

Preparation and evaluation of composite membrane for vanadium redox battery applications

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Abstract

A composite membrane has been fabricated from Daramic (a microporous separator), treated with Amberlite 400CG (an ion-exchange resin), and cross-linked using divinyl benzene. Coulombic, voltage and energy efficiencies of 95, 85 and 83%, respectively, have been achieved when this membrane is employed in the vanadium redox cell. Long-term charge/discharge cycling has been conducted on the membrane for more than 700 cycles (4000 h), without any appreciable drop in performance. The composite membrane satisfies the stability, low area resistance, selectivity, and low-cost requirements for use as a separator in the vanadium redox battery.

Introduction

Redox flow batteries, that are currently being developed for large-scale energy storage applications, require a membrane (or separator) to prevent cross-mixing of the electrolytes in the negative and the positive half-cells, whilst still allowing the transport of ions to complete the circuit during the passage of current. The ideal membrane should be permselective to the charge-carrying ions in order to provide high ionic conductance. In the vanadium redox cell [1], the membrane must suppress the diffusion of vanadium ions from one half-cell to the other without hindering the transport of the charge-carrying hydrogen ions. Both cation- and anion-exchange membranes have been tested and found to be satisfactory for use in the vanadium redox battery [1, 2]. This suggests that in the presence of high concentrations of hydrogen ions, as are required in the vanadium redox cell electrolyte, the transport of the charge-carrying hydrogen ions through the anion-exchange membranes is not severely impeded.

To date, the cation-exchange membrane, Selemion CMV (Asahi Glass Co.) has been the most widely used material in the research and development of the vanadium redox battery at the University of New South Wales. In fact, recent tests with a 1 kW prototype battery have shown that overall energy efficiencies of up to 90% can be achieved [3]. Despite these excellent results, the long-term stability of the Selemion CMV membrane in the vanadium redox cell is limited by the oxidizing nature of the V(V) electrolyte. By contrast, much higher stabilities, together with high energy efficiencies, are currently being exhibited by various anion-exchange membranes, and

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long-term testing in large battery stacks is presently being undertaken. Although the latter membranes are relatively inexpensive in comparison with the highly stable teflon-based membranes, the availability of an even cheaper and chemically inert separator material will reduce appreciably the cost of commercial redox battery systems.

In a separate paper [4], a report has been given of significant improvements in the ion selectivity of the Daramic microporous separator after treatment with Amberlite CG400 and further cross-linking using divinyl benzene. This treatment also reduced the pore size of the Daramic material.

In this communication, the parameters of the above treatment that affect both the selectivity and the area resistance of the membrane are investigated. The experimental conditions have been optimized to produce a membrane with high selectivity and low area resistance so as to meet the requirement of the vanadium redox battery.

Experimental

Membrane preparation

The composite membranes were prepared by immersing Daramic material (W. R. Grace; size: 12×14 cm) for 24 h in a mixture of divinyl benzene (DVB) and methanol (total volume: 50 ml) containing 1 g of Amberlite 400CG (Rohm & Haas). The DVB:methanol (vol.%) ratio was varied from 10 to 60%. The 'soaked membranes' were transferred to the reactor in which 1 g of NaS₂O₈ (Sigma Chemical Co.) was added to 200 ml of distilled water at 80 °C. The temperature of the reactor was slowly increased to 90 °C; this required a period of about 10 min. Polymerization was continued for 1 h at 90 °C and then for 1 h at 95 °C. Methanol was used as a diluent for the DVB and facilitated the penetration of the initiator, NaS₂O₈, into the membrane. Daramic separators with thicknesses of 0.15, 0.20, and 0.23 mm were employed.

Membrane characterization

The membrane diffusivity and the area resistance were evaluated by the methods described in ref. 4.

The electrolyte uptake of the membrane was determined by soaking the dry sample (weight W_d) in 1 M V(III)+1 M V(IV) (referred to as 2 M V^{3.5+}) in 2.5 M H₂SO₄ for 24 h. The membrane was taken out of the solution, wiped with filter paper and weighed to determine the final weight (W_s). The percent of electrolyte uptake was calculated using the formula:

$$E = (W_s - W_d)/W_d \times 100 \quad (1)$$

The ion-exchange capacity (IEC) of the membrane was determined by the method of Fisher and Kunin [5]. The composite membrane was converted to the Cl⁻ form by soaking the membrane in 0.1 M NaCl solution for 24 h. The excess Cl⁻ ions in the membrane were leached out by washing with ultra-pure water until the Cl⁻ concentration was <1 ppm. The IEC of the sample was obtained by leaching the Cl⁻-form membrane in fresh 0.05 M Na₂SO₄ solution for 5 days. This period ensured that all the chloride was removed. The IEC of the membrane was determined by analysing the amount of chloride in the leachate using ion-exchange chromatography (Waters, model 590, with IC-Pack column). The IEC is expressed as milliequivalents per gram of dry sample (mEq/dg), i.e.,

$$\frac{\text{millimole of Cl}^-}{\text{dry sample weight}} = \frac{\text{mEq. anion-exchange capacity}}{\text{g of dry Cl}^- \text{-form membrane}} \quad (2)$$

The average pore-size distribution of the membrane was determined using the bubble point technique with a Coulter porometer (Coulter Electronics Ltd.). The membrane was cut into discs of the required size for testing. The fluid used to wet the membrane was Porofils supplied by Coulter Electronics Ltd.

Membrane stability and performance in charge/discharge test

The redox flow cell and the set-up for the charge/discharge test are described in ref. 6. The cell was charged/discharged at constant current density. The charging and discharging current densities were equal and were in the range 20 to 80 mA cm⁻². A long-term charge/discharge cycle test was conducted at a constant current density of 40 mA cm⁻². The state-of-charge (SOC) of the electrolytes in both half-cells was balanced periodically when the performance of the cell dropped to an undesirable level. An imbalance in the SOC of the two half-cells can occur when air penetrates the unsealed negative half-cell causing oxidization of V(II) to V(III). No effort was made to seal the cell nor was nitrogen used to maintain an inert atmosphere in the negative half-cell. The cell was periodically rebalanced, however, by exchanging an appropriate volume of the charged positive (V(V)) solution with an equivalent volume of V(IV) solution. This procedure enabled the cell capacity to be fully restored by equalizing the SOC of the two half-cell electrolytes.

Results and discussion

Composite membrane properties

The area resistance and diffusivity (K_s) of the composite membrane after modification, are shown in Table 1 as a function of the DVB:methanol ratio used in the treatment. The degree of cross-linking would be expected to increase with the volume of DVB used in the treatment. The degree of cross-linking is usually determined by solvent extraction. A solvent that dissolves the polymeric material (membrane), but

TABLE 1

Area resistance and diffusivity values of composite membranes (0.15 mm)

<i>Treated Daramic</i> Divinyl benzene:methanol (vol.%)	Area resistance (Ω cm ²)	Diffusivity ($K_s \times 10^4$) (cm min ⁻¹)
0:100	0.95	6.8
10:90	1.24	11.0
20:80	0.77	9.5
30:70	1.42	6.4
40:60	1.25	1.6
50:50	7.68	1.1
60:40	7.12	3.2
<i>Untreated Daramic</i>		
0.15 mm	0.30	13.0
0.20 mm	0.39	12.0
0.23 mm	0.33	8.1

not the cross-linked polymer, is employed. The percentage of undissolved polymeric material represents the degree of cross-linking. In the present study, however, the actual percentage of cross-linking of the composite membrane was not determined since the base material was not soluble in any of the solvents examined. This could be due to the silica that was incorporated in the base material.

The area resistance of the composite membrane is seen to rise sharply when more than 40 vol.% DVB was used in the treatment of the membrane. On the other hand, the diffusion coefficient (K_s) of the composite membrane is lowered by a factor of 10 for 40 to 50 vol.% DVB. The swelling of the membrane is reduced by cross-linking using DVB. The degree of swelling decreases with increased cross-link density. The more highly cross-linked membranes are less permeable because of the reduced internal volume of the network.

When a Daramic sample was soaked in a mixture of Amberlite and ethanol, no significant improvement in selectivity was observed. This suggests that, without any cross-linking, the adsorbed ion-exchange resin on the substrate was incapable of preventing the vanadium ions from permeating through the membrane. Within the large pores of the Daramic, therefore, the ionic groups of the adsorbed ion-exchange resin are unable to produce a significant repulsion effect on the vanadium co-ions and, consequently, there is no reduction in the permeability of the membrane to vanadium ions. Furthermore, when Daramic was treated with DVB (without using Amberlite) to modify the membrane, no significant decrease in diffusivity was observed. The reduction in pore size of the membrane with cross-linking alone was thus ineffective in blocking the migrating ions. The above experiments show that the effect of the present treatment is to reduce the size of the pores with cross-linking while simultaneously 'locking' in the ion-exchange groups within the pores of the separator.

Following the results obtained in Table 1, composite membranes were prepared using 40 vol.% DVB with Daramic material of different thicknesses. The area resistance and diffusivity values of the resulting composite membranes are presented in Table 2.

Composite membranes obtained with substrates of different thickness exhibit only a slight variation in area resistance and diffusivity. For each of the different thicknesses employed, a significant improvement in selectivity was achieved with the treatment (cf., diffusivity of untreated Daramic listed in Table 1). The composite membrane with the highest selectivity was obtained with the 0.15 mm Daramic. This is the opposite of that expected since for the untreated membrane (Table 1), the 0.23 mm Daramic has the lowest diffusivity value. The probable reason for this finding is the different structural properties of the 0.15 and the 0.23 mm untreated Daramic. The technical

TABLE 2

Area resistance and diffusivity of composite membranes prepared with 40 vol.% divinyl benzene (DVB)

Composite membrane thickness (mm)	Area resistance ($\Omega \text{ cm}^2$)	Diffusivity $K_s \times 10^4$ (cm min^{-1})
0.15	1.25	1.6
0.20	1.60	2.5
0.23	1.50	2.4

information provided by the manufacturer revealed that the 0.15 mm membrane is in fact obtained from the 0.23 mm membrane by a hot-rolling process. This could change the tortuosity of the 0.23 mm membrane and would explain the observed selectivity behaviour.

The properties of the composite membrane (0.15 mm) produced with 40 vol.% DVB and those of the untreated microporous membrane, Daramic (0.15 mm) are given in Table 3. The composite membrane produced with 40 vol.% DVB exhibits a six-fold increase in area resistance while the diffusivity is reduced by a factor of eight. The average pore-size for Daramic determined using the bubble point technique was $0.095 \mu\text{m}$ and this value corresponds well with the manufacturer's specification, viz., $0.1 \mu\text{m}$. In fact, the same average pore-size was found for all three thicknesses of the Daramic material. Figure 1 shows the differential-pore-number distribution of Daramic (0.15 mm). The differential number of pores (expressed as a percentage) corresponds to the percentage of pores at each pore-size. The pore-size distribution of Daramic is thus seen to fall within a very narrow range. The composite membrane,

TABLE 3

Properties of composite membrane (40 vol.% divinyl benzene (DVB)) and Daramic (0.15 mm)

Properties (units)	Daramic (0.15 mm)	Composite membrane
Area resistance ($\Omega \text{ cm}^2$)	0.3	1.9
Diffusivity (cm min^{-1})	1.3×10^{-3}	1.6×10^{-4}
Average pore-size (μm)	0.095	<0.060
Ion-exchange capacity (mEq/dg)		0.4
Electrolyte uptake (%)	140	60

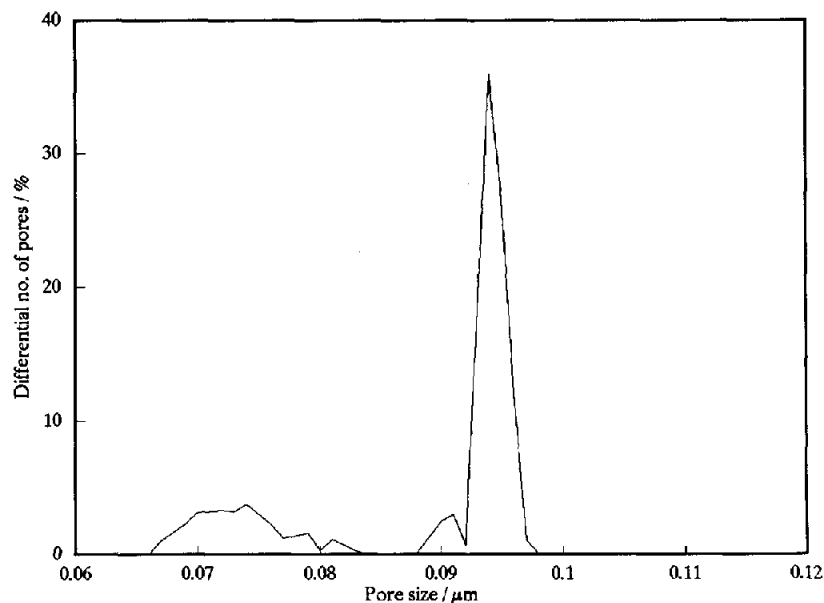


Fig. 1. Differential-pore-number vs. pore-size distribution for untreated Daramic (0.15 mm).

on the other hand, has pore sizes $< 0.06 \mu\text{m}$; these sizes are beyond the limit detectable by the Coulter porometer.

The IEC of the composite membrane was found to be 0.4 mEq/dg. This value is low compared with those usually exhibited by ion-exchange membranes, viz., 1–5 mEq/dg. The incorporation of even a very small IEC can, however, influence significantly the transport properties of the membrane. The electrolyte uptake of the membrane was tested by soaking in a solution of 2 M $\text{V}^{3.5+}$ in 2.5 M H_2SO_4 , since in the vanadium redox battery application, the predominant ions in the pores of the membrane are V(III) and V(IV). As seen in Table 3, the electrolyte uptake of the composite membrane shows a marked decrease of $\sim 80\%$.

From the above-mentioned properties of the composite membrane, the increase in selectivity can be attributed to the combined effects of the decrease in pore-size, or a change in tortuosity of the membrane, and the incorporation of ion-exchange sites into the cross-linking element. Tortuosity is defined as the effective path length of the migrating ions through the network of the interlocking pores in the membrane. This network acts as a physical barrier to the migrating ions so that the ion mobility is effectively reduced with increase in tortuosity. For large pore-sizes, the transport of the co-ions (i.e., vanadium ions) is hindered by the ion-exchange resin only near the pore walls. With decrease in pore size (due to cross-linking), the ion-exchange sites incorporated into the cross-linking element would be more effective in excluding the co-ions.

The increase in area resistance of the composite membrane can be attributed to the decrease in the percentage of electrolyte uptake [7]. The electrical conductivity is directly proportional to the concentration of the current-carrying species in the membrane; this species is predominantly H^+ ions in the vanadium redox cell.

The membrane treatment thus partially blocks the pores and produces a thin surface layer on the Daramic substrate. The resulting membrane is more selective and the diffusivity for vanadium ions is greatly reduced. Although composite membranes prepared using 40 vol.% DVB are mechanically weaker than untreated Daramic material, membranes sizes as large as 40×60 cm have been employed successfully in cell charge/discharge testing without any splitting or tearing problems.

Membrane stability and performance in charge/discharge test

The composite membrane (0.15 mm) produced with 40 vol.% DVB was chosen for performance testing in a small vanadium redox test cell with an electrode area of 25 cm^2 . The cell contained 65 ml of 2 M $\text{V}^{3.5+}$ in 3 M H_2SO_4 in each half-cell and had a theoretical capacity of 3 A h. A typical charge/discharge voltage profile obtained at 20 mA cm^{-2} is shown in Fig. 2. From this data, the coulombic, voltage and energy efficiencies were calculated as 94, 90 and 85%, respectively.

The efficiencies of the cell obtained at various current densities are shown in Fig. 3. The coulombic efficiency remains fairly constant within the range of current densities investigated, while the voltage efficiency declines with increasing current density due to increased internal resistance losses. The overall energy efficiency thus falls with increasing current density; a maximum of 85% is observed at 20 mA cm^{-2} . The efficiencies obtained for the composite membrane are comparable with those obtained with the cation-exchange membrane, Selemion CMV [6].

The long-term cycling data for the composite membrane (40 vol.% DVB) obtained at a charge/discharge current density of 40 mA cm^{-2} are presented in Fig. 4. The average current, voltage and energy efficiencies over 700 cycles (4000 h) were 95, 79 and 75%, respectively. The highest cell efficiencies, obtained at the 550th cycle, were

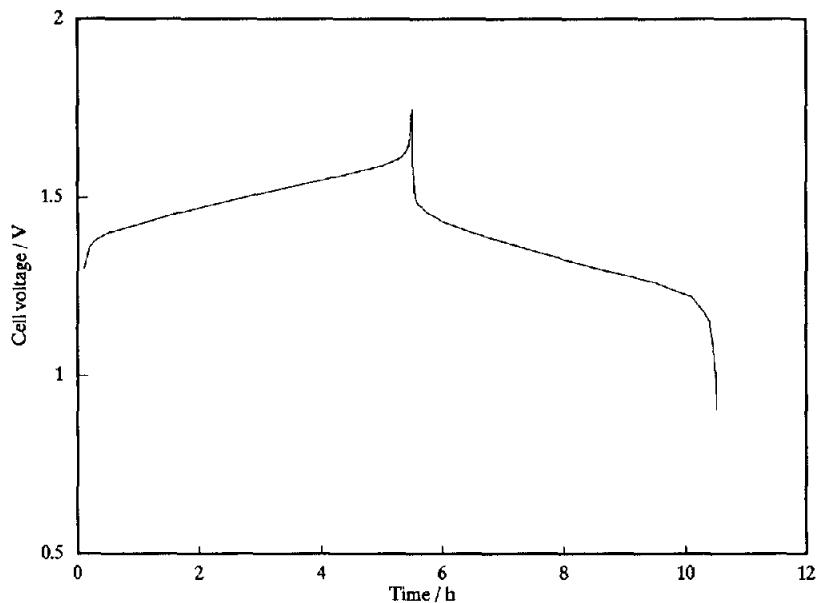


Fig. 2. Typical charge/discharge voltage profile of vanadium redox cell. Charging and discharging current densities = 20 mA cm^{-2} ; electrode area = 25 cm^2 ; electrolyte = $2 \text{ M V}^{3,5+}$ in $3 \text{ M H}_2\text{SO}_4$.

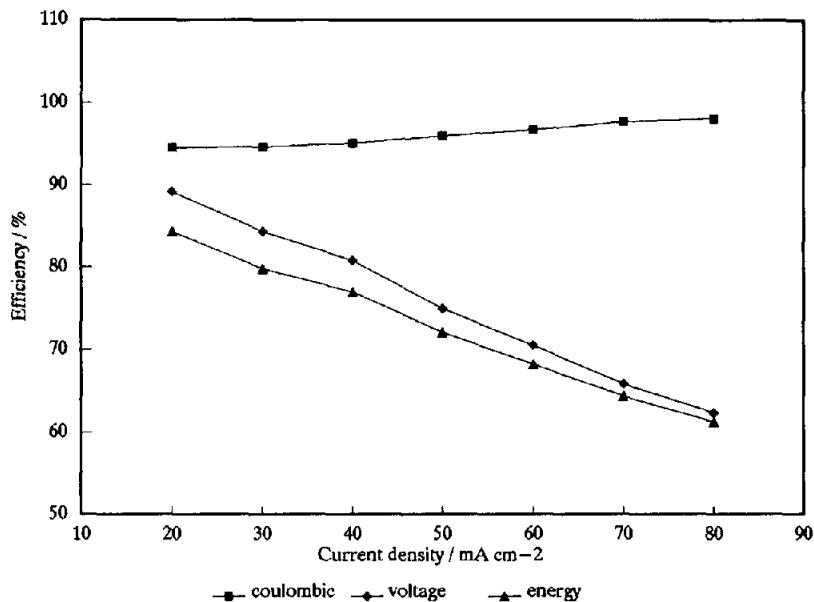


Fig. 3. Cell efficiencies with 0.15 mm composite membrane, (40 vol.% divinyl benzene (DVB)) at various current densities.

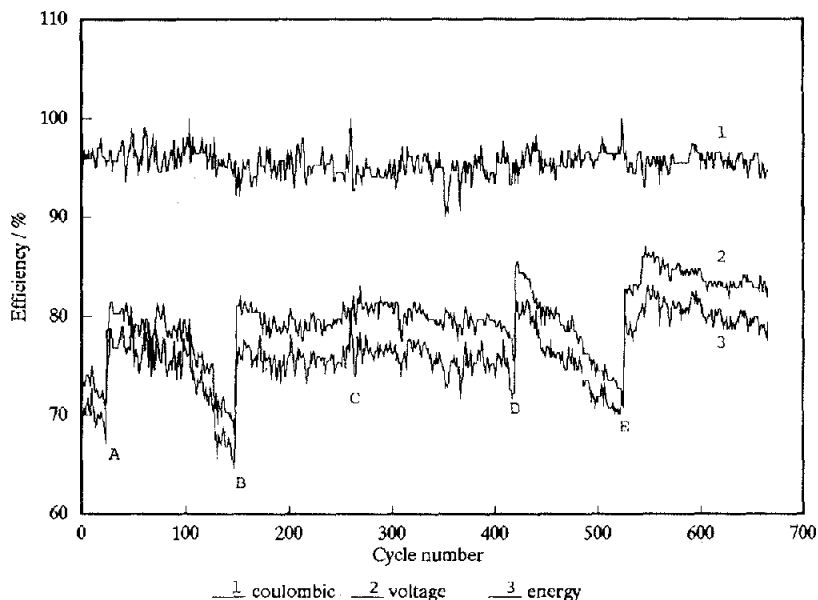


Fig. 4. Cell efficiencies vs. cycle number for vanadium redox cell employing 0.15 mm composite membrane; charging and discharging current densities = 40 mA cm^{-2} .

96, 85 and 83% for current, voltage and energy, respectively. The coulombic efficiency fluctuated between 93% and 100%, while the voltage efficiency exhibited a gradual decrease. The latter was due to the air oxidation of the negative half-cell electrolytes that resulted in an imbalance in the SOC of the electrolytes. This imbalance was also influenced by a volumetric cross-over of the electrolytes across the membrane in either direction during cycling. At points A to E, the solutions of the cells were rebalanced so as to bring the SOC of each of the half-cell electrolytes to the same level and restore the capacity of the system. This procedure also allowed the voltage efficiency of the cell, that declined after successive cycles, to recover.

At the 10th cycle, the cell resistance measured at 50% SOC was 2.65 and $2.75 \Omega \text{ cm}^2$ for charging and discharging, respectively. At the 550th cycle, the corresponding values of the cell resistance were 2.33 and $2.54 \Omega \text{ cm}^2$. This decrease in the cell resistance during cycling is believed to be due to activation of the graphite felt electrodes. The latter reduces the activation overvoltage during charging/discharging and results in a steady overall increase in voltage efficiency, as observed in Fig. 4.

The above long-term cycle tests demonstrate that the composite membrane is both chemically stable and resistant to fouling in the vanadium redox cell system. The composite membrane thus possesses the properties required of a separator for use in a redox battery.

Conclusions

A composite membrane has been developed using Daramic as substrate and the Amberlite ion-exchange resin. Further cross-linking using DVB has resulted in properties that are suitable for application in redox batteries. The performance of the membrane

in the charge/discharge testing of a vanadium redox cell is comparable with that observed with ion-exchange membranes available commercially. The chemical stability of the membrane was found to be excellent and the membrane was not susceptible to fouling.

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