Nafion-based composite membrane with a permselective layered silicate layer for vanadium redox flow battery

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A B S T R A C T
Layered silicate AMH-3 forms a 3D ordered microporous structure and is potentially useful as a permselective barrier. Nafion-based composite membrane containing delaminated AMH-3 (D-AMH-3) layer was prepared by solution casting and hot pressing. The membrane structure was analyzed by FE-SEM and EDS, revealing a sandwich-type structure that included double Nafion outer layers and a central D-AMH-3 layer. The Nafion/D-AMH-3 membrane was employed as an ion exchange membrane for VRB application, and the vanadium permeability and single cell performance were evaluated. The Nafion/D-AMH-3 membrane exhibited a lower VO2+ permeability compared to N117, resulting in higher Coulombic efficiency and lower capacity loss per cycle. The results indicated that D-AMH-3 layer is potentially suitable as a permselective barrier for reducing vanadium crossover and improving cell performance.

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1. Introduction

Vanadium redox flow batteries (VRBs), developed by Skyllas-Kazacos et al., have attracted attention for their utility in energy storage systems because of their long lifetime, flexible design, high efficiency and fast response time [1]. Ion exchange membranes (IEMs) are a key component of VRB systems. IEMs are employed to separate the positive and negative electrolytes and allow ion transport to complete the current circuit. An ideal IEM should possess low vanadium ion permeability, high proton conductivity, and good chemical stability. The membranes most commonly used in VRBs are perfluorosulfonic polymers, such as Nafion, which offers high proton conductivity and good mechanical and chemical stability under strongly acidic conditions [2]. However, Nafion suffers from vanadium crossover during cell operation, causing a reduction of the cell efficiency of VRB system [3,4]. The performance of VRB may be improved by reducing vanadium crossover through Nafion. Significant efforts have been applied toward the reduction of vanadium crossover by modifying Nafion. Inorganic materials have been introduced into Nafion clusters [5,6], Nafion surfaces have been modified [3], and Nafion has been blended with other polymers [7,8].

Layered silicate AMH-3 has a 3D ordered microporous structure [9,10] and has been applied in gas separators [11,12] and direct methanol fuel cells [13,14]. In our previous work [14], Nafion-based composite membrane coated with delaminated AMH-3 (D-AMH-3) can reduce methanol crossover by tortuous pathway effect while holding the proton conductivity constant. The permselective properties of the Nafion/D-AMH-3 membrane inspired us to attempt to reduce vanadium crossover in VRBs. In this study, Nafion-based composite membrane having a D-AMH-3 layer was prepared by solution casting and hot pressing. The performance of Nafion in a VRB has been shown to depend on the membrane thickness [15]. Thus, in order to examine the effect of D-AMH-3 layer, we controlled the thickness of Nafion/D-AMH-3 membrane, which is similar to the thickness of a neat Nafion.

2. Experimental

2.1. Membrane preparation

AMH-3 was synthesized and delaminated according to the methods described previously [14]. Nafion-based composite membrane with a D-AMH-3 layer (ND membrane) was prepared by solution casting. Nafion 117 (N117) was swollen in ethanol solution for 1 day and then placed in glass dish. A 10 wt.% of D-AMH-3 was added into Nafion solution, then the mixture was stirred at room temperature to yield a coating solution, which was slowly poured into glass dish containing swollen N117. The filled glass dish was evaporated in an oven at 40 °C for 1 day. After drying, the filled glass dish was cooled in water, and then the membrane was peeled off. Finally, in order to form the well-ordered D-AMH-3 layer, the membrane was hot pressed between polyimide films at 130 °C and 3000 psi for 10 min.
2.2. Vanadium permeability measurements

VO\textsuperscript{2+} permeability measurements were carried out at room temperature using a membrane-separated diffusion cell. The volume of each compartment was 100 mL, and the effective area of the membrane was 3.14 cm\textsuperscript{2}. The feed compartment was filled with 1 M VOSO\textsubscript{4} in 2 M H\textsubscript{2}SO\textsubscript{4}, and the permeate compartment contained 1 M MgSO\textsubscript{4} in 2 M H\textsubscript{2}SO\textsubscript{4}. The VO\textsubscript{2+} permeability of the membrane was determined by collecting 5 mL volumes of liquid sample using a syringe at prescribed time intervals. The samples extracted from the permeate compartment were analyzed by ICP-AES (ICPS-7510, Shimadzu).

2.3. VRB single cell test

A VRB single cell was assembled by sandwiching a membrane between two pieces of carbon felt electrodes (XF-30A, Toyobo Co., Ltd.). The VO\textsuperscript{2+} solution was prepared by dissolving VOSO\textsubscript{4} \cdot 3.5H\textsubscript{2}O (99.9%, Wako Pure Chemical Industries) in 2 M H\textsubscript{2}SO\textsubscript{4} solution. The V\textsuperscript{3+} solution was prepared by the electrochemical reduction of the VO\textsuperscript{2+} solution. 2 M VO\textsuperscript{2+} and V\textsuperscript{3+} in 2 M H\textsubscript{2}SO\textsubscript{4} solutions were used as the initial positive and negative electrolytes, respectively. The active area of the cell was 12 cm\textsuperscript{2}, and the volume of the electrolyte solution was 2.8 mL in each half cell. Charge–discharge cycling of the cell was carried out at room temperature using a battery cycler (Maccor 4000). The cutoff voltages of the cell tests were selected to be 1.6 V and 0.8 V to avoid the corrosion of the carbon felt electrodes and conductive plastic, which corresponds to ~100% and ~0% SOC, respectively.

3. Results and discussion

3.1. Membrane morphology study

Fig. 1 shows a cross-sectional FE-SEM image and the corresponding EDS mapping of ND membrane. The FE-SEM image confirmed that ND membrane had a sandwich-like structure comprising the double Na\textsuperscript{+} outer layers and a D-AMH-3 central layer. The nominal thickness of N117 is around 180 μm. The dry thickness of ND membrane was around 183 μm, similar to that of N117. These values were expected to minimize the effect of the membrane thickness. The EDS mapping confirmed the presence of D-AMH-3 between the Na\textsuperscript{+} layers rather than within the Na\textsuperscript{+} matrix, probably indicating the presence of a well-formed D-

![Fig. 1. FE-SEM cross-sectional image of ND membrane (inset is EDS mapping of ND membrane).](image)

3.2. Vanadium permeability

The change of VO\textsuperscript{2+} concentration with time for N117 and ND membrane is shown in Fig. 2. The VO\textsuperscript{2+} concentration increase with time for ND membrane was lower than that for N117. The VO\textsuperscript{2+} permeability of N117 and ND membrane were 3.07 × 10\textsuperscript{−6} cm\textsuperscript{2}/min and 8.64 × 10\textsuperscript{−7} cm\textsuperscript{2}/min, respectively, calculated according to the equation provided in Ref. [3]. These results showed that a reduction in VO\textsuperscript{2+} permeability can be achieved by D-AMH-3 layer, which acted as a permselective barrier by tortuous pathway effect.

3.3. VRB charge–discharge performance

Fig. 3 shows the charge–discharge curves of VRBs prepared with N117 and ND membranes at 40 mA/cm\textsuperscript{2}. As shown, the charge and discharge capacities of the ND-VRB were higher than those obtained from the N117-VRB, demonstrating that ND membrane improved the cell performance by reducing vanadium crossover. The Coulombic efficiency (CE) of the ND-VRB was 97.4%, and that of the N117-VRB was 94.7%, in good agreement with the results of VO\textsuperscript{2+} permeability. The ND-VRB had a higher cell resistance than the N117-VRB (0.15 Ω vs. 0.10 Ω), leading to a higher charge voltage and a lower discharge voltage. Accordingly, the voltage efficiency (VE) of the ND-VRB was 85.6%, lower than that (90.5%) of the N117-VRB. Because D-AMH-3 contains very few proton-hopping sites, such as sulfuric acid groups, the resistance of ND membrane having D-AMH-3 layer increased. The energy efficiency (EE) was calculated according to: CE × VE. The EE of the ND-VRB was...
lower than that of the N117-VRB because the cell resistance was higher: 83.4% (ND) versus 85.6% (N117); however, at a current density of 20 mA/cm², the EE of the ND-VRB exceeded that of the N117-VRB: 87.6% (ND) and 82.8% (N117), due to low vanadium crossover and minimization of IR drop.

3.4. VRB cycling performance

The charge–discharge curves for N117-VRB and ND-VRB over 100 cycles are shown in Fig. 4. The charge–discharge voltage of the ND-VRB remained constant and the capacity loss of the ND-VRB was small compared to that of N117-VRB over 100 cycles, indicating a low and stable vanadium permeation rate through ND membrane. As shown in Fig. 5(a), there is no efficiency decline after 100 charge–discharge cycles. The ND-VRB showed a stable performance in vanadium solutions under strongly acidic conditions. Fig. 5(b) shows the capacity loss curves of the N117-VRB and ND-VRB. The capacity retention of the ND-VRB was 84.6% after 100 cycles, much higher than the value obtained from the N117-VRB (14.3%). The low capacity retention of the N117-VRB was attributed to high vanadium crossover. These results indicated that the ND-VRB could operate longer than the N117-VRB because D-AMH-3 layer acted as a permselective layer to reduce vanadium crossover.

The VRB cycling tests confirmed that ND membrane offered good chemical stability in strongly acidic vanadium solutions and long lifetime suitable for VRB systems. In addition, the sandwich structure of ND membrane is expected to increase VRB operating lifetime because when one Nafion layer facing the catholyte breaks, the other Nafion layer can continue to operate. Pentavalent vanadium ions in a fully charged catholyte have highly oxidizing nature [16], causing the catholyte-facing membrane to degrade during repeated cycling.

4. Conclusions

Nafion-based composite membrane with a D-AMH-3 layer was prepared by solution casting and hot pressing, which had a sandwich structure. The D-AMH-3 layer acted as a permselective layer to reduce vanadium crossover. Although ND membrane delivered slightly lower energy efficiency compared with N117 at higher current density due to higher cell resistance, ND membrane showed lower vanadium permeability compared to N117, thereby improving the capacity. Coulombic efficiency and capacity retention in VRB single cell tests. ND membrane exhibited a stable performance over 100 cycles. Cell resistance may potentially be reduced by further optimizing D-AMH-3 layer content and by modifying D-AMH-3 surface.

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