Modification of anion-exchange membranes for vanadium redox flow battery applications

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Abstract

Modification of the Selemion AMV and New Selemion (Type 2) anion-exchange membranes (Asahi Glass, Japan) has improved their water transport properties in the vanadium redox cell. The AMV membrane is sulfonated using concentrated sulfuric acid, while poly(sodium-4-styrenesulfonate) (Aldrich, USA, mol. wt. ~70 000) is incorporated into the New Selemion (Type 2) membrane. A significant reduction in the amount of water transport across the membranes during operation of the vanadium redox battery is achieved.

Keywords: Ion-exchange membranes; Sulfonation; Vanadium redox batteries; Batteries; Water transfer

1. Introduction

The vanadium redox flow battery (VRB) employs V(II)/V(III) and V(IV)/V(V) redox couples in the negative and positive half-cell electrolytes, respectively. An ion-exchange membrane is required to prevent cross-mixing of the electrolytes, whilst allowing the transport of ions to complete the circuit during the passage of current. This transport of ions, together with the flux of water due to differences in ionic strength of the two solutions, leads to a flow of solution backwards and forwards across the membrane during charging and discharging.

Earlier evaluation of a number of commercial ion-exchange membranes showed that, depending on the type of membrane used during the charge/discharge cycling of the VRB, there is a net volumetric transfer in one direction across the membrane. For a cell that employs an anion-exchange membrane, it is observed that the net volumetric transfer over a complete charge/discharge cycle is towards the negative half-cell, whereas for a cation-exchange membrane, the net volumetric transfer is towards the positive half-cell. This phenomenon, which is common to ion-exchange membranes and to redox flow cells, is due to the fact that the transfer of water across different membranes is the net effect of a number of processes of water transport: (i) that resulting from the ions moving under the concentration gradient; (ii) that carried by the charge-carrying species, and (iii) that due to the osmotic

pressure difference between the two solutions. The contribution from each process varies for different membranes so that the net water transport properties also vary. This phenomenon can lead not only to a reduction in cell capacity because of concentration of active species on one side and dilution on the other, but also to possible flooding of the solution reservoirs [1].

It was suggested [2] that the amount of water transfer is related to the ion-exchange capacity (IEC) of the membrane. Thus, by reducing the IEC of an anion-exchange membrane, it should be possible to minimize the amount of water transfer across the membrane. A sulfonation treatment was applied to the AMV membrane to incorporate strong cation-exchange groups ($-SO_3, H^+$) so as to modify its permeation properties. Sulfonation was carried out using 98% sulfuric acid.

Due to the poor chemical stability of New Selemion (Type 2) in concentrated sulfuric acid, however, partial neutralization of anion-exchange groups of the membrane was performed using poly(sodium 4-styrenesulfonate), termed PSSS, which is a cationic poly-electrolyte. A composite membrane prepared by cross-linking of a microporous Daramic separator with divinylbenzene, was subjected to both treatment techniques [3–5] and a significant reduction was achieved in the rate of water transfer during operation of the vanadium redox cell. The results presented here show that both methods are also able to reduce the water transport across commercial anion-exchange membranes, and thus make them more suitable for application in the vanadium redox cell system.

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2. Experimental

2.1. Membrane preparation

To incorporate strong cation-exchange groups (-SO₃, H⁺) into the AMV membrane, sulfonation was carried out using highly concentrated sulfuric acid at different temperatures for different times. Silver sulfate (1 wt.%) was used as a catalyst for the sulfonation reaction. A piece of the membrane (size: 12 cm × 14 cm) was transferred to a reactor in which the sulfuric acid and silver sulfate solution was heated to the desired temperature. For modification of the New Selemion (Type 2) membrane, a sample (size: 12 cm × 14 cm) was soaked in a solution of PSSS (75 g PSSS/l distilled water) for a certain period at ambient temperature.

2.2. Membrane characterization

The area resistance and the permeability of the membranes were evaluated by the methods described by Grossmith et al. [6]. For the permeability measurement, the diffusion coefficient of V(IV) ions across the membrane was determined. The membrane was exposed to a solution of 1 M VOSO₄ in 2 M H₂SO₄ on one side and a solution of 1 M MgSO₄ in 2 M H₂SO₄ on the other side. MgSO₄ 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 VOSO₄ in 3 M H₂SO₄ on both sides. For each measurement, four samples were prepared and the results averaged, the typical scatter between samples was less than 12%.

The water transport across the membranes was evaluated by the method described by Hoong Ang [7] and illustrated in Fig. 1. Negative and positive half-cell electrolytes at 50% state-of-charge (SOC) (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 is equivalent to a transfer of 1 ml solution from one side to the other.

The IEC of the membranes was evaluated by the method described by Wycisk and Trochimczuk [8]. The membrane in the Na⁺ form was soaked in 1 M HCl solution to convert it to the H⁺ form. The membrane was then immersed in a
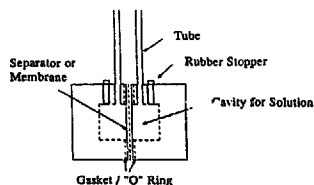
known volume of 0.05 M KOH for 48 h at room temperature. The amount of H⁺ (in mM) was determined by back titration with a 0.05 M HCl solution. The membrane in Cl⁻ form was soaked in 1 M KOH solution to convert it to the OH⁻ form. This was then immersed in a known volume of 0.05 M HCl for 48 h at room temperature. The amount of OH⁻ (in mM) was determined by back titration with a 0.05 M KOH 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⁺ (or OH⁻) to the weight of the dried membrane, i.e., millimole per dried gram weight (mM/dg). For each measurement, three samples were prepared and the results averaged, the typical scatter between samples was less than 8%.

The vanadium redox flow cell design used in the charge/discharge tests employed 2 M V(II)/V(III) and V(IV)/V(V) redox couples in H₂SO₄, with graphite-felt electrodes and graphite plates as current-collectors. The electrode and membrane area were 25 and 30 cm², respectively, while the volume of electrolyte was 65 ml in each half-cell. The cell was charged and discharged at a constant current-density of 30 or 40 mA cm⁻².

Morphological studies were undertaken with a Hitachi S-900, field emission scanning electron microscope (FESEM), X-ray dispersion analyses were also carried out using a JEOL JXA-840 scanning microanalyser and a Link An 10000, EDAX (energy dispersive X-ray analyser).

3. Results and discussion

The area resistance and V(IV) diffusivity values for AMV and sulfonated AMV membranes are presented in Table 1. The results show that the incorporation of cation-exchange groups into the anion-exchange AMV membrane has led to a significant increase in vanadium-ion diffusivity and a slight reduction in area resistivity. In general, cation-exchange membranes exhibit higher conductivity and vanadium-ion diffusivity compared with anion-exchange membranes when employed in the VRB. The former is due to the fact that, for cation-exchange membranes, the current is carried exclusively by H⁺ ions, while the current is carried by both H⁺ and SO₄²⁻ ions for anion-exchange membranes. Thus, the lower resistivity of the cation-exchange membranes is due to the higher mobility of H⁺ ions compared with SO₄²⁻ ions. The lower diffusivity of the vanadium ions through the anion-

Fig. 1. Apparatus used to measure water transfer properties of membranes.

Table 1
Diffusivity and area resistivity of AMV and sulfonated AMV membranes

Membrane	Sulfonation temperature (°C)/time (h)	Diffusivity (cm min⁻¹) × 10⁵	Area resistance (Ω cm²)
AMV	n.a.	0.32	2.80
Sulfonated AMV	60/24	38.5	2.45

n.a. = not applicable.

Table 2
Effect of incorporation of PSSS on area resistance and diffusivity of New Selemion (Type 2) membrane

Membrane	Soaking time (days)	Diffusivity (cm/min) $\times 10^5$	Area resistance (Ω cm^2)
New Selemion (Type 2)	n.a. [a]	11.6	0.98
PSSS Selemion (Type 2)	2	4.11	1.25
PSSS Selemion (Type 2)	4	1.54	1.46
PSSS Selemion (Type 2)	6	0.93	1.70
PSSS Selemion (Type 2)	8	0.85	1.77

[a] n.a. = not applicable.

exchange membranes can be attributed to the Donnan exclusion effect.

The anion-exchange capacity of the AMV membrane before and after sulfonation was 1.95 and 1.74 mM/dg, respectively. The reduction of the anion-exchange capacity of the membrane after sulfonation can be attributed to the destruction of some of the anion-exchange groups. The cation-exchange capacity of the sulfonated AMV membrane was found to be as high as 2.34 mM/dg.

This technique was also employed to modify the anion-exchange capacity of the New Selemion (Type 2) membrane, but was found to be unsuitable due to the very low chemical stability of its polysulfone substrate in the very corrosive environment. The New Selemion (Type 2) membrane was thus modified by soaking in the PSSS solution. The resultant membranes were soaked in distilled water for two to three days and washed several times with distilled water to ensure that all the unreacted PSSS had been removed. Table 2 presents the area resistance and diffusivity values of the untreated and PSSS-treated Selemion (Type 2) membranes, the latter were soaked in the PSSS solution for different periods. The results show that incorporation of PSSS leads to both a higher area resistance and a lower permeation of vanadium ions. This may be attributed to the fact that during the treatment process, the pores of the membranes are partially blocked by the PSSS which has a very high mol. wt. The results also show that the longer the soaking time, the higher the incorporation of PSSS into the membrane, and hence, the higher the area resistance and the lower the vanadium-ion diffusivity. It can also be concluded that neutralization of the anion-exchange groups in the membrane with PSSS solution is a very slow reaction.

Water transport measurements were also conducted on AMV, sulfonated AMV, New Selemion (Type 2) and PSSS Selemion (Type 2) membranes. The net water transfer across the modified membranes was found to decrease dramatically after treatment. Figs. 2 and 3 present the results for the AMV and the sulfonated AMV membranes, respectively, while data
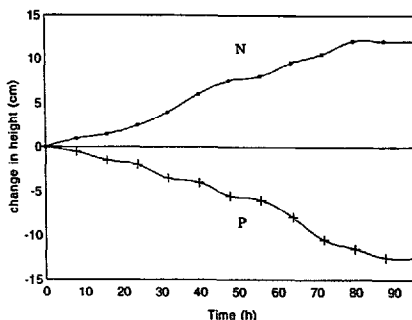

Fig. 2. Transport of water across an AMV membrane for vanadium electrolytes of 50% initial SOC. N: negative half-cell electrolyte, and P: positive half-cell electrolyte.
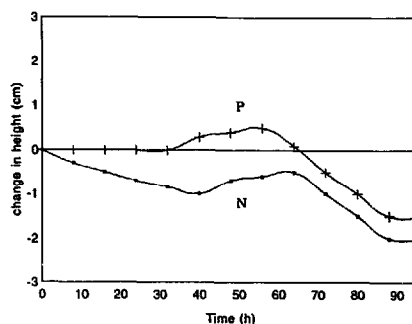

Fig. 3. Transport of water across sulfonated AMV membrane for vanadium electrolytes of 50% initial SOC. N: negative half-cell electrolyte, and P: positive half-cell electrolyte.

for New Selemion (Type 2) membrane and PSSS Selemion (Type 2) membranes are given in Fig. 4. It can be concluded that sulfonation of the AMV membrane can reduce water transfer. It should be noted that the mixing of the two electrolytes is not ideal and displays a negative deviation. In other words, the total volume of the two electrolytes after mixing is less than the summation of their individual volumes. The final reduction of the electrolyte levels in Fig. 3 may be attributed to this negative deviation. The results also reveal that longer soaking times in the PSSS solution result in less transport of water across the PSSS Selemion (Type 2) membrane. The reduction of water transferred across New Selemion (Type 2) membrane after soaking in the PSSS solution can be attributed to both the neutralization of the anion-exchange groups and the partial blockage of the membrane pores.

Measurements of volumetric cross-over of the electrolytes across sulfonated AMV and PSSS Selemion membranes during charge/discharge cycling of a VRB also showed that both
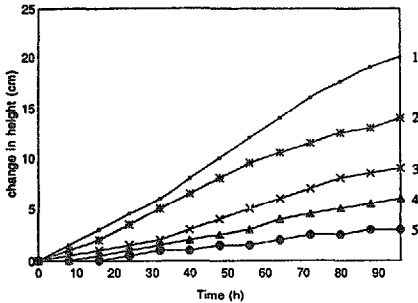
Fig. 4. Change in negative electrolyte level for Selemion (Type 2) membrane and PSSS Selemion (Type 2) membranes soaked in PSSS solution for vanadium electrolytes of 50% initial SOC. Soaking time (days): (1) not applicable; (2) two; (3) four; (4) six, and (5) eight.
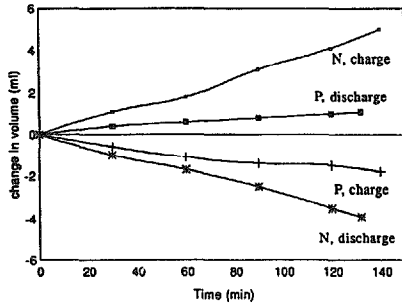
sulfonation and PSSS incorporation can eliminate problems caused by the accumulation of solution in one reservoir. Figs. 5–8 can be used to compare the volumetric cross-over behaviour of the treated and untreated AMV and New Selemion (Type 2) membranes during charge/discharge cycling of a VRB. The PSSS Selemion (Type 2) membrane had been soaked in the PSSS solution for eight days. The results demonstrate that not only is less water transferred across the treated membranes during a charge or a discharge cycle, but also the amount of water transferred in one direction across the treated membranes during the charge cycle is almost identical to that transferred in the opposite direction during the subsequent discharge cycle. This results in a lower net transfer of water during a complete cycle. The amount of water transferred across different membranes during charge/discharge cycling of a VRB is given in Table 3.

After sulfonation of the AMV membrane, the water transport per cycle was reduced from 0.7 to 0.3 ml, while after
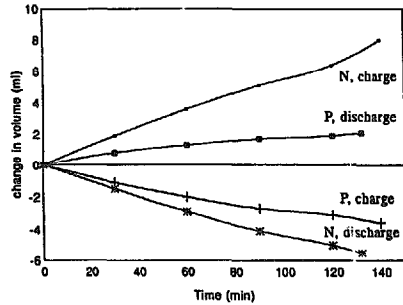

Fig. 5. Transport of water across AMV membrane during charge/discharge cycling of VRB at a current density of 20 mA cm^{-2}. N: negative half-cell electrolyte, and P: positive half-cell electrolyte.

Fig. 7. Transport of water across New Selemion (Type 2) membrane during charge/discharge cycling of a vanadium redox flow battery at a current density of 20 mA cm^{-2}. N: negative half-cell electrolyte, and P: positive half-cell electrolyte.
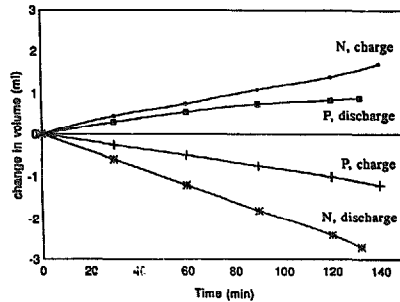

Fig. 6. Transport of water across sulfonated AMV membrane during charge/discharge cycling of a vanadium redox flow battery at a current density of 20 mA cm^{-2}. N: negative half-cell electrolyte, and P: positive half-cell electrolyte.

Fig. 8. Transport of water across PSSS Selemion (Type 2) membrane during charge/discharge cycling of a vanadium redox flow battery at a current density of 20 mA cm^{-2}. N: negative half-cell electrolyte, and P: positive half-cell electrolyte.

Table 3
Net volumetric transfer of water during one complete charge/discharge cycle of vanadium redox flow cells that employ different membranes at a charge/discharge current density at 20 mA cm^{-2}

Membrane	Observed net volumetric transfer of solution in a complete cycle (ml)
AMV	0.7 from +ve to −ve
Sulfonated AMV	0.3 from −ve to +ve
New Selemion (Type 2)	1.5 from +ve to −ve
PSSS Selemion (Type 2)	0.3 from +ve to −ve

Table 4
Amount of water transferred for 50% SOC solutions across sulfonated AMV membranes vs. their sulfonation time

Membrane	Sulfonation time (h)	Volume of water transferred (ml)
AMV	n.a.[a]	1.74
Sulfonated AMV	6	1.06
Sulfonated AMV	12	0.50
Sulfonated AMV	18	0.25
Sulfonated AMV	24	[b]

[a] n.a. = not applicable.
[b] Direction of water transfer was from the positive electrolyte to the negative electrolyte.

PSSS treatment of the New Selemion (Type 2) membrane, it decreased from 1.5 to 0.3 ml. For the PSSS Selemion (Type 2) membrane, the anion-exchange groups are partially neutralized, and thus, the water transport direction does not change. In the case of the sulfonated AMV membrane, however, the change in direction of water transport can be attributed to the fact that the cation-exchange capacity of the membrane is greater than its anion-exchange capacity.

Further optimization of the sulfonation was thus carried out in order to investigate the relationship between the sulfonation time and the water transport behaviour. The AMV membrane samples were sulfonated at 60 °C for different periods. The water transfer results for 50% SOC solutions are presented in Fig. 9, which also provides a comparison with the results for the unsulfonated membrane. As expected, the longer the sulfonation reaction time, the smaller the amount of water transferred across the resulting membrane. For even longer times, deformation (or in severe cases destruction) of the substrate is observed.

The amount of water transfer across the membranes is also presented in Table 4. Due to the negative deviation of the mixing of the two electrolytes, again, the increase in height for one side is generally less than the corresponding reduction for the other side. The smaller of the two values was thus considered in the calculations. In the case of the sulfonated AMV membrane that had been treated for 24 h the final

heights in both sides were negative and the amount of water transferred could not therefore be calculated. The diffusion of the vanadium ions in both directions, which causes the electrolytes to be mixed to some extent, may lead to the observed decrease in the total volume of the electrolytes.

FESEM images of membrane samples coated with chromium (Figs. 10 and 11) allow a study to be made of the surface morphology of the AMV membrane before and after sulfonation. The micrographs generally show that the sulfonation process that used concentrated sulfuric acid solution leads to a change in surface morphology of the membrane. This result is consistent with that reported previously [4].

Elemental analysis of the New Selemion (Type 2) membrane and PSSS Selemion (Type 2) membrane was carried out to further investigate the reaction between PSSS and the membrane. The samples were coated with carbon before analysis and the results are presented in Figs. 12 and 13 for New Selemion (Type 2) and PSSS Selemion (Type 2) membranes, respectively. The New Selemion (Type 2) membrane is fabricated from a backbone of polysulfone, and a chloromethylation/amination technique is employed to incorporate anion-exchange groups. Strong peaks associated
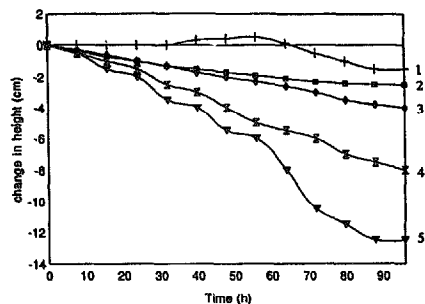
Fig. 9. Decrease in positive electrolyte level for sulfonated AMV membranes for vanadium electrolytes of 50% initial SOC. Sulfonation time: (1) 24 h; (2) 18 h; (3) 12 h; (4) 6 h, and (5) not applicable.

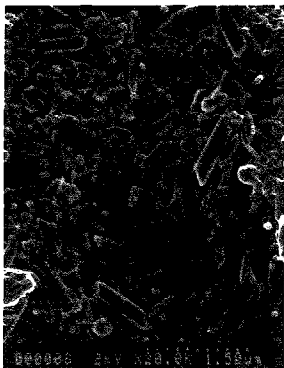Fig. 10. FESEM micrograph of AMV membrane (surface).

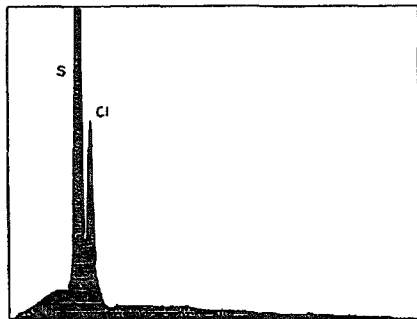Fig. 11. FESEM micrograph of sulfonated AMV membrane (surface).

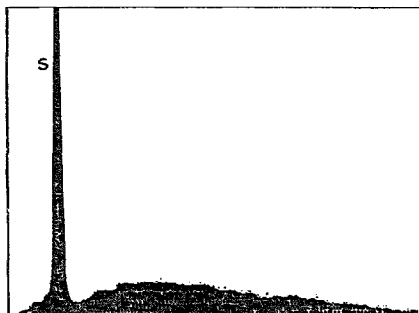Fig. 12. X-ray dispersive analysis of New Selemion (Type 2) membrane.

Fig. 13. X-ray dispersive analysis of PSSS Selemion (Type 2) membrane.

with the presence of sulfur and chlorine, as mobile ions, in the New Selemion (Type 2) membrane are evident in Fig. 12. The chlorine peak disappears for the PSSS Selemion (Type 2) membrane (see Fig. 13). This can be attributed to a neutralization reaction between the chloride ions of the membrane and sodium ions of PSSS. Thus, poly(styrene-sulfonate) ions, which are anions with a very large mol. wt., may exchange with chloride ions and, to some extent, block the pores of the membrane to yield a higher area resistivity and a lower vanadium ion diffusivity of the membrane. The only detectable element of PSSS is sulfur, thus elemental analysis of PSSS Selemion (Type 2) membrane only shows the presence of sulfur.

A comparison of the pore-size distribution for the New Selemion (Type 2) and PSSS Selemion (Type 2) membranes is given in Fig. 14. After treatment, a slight shift to smaller pore size is evident. The reduction in porosity can be attributed to the fact that, during treatment, the pores of the membrane are partially blocked by the PSSS which has a very high mol. wt. It can thus be concluded that the reduction in vanadium ion permeability and increase in area resistivity of the membrane is partially associated with the reduction in the pore size of the membrane.

A typical charge/discharge curve for a VRB with an AMV membrane is shown in Fig. 15. Continuous charge/discharge
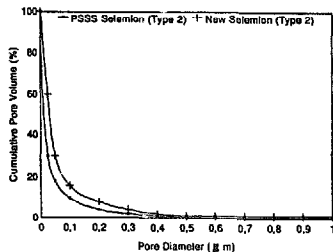

Fig. 14. Comparison of cumulative pore volume (%) for a New Selemion (Type 2) membrane with an average pore size of 0.059 μm and a PSSS Selemion (Type 2) membrane with an average pore size of 0.036 μm.
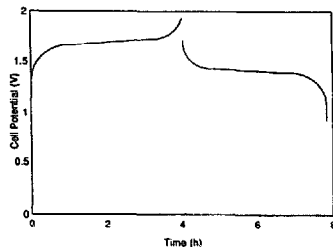

Fig. 15. A typical charge/discharge cycle for AMV membrane at a constant current-density of 30 mA cm^{-2}.

Table 5
Cell performance characteristics of vanadium redox batteries that employ AMV, sulfonated AMV, New Selemion (Type 2) or PSSS Selemion (Type 2) membranes

Membrane	Coulombic efficiency (%)	Voltage efficiency (%)	Energy efficiency (%)
AMV [a]	98.5	81.4	80.2
Sulfonated AMV [a]	96.0	82.5	79.2
New Selemion (Type 2) [b]	98.6	87.5	86.3
PSSS Selemion (Type 2) [b]	100	83.4	83.4

[a] At a current density of 30 mA cm^{-2}.

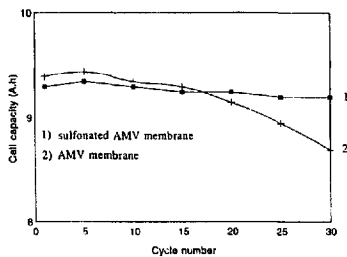[b] At a current density of 40 mA cm^{-2}.

Fig. 16. Cell capacity of a vanadium redox flow battery that employs AMV or sulfonated AMV membranes vs. cycle number.
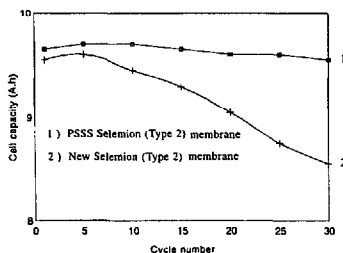

Fig. 17. Cell capacity of a vanadium redox flow battery that employs New Selemion (Type 2) or PSSS Selemion (Type 2) membranes vs. cycle number.

cycling of a VRB with a sulfonated AMV membrane over more than 100 cycles at a current density of 30 mA cm^{-2} showed an overall energy efficiency of 79.2% compared with 80.2% for the untreated AMV membrane. As expected, due to its lower area resistance, the sulfonated AMV membrane has a higher voltage efficiency of 82.5% compared with 81.4% for the AMV membrane. On the other hand, due to the greater permeation of vanadium ions through the sulfonated AMV membrane, a lower coulombic efficiency of

96.0% was obtained compared with 98.5% for the AMV membrane. As seen in Table 5, a VRB with the New Selemion (Type 2) membrane displayed an overall energy efficiency value of 86.3% over more than 50 cycles at a current density of 40 mA cm^{-2}, while the PSSS Selemion (Type 2) membrane gave an overall energy efficiency of 83.4%. As expected, due to its higher area resistance, the PSSS Selemion (Type 2) membrane showed a low voltage efficiency of 83.4% (compared with 87.5% for the untreated counterpart), while its lower permeability for vanadium ions resulted in the highest coulombic efficiency of 100% (compared with 98.6% for the untreated membrane). While the treatment process for the New Selemion (Type 2) membrane resulted in a slight decrease in overall energy efficiency, however, the operation of a VRB improved considerably after the membrane treatment due to the reduced absolute and net water transfer during the charge/discharge cycling.

The capacities of VRBs with AMV, sulfonated AMV, New Selemion (Type 2) or PSSS Selemion (Type 2) membranes were measured as a function of cycle number during charge/discharge cycling; the results are given in Figs. 16 and 17. The results showed that the both treatment methods were able to reduce the capacity loss of a VRB during long-term continuous operation.

4. Conclusions

This study has shown that sulfonation of the anion-exchange AMV membrane leads to the incorporation of some cation-exchange capacity into the membrane that results in reduction in the water transfer across the membrane when used in a vanadium redox battery. The results also show that incorporation of PSSS into the anion-exchange New Selemion (Type 2) membrane leads to partial neutralization of its anino-exchange capacity which, in turn, causes a reduction in water transfer. These methods are capable of reducing the capacity loss and possible reservoir flooding during long-term continuous operation of a vanadium redox battery.

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