

## Poly(vinylbenzyl chloride-glycidyl methacrylate)/Polyethylene Composite Anion Exchange Membranes for Vanadium Redox Battery Application

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Anion exchange membranes for a vanadium redox flow battery (VRB) were prepared by pore-filling on a PE substrate with the copolymerization of vinylbenzyl chloride (VBC) and glycidyl methacrylate (GMA). The ion exchange capacity, water uptake and weight gain ratio were increased with a similar tendency up to 65% of GMA content, indicating that the monomer improved the pore-filling degree and membrane properties. The vanadium ion permeability and open-circuit voltage were also investigated. The permeability of the VG65 membrane was only  $1.23 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$  compared to  $17.9 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$  for Nafion 117 and  $1.8 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$  for AMV. Consequently, a VRB single cell using the prepared membrane showed higher energy efficiency (over 80%) of up to 100 cycles compared to the commercial membranes, Nafion 117 (ca. 58%) and AMV (ca. 70%).

**Key Words :** Vanadium redox battery, Anion exchange membrane, Vinylbenzyl chloride, Glycidyl methacrylate

### Introduction

Recently, redox flow battery (RFB) has received attention as a large-scale energy storage technology for intermittent renewable energy sources due to their independently tunable power and capacity, long cycle life, rapid response time, and high energy efficiency. A RFB is a form of rechargeable battery in which an electrolyte containing one or more dissolved electroactive species flows through an electrochemical cell that directly converts chemical energy to electric energy. In addition, the electrolyte is externally stored, generally in tanks, and is usually pumped through the cells of the reactor.

Since the first concept of RFB was reported in 1973 by L.H. Thaller of NASA, it has been developed as a massive energy storage system and used for large stationary applications, loading levels, renewable energy storage systems, uninterrupted power supply, and in electric vehicle applications. Among the various types of RFBs, vanadium redox batteries (VRBs) have been investigated as an energy storage device for these purposes since Skyllas-Kazacos and Grossmith initially studied them.<sup>1</sup> The VRB has the advantages of a long life time, a quick response time, deep-discharge capability and a low maintenance cost. In particular, the VRB has a higher electromotive force (1.4 V in VRB systems) and a higher energy density compared to other RFB systems.<sup>1-4</sup>

The ion-exchange membrane (IEM) is a key component of VRB systems. The function of the IEM is to separate the positive and negative electrolytes and to prevent the cross-mixing of both electrolytes while allowing proton transport. Nafion membranes, which have excellent chemical stability

and high proton conductivity, are the most widely used cation-exchange membrane (CEM) in VRB systems. In spite of these advantages, there are serious obstacles preventing the application of VRBs, specially their high cost and most significantly the problem of "vanadium ion crossover." Ion crossover through the IEM is caused by an undesired exchange of  $\text{H}_3\text{O}^+$  ions with vanadium ions at different oxidation states. The crossover of vanadium ions leads to loss of the cell capacity and a reduction of the energy efficiency in VRB systems.<sup>5,6</sup> On the other hand, an anion-exchange membrane (AEM) can reduce the crossover phenomenon due to the coulomb repulsion between the cation groups of the AEM and vanadium ions.<sup>7</sup> Therefore, the AEM is currently being applied to VRB systems as a separator.<sup>5,8-11</sup>

The glycidyl methacrylate (GMA) monomer containing acrylic and epoxy groups offers good flexibility in polymer design. The epoxy groups in this monomer can react with other functional groups such as carboxyl, hydroxyl and amine groups.<sup>12</sup> It was also reported that the GMA monomer leads to a significant increase in the polymerization rate and improves the wet-strength of the polymer.<sup>13,14</sup> In this study, anion-conducting membranes were prepared by filling pores of a polyethylene (PE) substrate with the proper copolymerization of vinylbenzyl chloride (VBC) and GMA for the composite membrane. These pore-filling membranes with a reinforced structure are composed of two different polymer materials: a porous substrate, PE film, and an impregnating polymer that fills the pores of the substrate. The filling polymer with anion-conducting functional groups reduces vanadium ion crossover, and the porous substrate matrix prevents the swelling of the filling polymer due to its excellent mechanical properties. The ion exchange capacity,

water uptake and vanadium ion permeability of the prepared membranes were determined in comparison with those of commercial membranes. The cell performances of a prepared VBC-GMA composite membrane and commercial membranes (Nafion 117 and AMV) were also tested using a non-flow system for simple assembly and fast determination.

### Experimental

**Materials.** As a pore-filling substrate, a microporous PE film (F20BHE, thickness = 20  $\mu\text{m}$ , ExxonMobil Chemical) was chosen. 4-Vinylbenzyl chloride (VBC, Tokyo Kasei Kogyo Co. Ltd.), divinylbenzene (DVB, Sigma-Aldrich), glycidyl methacrylate (GMA, Sigma-Aldrich), 2,2-azobis(2-methylpropionitrile) (AIBN, Fluka) and trimethylamine (TMA, 25% in water, Sigma-Aldrich) were used to prepare the anion exchange composite membranes.

**Membrane Preparation.** The PE film was soaked in a monomer solution containing VBC, GMA, DVB and AIBN (0.01 g/mL of monomer solution) for 30 min at room temperature. The monomer-sorbed PE was placed between two polyester films to prevent the evaporation of the monomer. Thermal polymerization was then carried out in an oven at 80  $^{\circ}\text{C}$  for 12 h. After the polymerization process, the membrane was aminated by soaking in 1 M of TMA solution for 24 h at room temperature. The aminated membrane was then washed with purified water to remove any residual base. The prepared membrane was subsequently soaked in 1 M NaOH for 24 h, washed and stored in deionized water. The composition of the monomer solution is listed in Table 1.

**Characterization.** The chemical structure of the prepared membranes was analyzed by the Fourier transform infrared (FT-IR) spectrometer (AIM-8800, Shimadzu, Kyoto Co., Japan) to confirm the functional groups the synthesized membranes. All spectra were recorded in the range of 4000–600  $\text{cm}^{-1}$  from an average of 20 scans at a resolution of 4  $\text{cm}^{-1}$ . The weight gain ratio (WGR) reflects the polymerization yield. This value is defined by the Eq. (1):

$$\text{WGR}(\%) = \frac{W_P - W_O}{W_O} \times 100 \quad (1)$$

Here,  $W_O$  is the weight of the PE substrate and  $W_P$  is the weight of the pore-filling membrane after polymerization. To measure the water uptake ( $W_U$ ), the membranes were

immersed in deionized water for 24 h, and the weight of the wet membrane was measured after removing the free water on the membrane surface. On the other hand, the weight of the dry membrane was obtained after the membrane was dried at 60  $^{\circ}\text{C}$  under a vacuum for 24 h. The  $W_U$  value can be calculated with the Eq. (2):

$$W_U(\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \quad (2)$$

In this equation,  $W_{\text{wet}}$  and  $W_{\text{dry}}$  are the weight of the membrane in wet and dry state, respectively. For the ion exchange capacity (IEC), a sample was soaked in a large volume of 1 M NaOH for 1 day to obtain a membrane in the  $\text{OH}^-$  form. This membrane was washed with deionized water to remove the residual NaOH, after which it was equilibrated with 0.1 N HCl for 24 h. Subsequently, the solution was used for back titration with 0.1 M NaOH so that it would be neutral. The sample was dried at 60  $^{\circ}\text{C}$  under a vacuum until its weight reached a constant value. The experimental IEC value was calculated *via*

$$\text{IEC}(\text{meq/g}) = \frac{C_{\text{HCl},0} V_{\text{HCl},0} - C_{\text{NaOH}} V_{\text{NaOH}}}{W_{\text{dry}}} \quad (3)$$

in which  $C_{\text{HCl},0}$  and  $V_{\text{HCl},0}$  are the concentration and volume of the HCl standard solution, respectively. In addition,  $C_{\text{NaOH}}$  and  $V_{\text{NaOH}}$  are respectively the concentration and the volume of the NaOH which used for titration.

To determine the permeability of the vanadium ion (here  $\text{V}^{4+}$ ), representing ion crossover, the membranes were sandwiched between two chambers. The left reservoir was filled with 2.0 mol  $\text{L}^{-1}$   $\text{VOSO}_4$  in 2.0 mol  $\text{L}^{-1}$   $\text{H}_2\text{SO}_4$ , while the right one was filled with 2.0 mol  $\text{L}^{-1}$   $\text{MgSO}_4$  in 2.0 mol  $\text{L}^{-1}$   $\text{H}_2\text{SO}_4$ .  $\text{MgSO}_4$  was used to balance the intensity of the ions in the solutions in both sides and to minimize the osmotic pressure. The effective area of the exposed membrane is 3.14  $\text{cm}^2$  while the volume of the solutions in each reservoir is 125 mL. To determine the vanadium ion permeability of each membrane, 3.5 mL of the solution from the right reservoir was taken at regular time intervals and the concentration of vanadium ions was analyzed by a UV-Vis spectrometer (Lambda 2, Perkin-Elmer Corp., USA). To calculate the permeability of the vanadium ion through the membrane, the concentration of vanadium ions in  $\text{MgSO}_4$  solution as a function of time was determined by the following equation:

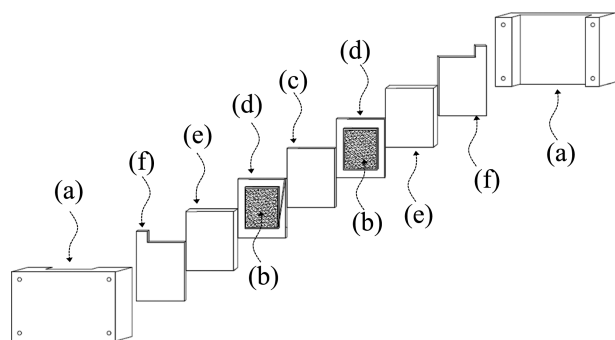
$$V_B \frac{dC_B(t)}{dt} = A \frac{P}{L} (C_A - C_B(t)) \quad (4)$$

Here,  $V_B$  is the volume of the right reservoir,  $A$  and  $L$  are the area and thickness of the membrane exposed to the solution,  $P$  is the permeability of vanadium ions,  $C_A$  is the initial concentration of the left reservoir, and  $C_B(t)$  is the vanadium concentration in the right reservoir at time  $t$ .<sup>6,15</sup>

VRB single cell experiments. In this study, an in-house-designed non-flow single cell created for the purpose of simple assembly and fast determination was employed to

**Table 1.** Chemical composition of monomer solution

Membranes	VBC (vol %)	GMA (vol %)	DVB (vol %)
VG0	95	0	5
VG25	70	25	5
VG45	50	45	5
VG55	40	55	5
VG65	30	65	5
VG70	25	70	5



**Figure 1.** Schematic diagram of a non-flow single cell: (a) acrylic endplate, (b) carbon felt electrode, (c) membrane, (d) polypropylene frame, (e) graphite polar plate and (f) copper plate as a current collector.

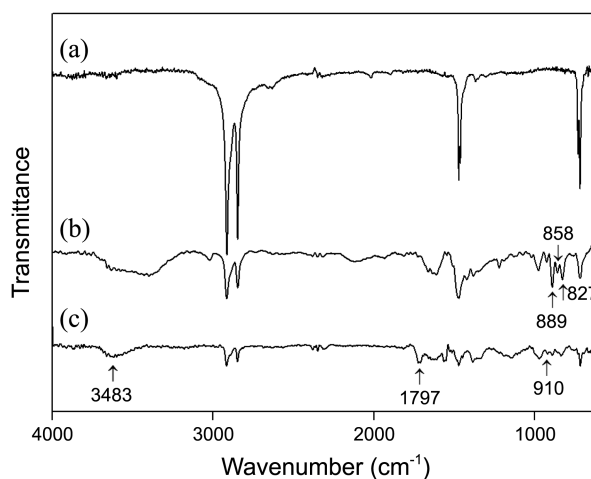
evaluate the properties of the IEMs for VRB performance. As shown in Figure 1, the VRB cell was assembled by sandwiching the membrane between two pieces of air-oxidized carbon felt electrodes which were 5 mm thickness (effective area = 12 cm<sup>2</sup>, XF-30A, Toyobo Co., Ltd.) with a polypropylene frame, and two graphite polar plates (thickness = 5 mm, SK507, Morgan Korea Co., Ltd.) to avoid the corrosion of the copper plates used as current collectors. The VO<sup>2+</sup> solution was prepared by dissolving VOSO<sub>4</sub>·3.5H<sub>2</sub>O (99.9%, Wako Pure Chemical Industries, Osaka, Japan) in 2.0 M of H<sub>2</sub>SO<sub>4</sub> solution. The V<sup>3+</sup> solution was prepared by the electrochemical reduction of the VO<sup>2+</sup> solution. Small volumes (*ca.* 3 mL) of 2.0 mol L<sup>-1</sup> V<sup>3+</sup> solution and VO<sup>2+</sup> solution were injected into the single-unit cell for the negative and positive electrolytes, respectively.

The cell was initially charged to 1.45 V (at 81% state of charge) with a current density of 20 mA cm<sup>-2</sup>, after which the change of the open-circuit voltage (OCV) was measured. The charge/discharge test was performed with the single-unit VRB cell for 100 cycles. It was charged and discharged between 1.6 V and 0.8 V at a constant current density of 40 mA cm<sup>-2</sup>.

## Results and Discussion

Figure 2 shows the FT-IR spectra of the prepared membranes. The spectrum, as shown in curve (b), has an absorption band at 827 cm<sup>-1</sup> which can be attributed to the C-Cl stretch of the CH<sub>2</sub>Cl groups that are derived from the VBC monomer. For the polymer aminated with trimethylamine, the observed infrared absorption levels due to the quaternary amine were 858 cm<sup>-1</sup> and 889 cm<sup>-1</sup>. It was also observed that the peaks at 1797 cm<sup>-1</sup> and 910 cm<sup>-1</sup> were respectively assigned the carbonyl (>C=O) and epoxy (-COC-) stretching vibration band as a characteristic of GMA (curve (c)).<sup>16</sup> These observations show that the VBC and GMA copolymer was successfully synthesized and that the amine group was introduced to the base polymer through the functionalization process.

We measured the IEC, water uptake, weight gain ratio, and the permeability of the vanadium ion for the prepared com-



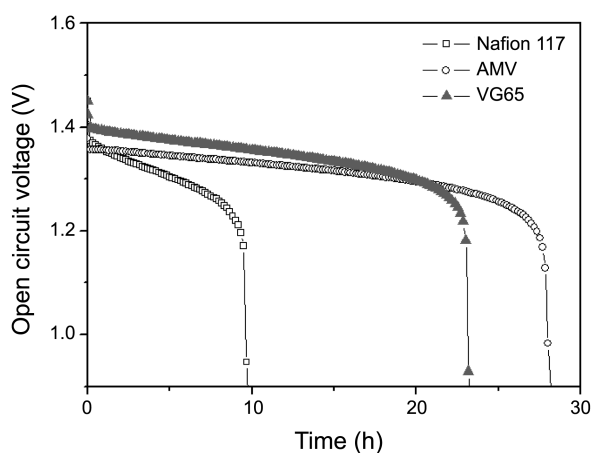
**Figure 2.** Confirmation of membrane structure using FT-IR spectra: (a) PE substrate, (b) VG0 and (c) VG70 membranes.

**Table 2.** Membrane properties of the prepared membranes

Membranes	IEC (meq/g)	W <sub>U</sub> (%)	WGR (%)	Permeability (10 <sup>-7</sup> cm <sup>2</sup> /min)
Nafion 117	1.22	17.3	-	17.9
AMV	1.78	22.1	-	1.8
VG0	3.35	33.6	133.2	15.5
VG25	7.86	34.5	104.2	30.0
VG45	6.39	36.0	112.6	18.0
VG55	15.2	42.1	179.7	2.9
VG65	16.7	48.0	197.1	1.2
VG70	11.9	30.5	163.0	1.6

posite membranes for a comparison with two commercial membranes (Nafion 117 and AMV). The results are shown in Table 2. The IEC value is known to be related to the water uptake, and a high water uptake is advantageous for a high ion exchange capacity.<sup>17</sup> The water uptake tends to increase with an increase in the GMA content, which indicates that the monomer increases the presence of hydrophilic sites within the membranes. It is known that both VBC and GMA can be easily quaternary-aminated. The highest IEC (16.7 meq/g) was obtained at a GMA content of 65%. This arose due to the increase in the hydrophilicity imparted to the membranes by the incorporation of -NR<sup>3+</sup> groups as a consequence of the increase in the degree of grafting. The weight gain ratio was found to be strongly affected by the GMA content because an increase in the concentration leads to a significant increase in the reaction rate for polymerization.<sup>13</sup> The weight gain ratio vividly increased from 104.2 to 197.1% in proportion to the GMA content, except for the VG70 membrane. It is assumed that the GMA can improve the degree of pore-filling, *i.e.*, the amount of polymer which was impregnated into pores of the PE film.

The crossover of vanadium ions through the membrane affects the performance of a VRB, as it will cause serious self-discharge of the battery, resulting in lower energy efficiency. According to Eq. (4), the permeability through the

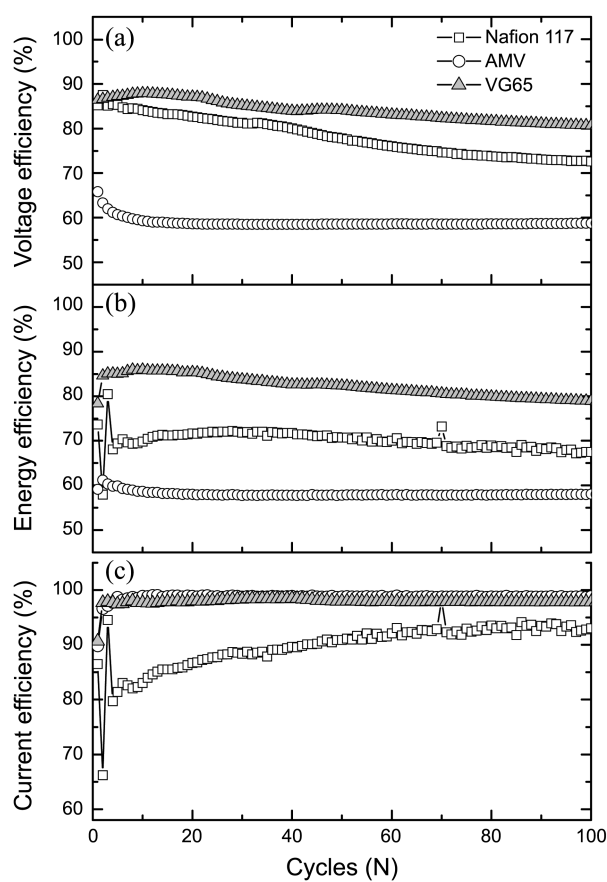


**Figure 3.** Open circuit voltage of VRB with the ion exchange membranes.

membranes was calculated, as listed in Table 2. Generally, the diffusion of vanadium ions, a metallic cation, is much slower in AEMs than it is in CEMs. The permeability of the AMV membrane is only  $1.8 \times 10^{-7}$  cm<sup>2</sup>/min compared to  $18 \times 10^{-7}$  cm<sup>2</sup>/min for Nafion 117. The permeability of the prepared membranes decreased with an increase in the GMA content. As a result of the change in the weight gain ratio, the composite membrane can be denser with GMA copolymerization, leading to the reduction of vanadium ion crossover. The significantly low permeability of the prepared membranes is mainly attributed to the coulomb repulsion between the cation groups of the AEM and vanadium ions.<sup>11</sup> As low crossover can induce a reduction of the self-discharge in the battery, it is expected that VRB cell assembled with the prepared membrane (VG65) will show higher performance in comparison with Nafion 117.

The diffusion of vanadium ions through the membrane will lead to the self-discharge, representing the decrease of the OCV.<sup>15</sup> Therefore, the change in the OCV value can be used to predict the VRB performance. The OCV values obtained from a VRB single cell assembled with different membranes (Nafion 117, AMV and VG65) are shown in Figure 3. To determine the maintenance time, it was charged to a state of charge of 81%. The OCV values gradually decreased from the initial voltage of 1.45 V. The maintenance time with an OCV that exceed 0.8V with the AMV is *ca.* 28 h, which is nearly three times longer than that of a VRB with Nafion 117 due to the lower crossover of vanadium ions across the AEM, resulting in delayed self-discharge of the battery. For the prepared membrane, VG65, the time that the OCV value remained higher than 0.8 V was 23 h; this value is shorter than that of the AMV. Compared to the thickness of the AMV (200  $\mu$ m), that of the VG65 membrane (43  $\mu$ m), however, was much thinner, indicating the lower area resistance of the prepared membrane. Consequently, the VG65 membrane is expected to show better prospects as a separator for the VRB system.

The cycle performance of the VRB single cell with the VG65 membrane was measured and compared to that of the



**Figure 4.** Cell performances of VRB system in the different membranes: (a) current, (b) energy and (c) voltage efficiencies.

VRBs with the commercial membranes (Nafion 117 and AMV), as shown in Figure 4. In general, the lower vanadium ion permeability of the membrane for the VRB system results in higher current efficiency. The VRB single cell using the VG65 membrane exhibited a current efficiency ranging from 97.8 to 98.2%, which was higher than the value of 93% for the Nafion 117 membrane. The energy efficiency and voltage efficiency of the cell with the VG65 membrane were higher compared to those using the commercial membranes. This was mainly due to the lower permeability and thinner thickness of the prepared membrane. There is also less decay of the energy efficiency, which remained at nearly 80% up to 100 cycles in the VRB single cell using the VG65 membrane. This indicates that the prepared membrane possesses high stability in the VRB system and is thus able to maintain good cell performance. The results show that the prepared AEM is a good candidate as a separator for VRB applications.

## Conclusion

Anion exchange composite membranes were prepared by filling pores of a PE substrate with the appropriate copolymerization of VBC and GMA for VRB applications. The primary properties of the prepared membranes and the VRB performances using an in-house-designed non-flow single

cell for simple assembly and fast determination were investigated. Based on the results, the ion exchange capacity, water uptake and weight gain ratio increased with the GMA content, implying that the properties of the prepared membranes were improved through the copolymerization of VBC with GMA. The vanadium ion permeability of the VG65 membrane was significantly lower than that of the commercial membranes. Subsequently, a VRB single cell with the VG65 membrane showed high energy, current and voltage efficiencies, thus retaining good performance with a low self-discharge rate. Consequently, given the good battery performances, the prepared anion exchange composite membrane is expected to have excellent commercial prospects as a separator for VRB applications.

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