Modification of a Composite Membrane for Redox Flow Battery Applications

Touraj Mohammadi* and Vahid Haddadi-Asl**
School of Chemical Engineering and Industrial Chemistry, The University of New South Wales, Sydney, Australia

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ABSTRACT

A composite membrane from a single sheet of Daramic, a microporous separator, is prepared by incorporation of an anion exchange resin, Amberlite CG 400, and further cross-linking with divinylbenzene [1]. Further modification and characterization of the composite membrane are now described. A detailed FESEM, TGA, FT-IR and $^{13}$C NMR analyses of the composite membrane have been carried out. The ion exchange capacity of the composite membrane has been also evaluated. Formation of thin layer of polydivinylbenzene after cross-linking is confirmed by morphological studies. None of the experiments show incorporation of the ion exchange resin into the composite membrane.

Key Words: polymerization, cross-linking, divinylbenzene, ion exchange, composite membrane

INTRODUCTION

Membranes and separators are widely used in batteries and fuel cells, as well as in electrochemical processes in many industrial applications. More and more novel electrochemical processes are being developed which require a membrane or a separator to play in integral function in the whole process. In the vanadium redox flow battery, the function of a membrane/separator is to prevent cross mixing of the positive, V(IV) and V(V); and negative, V(II) and V(III), electrolytes in sulphuric acid solution, while still allowing the transport of ions to complete the circuit during the passage of current. The evaluation of commercial ion exchange membranes for the vanadium redox battery has shown that except for a few which are currently too expensive for commercial use, most are unsuitable due to their poor chemical stability in the vanadium solutions.

Modification of low cost separators can lead to significant cost reduction for the production of a commercial redox flow battery. Daramic, a microporous separator, has been chosen due to its low cost and also its chemical stability in the V(V) solution. The approach taken to impart selectivity to
the separator is to partially block or to reduce the pore size, as well as to impart some ion selective capability to the separator.

It is believed that direct introduction of ion exchange groups, sorption of an ion exchange resin onto the porous structure of the separator and further cross-linking should lead to the production of an ion selective membrane which has good performance in the vanadium redox cell [1].

A number of polyelectrolytes and ion exchange resins are tested with or without further cross-linking with divinylbenzene (DVB) [2], and the best results are obtained by soaking of Daramic in a mixture of an anion exchange resin (Amberlite CG 400), divinylbenzene (DVB) and methanol. DVB is cross-linked into the porous structure of Daramic in the next step.

The composite membrane obtained by this method gives an overall energy efficiency of 75% at a charge/discharge current density of 40 mAX cm⁻² when tested in the vanadium redox flow battery, compared with only 40% for the untreated Daramic.

However, this study has revealed that in the absence of Amberlite, cross-linking of Daramic with DVB can produce a composite membrane with almost the same permeability of vanadium ions and conductivity as those prepared using the Amberlite. Also, this has been surprising since the initial particle size of the Amberlite is found to be much greater than the pore size of the Daramic.

Further characterization of the composite membrane which has been recently carried out, however, has shown that the procedure does not impart any significant ion exchange capability into the composite membrane, although the presence of the Amberlite seems, to some extent affect the final properties of the composite membrane. The composite membrane produced by this method does show properties which makes it suitable for use in the vanadium redox flow battery.

Further modification and optimization of the membrane treatment method have been undertaken and are described in this paper together with the results of detailed characterization of the membrane produced.

**EXPERIMENTAL**

**Membrane Preparation**

A piece of Daramic of 0.1 μ pore size (W.R. Grace; size: 12×14 cm) was soaked for 12 h in a solution of DVB, a selected solvent [2, 3] and Amberlite CG 400 of mesh size 40–80 μ (an anion exchange resin; 1 g per 50 mL of the solution). Daramic consists of 44% polyethylene, 54% silica and 2% mineral oil as a stabilizer against oxidation. Amberlite is made by copolymerization of DVB and styrene with further incorporation of some functional groups. The optimization experiments showed that immersion periods of Daramic in the mixture of more than 12 h do not affect the results. The selected solvents were methanol, ethanol and acetone whose optimized ratios were determined. They were selected because they are miscible with DVB and water and also they have different constants. A cation exchange resin, Amberlite CG 120, of 40–80 μ mesh size was also used to incorporate some cation exchange capacity into the sample.

The soaked Daramic was transferred to a reactor in which a solution of sodium persulphate (5 g per 100 mL of distilled water) was heated at 95 °C. Sodium persulphate was used as an initiator for polymerization of DVB. The temperature was increased to 98 °C in 10 min. The reaction time was being different for each solvent and for acetone and ethanol shorter times were required.

**Membrane Characterization**

The area resistance and the diffusion coefficient (Kₐ) of the membranes were evaluated by the methods described in ref 3. For the diffusion coefficient measurements, the membrane was exposed to a solution of 1M VOSO₄ in 2M H₂SO₄ on one side and a solution of 1 M MgSO₄ in 2 M H₂SO₄ on another side. The salt 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.

The water transfer across the membranes
was evaluated by method described in ref 4.

Negative and positive electrolytes at 50% state of charge (1M V(II) + 1M V(III) on one side and 1M V(IV) + 1M V(V) on the other side) were used to evaluate the water transport behaviour of the composite membranes. Generally, for cation exchange membranes, the solution transfer is from the negative half cell to the positive half cell. The solution transfer for anion exchange membranes and non-selective membranes is from the positive side to the negative side [4].

The ion exchange capacity (IEC) of the membranes was evaluated by the method described in ref 5. The membrane in Na⁺ form was soaked in 1 N HCl solution to convert it to an H⁺ form membrane. The membrane was then immersed in a known volume of 0.05 N KOH solution for 48 h at room temperature. The amount of H⁺ (mmol) was determined by back titration with a 0.05 N HCl solution. The membrane in Cl⁻ form was soaked in 1 N KOH solution to convert it to an OH⁻ form membrane. This was then immersed in a known volume of 0.05 N HCl solution for 48 h at room temperature. The amount of OH⁻ (mmol) was determined by back titration with a 0.05 N 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.

Morphological studies were undertaken with a field emission scanning electron microscope (FESEM). Nuclear magnetic resonance (NMR) and Fourier transform infrared (FT-IR) spectra were also obtained to establish whether any ion exchange resin was incorporated into the composite membrane using Bruker MSL 300 NMR and Perkin Elmer 2000 FT-IR machines, respectively.

Thermogravimetric analysis (TGA) studies were performed using a Du Pont Instruments 951 thermogravimetric analyzer.

### RESULTS AND DISCUSSION

The solvent is the medium between the monomer and distilled water. The initiator can transfer from the water to the monomer through the solvent. Another function of the solvent 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 in the pores.

The dielectric constants of the materials and chemicals used in the membrane treatment are presented in Table 1. The approximate composition of Daramic considered as (45%) polyethylene and (55%) silica. The dielectric constant of Daramic (D₄) was directly from that of polyethylene and silica as follows:

\[
D_4 = D_{\text{polyethylene}} \times \text{polyethylene} \% + D_{\text{silica}} \times \text{silica} \%
\]

From the table, it can be seen that the difference between dielectric constants of solution and substrate is lower when acetone is used as a solvent (D₃−D₄) and the difference is higher when methanol is used as a solvent (D₁−D₄). The adsorption of polyelectrolyte has been shown to depend strongly on the charge of the polyelectrolyte and the difference between the dielectric constant of the solution and that of the substrate [6]. The latter may also affect the polymerization of the monomer into the swollen substrate. The results show that the vanadium ion permeability of the

<table>
<thead>
<tr>
<th>Substance</th>
<th>Dielectric constant</th>
<th>Substance</th>
<th>Dielectric constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>DVB</td>
<td>2.60</td>
<td>Solution (1)</td>
<td>20.62</td>
</tr>
<tr>
<td>Methanol</td>
<td>32.63</td>
<td>Solution (2)</td>
<td>15.62</td>
</tr>
<tr>
<td>Ethanol</td>
<td>24.30</td>
<td>Solution (3)</td>
<td>13.46</td>
</tr>
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<td>Acetone</td>
<td>20.70</td>
<td>D₋D₄ (4)</td>
<td>17.72</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>2.15</td>
<td>D₋D₅ (5)</td>
<td>12.72</td>
</tr>
<tr>
<td>Silica</td>
<td>3.51</td>
<td>D₋D₆ (6)</td>
<td>10.56</td>
</tr>
<tr>
<td>Daramic</td>
<td>2.90</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(1) DVB: Methanol (40:60); (2) DVB: Ethanol (40:60); (3) DVB: Acetone (40:60).
Modification of a Composite Membrane for Redox Flow Battery Applications

Table 2. Characteristics of different composite membranes.

<table>
<thead>
<tr>
<th>Composite membrane assignment</th>
<th>DVB (%)</th>
<th>Methanol (%)</th>
<th>Ethanol (%)</th>
<th>Acetone (%)</th>
<th>Reaction time (h)</th>
<th>Diffusivity, $K_x \times 10^4$ (cm/min)</th>
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<tr>
<td>1</td>
<td>25</td>
<td>75</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>7.95</td>
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<tr>
<td>2</td>
<td>40</td>
<td>60</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>2.84</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>60</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>2.77</td>
</tr>
<tr>
<td>4</td>
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<td>50</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>1.10</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>0</td>
<td>75</td>
<td>0</td>
<td>4.5</td>
<td>6.84</td>
</tr>
<tr>
<td>6</td>
<td>40</td>
<td>0</td>
<td>60</td>
<td>0</td>
<td>1.5</td>
<td>4.75</td>
</tr>
<tr>
<td>7</td>
<td>40</td>
<td>0</td>
<td>60</td>
<td>0</td>
<td>3</td>
<td>2.15</td>
</tr>
<tr>
<td>8</td>
<td>50</td>
<td>0</td>
<td>50</td>
<td>0</td>
<td>3</td>
<td>0.384</td>
</tr>
<tr>
<td>9</td>
<td>25</td>
<td>0</td>
<td>0</td>
<td>75</td>
<td>3</td>
<td>5.90</td>
</tr>
<tr>
<td>10</td>
<td>40</td>
<td>0</td>
<td>0</td>
<td>60</td>
<td>1.5</td>
<td>2.27</td>
</tr>
<tr>
<td>11</td>
<td>40</td>
<td>0</td>
<td>0</td>
<td>60</td>
<td>3</td>
<td>1.41</td>
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<td>0</td>
<td>0</td>
<td>50</td>
<td>3</td>
<td>0.267</td>
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</table>

membranes should increase for the different solvents in the order using acetone, ethanol, and methanol, respectively. The more selective the composite membrane, the less the diffusion of the vanadium ions through the composite membrane. From the results presented in Table 2, it may be said that the lower the difference between the dielectric constant of the solution and that of the substrate, the more selective the composite membrane, or in other words, the higher degree of polymerization of the monomer.

With the higher ratio of DVB to solvent which leads to a greater degree of polymerization, the higher degree of cross-linking of composite membrane would occur. Results also show that DVB/solvent ratios less than 40% cannot lead to the production of a composite membrane with low enough permeability of the vanadium ions for application in the vanadium redox cell, where a diffusivity of less than $2 \times 10^{-4}$ cm/min being considered the maximum value to allow practical coulombic and voltage efficiencies to be achieved in the system.

Three samples were prepared for each experiment and the presented results are averages. The typical divergence between samples being less than 12%, and the diffusivity measurements have been carried out at ambient temperature.

The results in Table 2 show that the lowest permeability of the vanadium ions is obtained when acetone and ethanol are used as solvents. Also, increasing the reaction time leads to a decrease in the diffusivity, however, in general, the change in diffusivity of vanadium ions through the composite membranes after 3 h in the reactor was not significant. In the preparation of the composite membranes, the cation exchange resin, Amberlite CG 120 was used, as well as the anion exchange resin, Amberlite CG 400.

The results presented in Table 3 show that with acetone as solvent, the composite membrane prepared with the cation exchange resin had a lower area resistance but slightly higher vanadium permeability than when the anion exchange resin was employed. In general, the permeation of cations through a cation exchange membrane is higher than that through an anion exchange resin due to the Donnan exclusion effect. This effect states that the diffusion of similar charge ions is ideally restricted across an ion exchange membrane, while counter ions can diffuse freely. The results in Table 3 are the average values of three samples. The reaction time for all samples was 3 h.

An experiment (sample designated as 4 in Table 3) was carried out with no Amberlite, and a slight difference in area resistance and diffusivity of
Table 3. Area resistivity and diffusivity of composite membranes.

<table>
<thead>
<tr>
<th>Composite membrane designates*</th>
<th>DVB (%)</th>
<th>Acetone (%)</th>
<th>Ethanol (%)</th>
<th>Amberlite CG 120 (cation g/L)</th>
<th>Amberlite CG 400 (anion g/L)</th>
<th>Diffusivity, $K \times 10^{-4}$ (cm/min)</th>
<th>Sheet resistance, $R$ (Ω.cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40</td>
<td>0</td>
<td>60</td>
<td>0</td>
<td>20</td>
<td>2.15</td>
<td>2.20</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>60</td>
<td>0</td>
<td>0</td>
<td>20</td>
<td>1.41</td>
<td>3.63</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>60</td>
<td>0</td>
<td>20</td>
<td>0</td>
<td>2.94</td>
<td>2.56</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>0</td>
<td>60</td>
<td>0</td>
<td>0</td>
<td>3.02</td>
<td>1.84</td>
</tr>
</tbody>
</table>

* Four samples were selected for evaluation, in which numbers 1 and 2 are the sample numbers indicated as 7 and 11 in table 2, and the numbers 3 and 4 are the new samples considered for resistivity testing.

The treated sample was observed. Area resistance and diffusivity measurements of sample numbers 1 & 2, and 3 & 4 in Table 3 were carried out simultaneously so that the variation of ambient temperature did not affect the results.

It is well known that the higher ambient temperature, the slightly higher the permeability of the vanadium ions and also the conductivity of the composite membrane.

It must be mentioned that the thickness of Daramic was increased after treatment. The thickness of Daramic used in this study was 0.20 mm, while the thickness of the composite membrane varied from 0.23 mm to 0.25 mm depending on the reaction time and the solvent employed in the process. The thickness of the composite membranes was measured when they were dried.

Further studies were undertaken to establish whether the ion exchange resin was incorporated into the substrate during the membrane modification process. The IEC measurements of the composite membranes, prepared in this study, using either amberlite CG 400 or amberlite CG 120 showed neither an anion exchange nor a cation exchange capacity, respectively, after treatment. From the present results, therefore, it can be concluded that no ion exchange capability is incorporated into the Daramic during the modification process.

Water transport measurements of the composite membranes were carried out. Surprisingly, the direction of the electrolyte transfer was the same...
for all of the samples, and it occurred from the positive half cell to the negative half cell.

Earlier water transport studies of variety of commercial ion exchange membranes in the vanadium redox cell have shown that the water transport through anion exchange membranes in the vanadium redox cell is from the positive half cell to the negative half cell, but for cation exchange membranes it is the opposite. This phenomenon is common to ion exchange membranes and it is due to the fact that the transfer of water across different membranes is the net effect of a number of processes: the water transported by ions moving under the concentration gradient, that carried by the charge carrying species, and that due to the osmotic pressure difference between the two solutions [8]. Since the observed water transfer of the composite membranes prepared using anion and cation exchange resins was the same, it can be concluded that the procedure used was not able to incorporate any ion exchange capability into the treated membranes.

Using the FESEM micrographs shown in Figures 1–4, the membrane morphology of the untreated Daramic and treated Daramic membranes for both the surface and the cross section can
Figure 7. $^{13}$C NMR spectrum of Daramic.

Figure 8. $^{13}$C NMR spectrum of composite membrane.

The FT-IR spectra of Daramic and the composite membrane using KBr pellet technique are shown in Figures 5 and 6. In Figure 5, the predominant peak of the FT-IR spectrum in the range of 1700–600 cm$^{-1}$ is at about 1100 cm$^{-1}$ and is due to the high silica content in Daramic.

In Figure 6, however, another two peaks of the FT-IR spectrum for the composite membrane can be observed at 1630 cm$^{-1}$ (C=C stretching vibration) and 700 cm$^{-1}$ (-CH out-of-plane deformation and benzene ring substitution) [8] confirming the incorporation of DVB with Daramic. In Figure 6, the silica peak at 1100 cm$^{-1}$ is still evident, but its intensity is subsided. This also shows that Daramic surface was covered with a polydivinylbenzene layer.

Therefore, it can be concluded that Daramic

be studied. Chromium was used to coat all samples except for Daramic in the surface analysis. In this case, the photographs were not clear. So gold was employed for coating of the sample. The photograph may thus be slightly different from the real surface, as chromium particles are much finer than gold particles.

Generally, the photographs show that cross-linking of Daramic leads to a change in the surface morphology of the membrane. The pores on the surface of the treated Daramic membrane (black area in Figure 3) are smaller than those on the surface of the untreated Daramic membrane in Figure 1.

Cross-sectional micrographs of the treated and untreated Daramic membranes are also different. Formation of thin surface layers on both sides of the Daramic after cross-linking was also confirmed. The layers are thought to be polymerized DVB.
was cross-linked with DVB after treatment.

Figures 7 and 8 represent the $^{13}$C NMR spectra of Daramic and the composite membrane, respectively. In Figure 7 the peak characteristic of polyethylene is evident at 32 ppm. The peak area of the benzene ring in $^{13}$C NMR is at about 127 ppm, and the peak areas of polyethylene and benzene ring at 32 and 127 ppm are also evident in Figure 8. These result thus confirm the presence of DVB on the surface of the composite membrane. The peak area of Amberlite CG 400 which is at 52 ppm is not observed in Figure 8 and again shows that there is no ion exchange resin incorporated into the treated Daramic.

TGA was also employed to determine the composition of Daramic and the composite Daramic. Figures 9 and 10 show these materials respective TGA traces. The TGA trace of Daramic shows a SiO$_2$ content of about 58.8%, while that of the composite membrane indicates a SiO$_2$ content of about 52.1%. The decrease in the SiO$_2$ content is due to the weight gain, which is 6.7%, due to polymerization of DVB during the treatment.

A comparison of the pore size distribution for the composite membrane and Daramic is shown in Figure 11. A shift to smaller pore size after treatment is evident. The reduction in porosity is expected and is due to the polymerized DVB networks formed on the surface and to some extent in the porous structure of the Daramic.

The overall energy efficiency measurements of the vanadium redox flow cell employing the composite membrane show a high value of 85% at a current density of 20 mA.cm$^{-2}$. The long term cycling (700 cycles= 4000 h) of the vanadium redox flow cell at a charge/discharge current density of 40 mA.cm$^{-2}$ show an overall energy efficiency of 75% averaged over the 700 cycles. The efficiencies obtained by employing the composite membrane are comparable with those obtained with the cation exchange membrane, Sellemion CMV (Asahi Glass Co., Japan).

**CONCLUSION**

The area resistance, diffusivity, FESEM, TGA and pore size distribution results show that an interpenetrating polymer network of polymerized DVB can be formed within the porous structure of Daramic and that the network is able to partially block or reduce the porous structure of the substrate. The water transfer measurements, IEC, FT-IR and $^{13}$C NMR spectrographs indicate that the incorporation of the ion exchange resin into the substrate does not occur, however, the slight difference in vanadium ion permeability and area resistance obtained in the presence of the Amberlite suggests that there may be some catalytic effect of the ion exchange resin on the polymerization reaction. Incorporation of ion exchange groups into Daramic by another methods are studied to allow a higher selectivity to be achieved at lower membrane area resistance [8, 9].

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