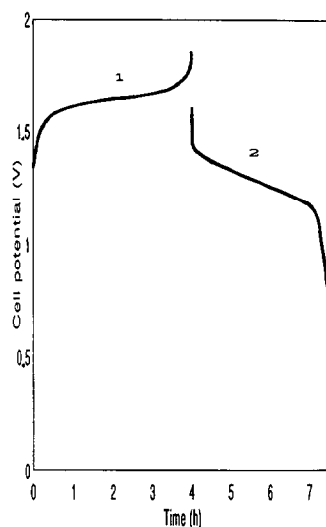


Fig. 4. Typical (1) charge and (2) discharge curves for vanadium redox cell at a charge/discharge current density of  $40 \text{ mA cm}^{-2}$ .

ciency obtained with this membrane are thus comparable with those obtained with the cation-exchange membrane, Selemion CMV (Asahi Glass Co., Japan) [1]. Long-term charge/discharge cycling of a vanadium redox flow cell that employed the PSSS composite membrane at various charge/discharge current densities is currently being undertaken to establish its long-term stability in vanadium solutions.

#### 4. Conclusions

A novel ion-exchange membrane was prepared by soaking the microporous separator, Daramic, in a solution of poly(sodium 4-styrenesulfonate) (PSSS) and crosslinking with divinylbenzene. Ion-exchange capacity measurements, water-transfer measurements,  $^{13}\text{C}$  NMR and X-ray dispersive analysis have all confirmed the incorporation of PSSS into the composite membrane during the initial soaking process. The method diminished the capacity loss and reservoir flooding during operation of a vanadium redox battery and also improved the battery performance compared with the cross-linked Daramic separator which had not been soaked in the

PSSS solution. The area resistance of the PSSS composite membrane reduced to a value of  $1.36 \Omega \text{ cm}^2$  from a value of  $2.68 \Omega \text{ cm}^2$  for the cross-linked Daramic separator, while the diffusivity of the PSSS composite membrane increased to a value of  $3.31 \times 10^{-4} \text{ cm min}^{-1}$  from a value of  $2.15 \times 10^{-4} \text{ cm min}^{-1}$  for the cross-linked Daramic separator. The vanadium redox flow cell with the PSSS composite membrane showed an overall energy efficiency of 77% at a current density of  $40 \text{ mA cm}^{-2}$ , compared with 74% for the cross-linked Daramic separator. It has been shown that the membrane treatment method can be used successfully to impart cation-exchange selectivity to the low cost, stable separator, Daramic. Long-term chemical stability tests of the PSSS composite membrane in vanadium(V) solution and in the battery system itself are currently in progress.

#### Acknowledgements

This project was funded by grants from Unisearch Ltd. and the Australian Research Council. T. Mohammadi was supported by a scholarship from the Ministry of Culture and Higher Education of IRAN. The authors thank Dr J. Hook (School of Chemistry, University of NSW) for the NMR spectra analysis and Mrs V. Piegerou (School of Materials Science and Engineering, University of NSW, Australia) for the electron dispersive analysis.

#### References

- [1] S.C. Chieng, *Ph.D. Thesis*, University of New South Wales, Sydney, NSW 2052, Australia.
- [2] T. Mohammadi and M. Skyllas-Kazacos, *J. Membr. Sci.*, 98 (1995) 77.
- [3] T. Mohammadi and M. Skyllas-Kazacos, *J. Membr. Sci.*, in press.
- [4] F. Grossmith, P. Liewellyn, A.G. Fane and M. Skyllas-Kazacos, *Proc. Symp., The Electrochemical Society, Honolulu, HI, USA, Oct. 1988*, Proc. Vol. 88-11, p. 363.
- [5] C.P.H. Ang, *M.E. Thesis*, University of New South Wales, Sydney, NSW 2052, Australia.
- [6] R. Wycisk and W.M. Trochimczuk, *J. Polym. Sci.: Part C*, 27 (1989) 321.
- [7] S.C. Chieng, M. Kazacos and M. Skyllas-Kazacos, *J. Membr. Sci.*, 75 (1992) 81.
- [8] *Atlas of  $^{13}\text{C}$  NMR Data*, Heyden and Son, London, 1979.