A Permselective Layered Silicate Modified by Acid-treatment and Its Use for Blocking of Methanol Crossover in DMFC

Ji Hoon Kim*, Hyonggoo Yoo** and Seung-Yeop Kwak***

Department of Materials Science and Engineering, Seoul National University,
599 Gwanak-ro, Gwanak-gu, Seoul 151-744, Korea,
*zalyong@hanmail.net, **friends1@snu.ac.kr ***sykwak@snu.ac.kr

ABSTRACT

Permselective layered silicate AMH-3 were synthesized by the hydrothermal method and modified by the acid treatment. As-made AMH-3 and acid-treated AMH-3 were characterized by XRD and FE-SEM, ^{29}Si MAS NMR. Layered silicate/polyelectrolyte multilayered composite membranes were prepared by layer-by-layer self-assembly (LBL) with various LBL cycle numbers. The methanol permeability and proton conductivity of multilayered composite membranes decreased with an increase number of LBL cycle. From methanol permeability and proton conductivity results, it was confirmed that the selectivity parameter of the AP5 multilayered composite membrane was the highest value.

Keywords: layered silicate, layer-by-layer self-assembly, DMFC, Nafion, methanol crossover

1 INTRODUCTION

Layered silicates are widely used various fields such as adsorption, catalysis and fabrication of nanocomposites [1]. Several layered silicates have channel systems or open frameworks within layers, so these silicates can be applied permselective barrier. Hence permselective property of layered silicate can be used to solve the problem for direct methanol fuel cells (DMFCs). One of the critical problems hindering the commercialization of DMFCs is high methanol crossover [2]. High methanol crossover caused loss of fuel, reduced fuel efficiency, mixed potential at the cathode and poisoned catalyst.

There have been many attempts to reduce the methanol permeability through the membranes: (1) to modify the surface of the membranes to block the methanol transport, (2) to reduce the size of ion-cluster channel, (3) to introduce inorganic materials within membrane use as a tortuous pathway, and (4) to develop new types of electrolyte polymers. Among these attempts surface modification is effective method to reduce methanol crossover because of its facile manipulation and high efficiency.

Layer-by-Layer self-assembly (LBL) is one of the most promising methods for thin film fabrication, as reported by Decher [3]. LBL is described as sequential adsorption of positive or negative charged species by alternatively dipping, spraying. There are a wide variety of materials that can be deposited by LBL including polyions, metals, and nanoparticles.

In this study, in order to block the methanol crossover through Nafion while maintaining proton conductivity, selective multilayer formation on the surface of Nafion by layer-by-layer self-assembly with permselective layered silicate (AMH-3). AMH-3 has three-dimensional micro-porous layers containing eight-membered rings opening (Figure 1). AMH-3 can be used as selective permeable barrier for DMFCs because of its pore size has smaller than diameter of methanol, and bigger than that of water, its three-dimensional micro-porous structure, and its high aspect ratio.

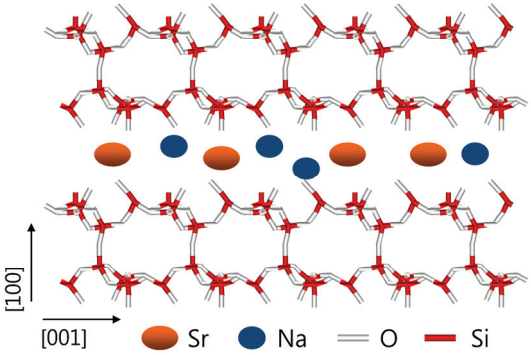

Figure 1: Framework of AMH-3

2 EXPREMENTAL

2.1 Materials

AMH-3 was synthesized by hydrothermal reaction using gels of the following molar compositions; 1 TiO_2: 10 SiO_2: 14 NaOH: 2 $SrCl_2$: 675 H_2O[1]. $TiCl_3$ solution (20 wt% $TiCl_3$), $SrCl_2 \cdot 6H_2O$ (99 wt%), Sodium silicate solution (27 wt% SiO_2, 14 wt% NaOH) were used as titanium, strontium and silicon sources, respectively. In a typical synthesis, NaOH was dissolved in deionized water. This solution was heated at 80 °C, then $SrCl_2 \cdot 6H_2O$ was added. The solution was stirred for 30 min. After stirring, sodium silicate solution was added drop wise and stirred for 30 min. Finally, $TiCl_3$ was added drop wise. Then, the mixture was stirred for 1 h. The resulting mixture was poured into a

Teflon-lined stainless steel autoclave and crystallized at 200 ^{o}C for 1 day. The product was washed with deionized water, and dried at 80 °C overnight.

2.2 Delamination and Exfoliation of AMH-3

The thickness of AMH-3 used in this study was too thick to prepare appropriate multilayer. Thus, AMH-3 was modified by acid-treatment. The acid-treatment of AMH-3 was carried out by hydrothermal reaction using 0.1 N HCl solution at various temperatures for 1 day. Inorganic cations (Na^+, Sr^{2+}) located between the layers of AMH-3 would remove and/or exchange with H^+ in the acid-treatment [4]. The exchange would result in variation of the surface charge, leading to repulsion of the individual layers of AMH-3. So, AMH-3 was delaminated by acid-treatment. Then, for exfoliating of AMH-3 layers, ultra-sonication was carried out for 2 h.

2.3 Fabrication of Multilayered Composite membranes

The multilayered composite membranes were prepared by LBL. Prior to LBL, Nafion 115 was treated according to the standard procedure of 30 min in a 5 wt% H_2O_2 solution at 80 °C, then 30 min in deionized water at 80 °C and 30 min in 8 wt% H_2SO_4 solution at 80 °C [5]. Then, the LBL was carried out by alternate dipping of the pre-treated Nafion membrane into cationic and anionic solutions under various LBL cycle numbers (5, 10, 15, and 20 cycles). The pre-treated Nafion was dipped into a cationic solution, poly(diallyldimethyl ammonium chloride), PDAC for 10 min. Subsequently, the pre-treated Nafion was washed with deionized water, and then dipped into an anionic solution, AMH-3 colloid for 10 min. The alternate dipping of cationic and anionic solution was repeated to increase the multilayer on Nafion surface. In this study, AP*x* denotes AMH-3/PDAC multilayered composite membranes under *x* LBL cycle number.

2.4 Characterization

The morphology of the AMH-3, delaminated AMH-3, and exfoliated AMH-3 was observed by Field emission scanning electron microscopy (FE-SEM, JEOL, JSM-6330F). The X-ray diffraction (XRD) was used to investigate the crystal properties of AMH-3 series by using a MAC Science MXP 18A-HF X-ray diffractometer with CuK_α radiation (λ = 1.5406 Å). Data were collected from 5 to 40°. In order to confirm the framework of AMH-3 series, ^{29}Si magic-angle-spinning nuclear magnetic resonance (MAS NMR) measurement was carried out by using a Bruker Avance II.

Methanol permeability measurements were carried out using home-made methanol permeation measurement cell that consisted of two glass compartments (A for feed and B for permeate) separated by a composite membrane with an effective area of 3.8 cm^2. In order to determine the methanol permeability of each membrane, liquid samples of 2 mL were taken from compartment B using a syringe at prescribed time intervals (15, 30, 60, and 120 min). The samples extracted from compartment B were analyzed using a calibrated gas chromatograph (HP 5980, Hewlett-Packard, USA). The methanol permeability was calculated according the equation.

$$C_B(t) = \frac{A}{V_B} \times \frac{DK}{L} C_A(t - t_0) \quad (1)$$

where C_A and C_B are the concentration of methanol in the compartment A and B, respectively. V_B is the volume of the compartment B. A and L are area and the thickness of the membrane, respectively. D and K are the methanol diffusion and partition coefficient, respectively. The product DK is the membrane permeability (P) ($P = DK$). Eq. (1) can be solved to give

$$P = \alpha \times \frac{V_B}{A} \times \frac{L}{C_A} \quad (2)$$

The methanol permeability was then calculated from the slope of the straight line (α).

The proton conductivity measurements on fully hydrated membrane samples were carried out with the cell immersed in liquid water. The installed cell was placed in a chamber. The impedance measurements were carried out in the frequency range from 0.1 Hz to 10^5 Hz using a CH instruments electrochemical analyzer with ZPLOT software. The proton conductivity was calculated from Eq. (3).

$$\sigma = \frac{L}{R \times A} \quad (3)$$

where R is the bulk resistance, L is the thickness of the membranes and A is the cross-sectional area of the membrane.

3 RESULTS AND DISCUSSION

3.1 Characterization of Delaminated AMH-3 and Exfoliated AMH-3

Figure 2 shows the FE-SEM images of AMH-3, delaminated AMH-3 and exfoliated AMH-3. On the basis of the FE-SEM results, we confirmed AMH-3 has hexagonal plate-like shape, and thickness of AMH-3 is about 3 μm. From the FE-SEM images of delaminated AMH-3 (figure 2b-c), it can be seen that the interlayer space of AMH-3 was expanded. These results indicate that AMH-3 layers are delaminated by acid-treatment. The thickness of delaminated AMH-3 individual layers is approximately 100–400 nm. At the higher hydrothermal

reaction temperature, it can be expected that the degree of delamination is increased and thickness of individual layer is decreased. The FE-SEM images as shown in Figure 2d present the morphology of exfoliated AMH-3. From the FE-SEM results, it was confirm that delaminated AMH-3 was successfully exfoliated by ultra-sonication and the thickness of individual layer is about 150 nm.

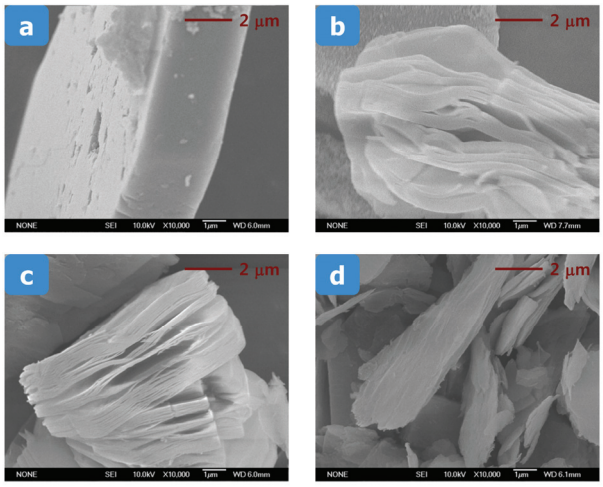

Figure 2: FE-SEM images of (a) AMH-3, and delaminated AMH-3 with hydrothermal reaction at (b) room temperature, (c) 200 °C, and (d) exfoliated AMH-3

The XRD patterns for AMH-3, delaminated AMH-3, and exfoliated AMH-3 are given in Figure 3. Comparing the XRD pattern of delaminated and exfoliated AMH-3 with original AMH-3, it can be seen that the XRD patterns were changed, and broadened. We have treated AMH-3 with HCl which can be removed and/or exchanged Na^+, Sr^{2+} with H^+, producing disorder along the [100] direction and random orientation. These facts are the reason why (100) XRD peak disappeared and other XRD peaks broadened [6].

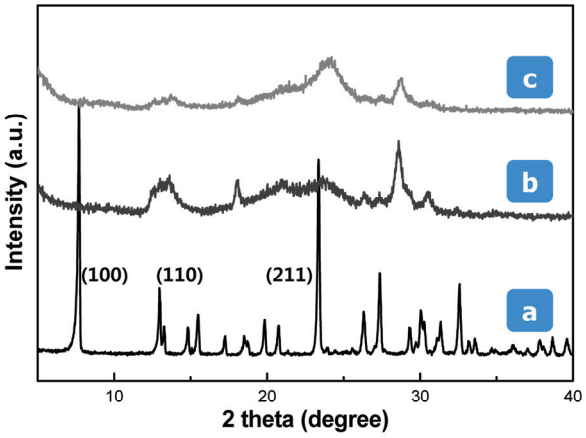

Figure 3: The X-ray diffraction patterns of (a) AMH-3, (b) delaminated AMH-3, and (c) exfoliated AMH-3

The ^{29}Si MAS NMR spectra of AMH-3 (figure 4a) contain three peaks located at -89.4, -90.8 and -93.5 ppm, corresponding to Q_3 and Q_4 Si sites respectively [1]. This result indicates that the framework of AMH-3 is constructed by Q_3 and Q_4 silicate unit. Q_3 and Q_4 peaks were shifted by the acid-treatment due to the different environment of the exposing (figure 4b). From this result, the framework of AMH-3 was almost retained after acid-treatment.

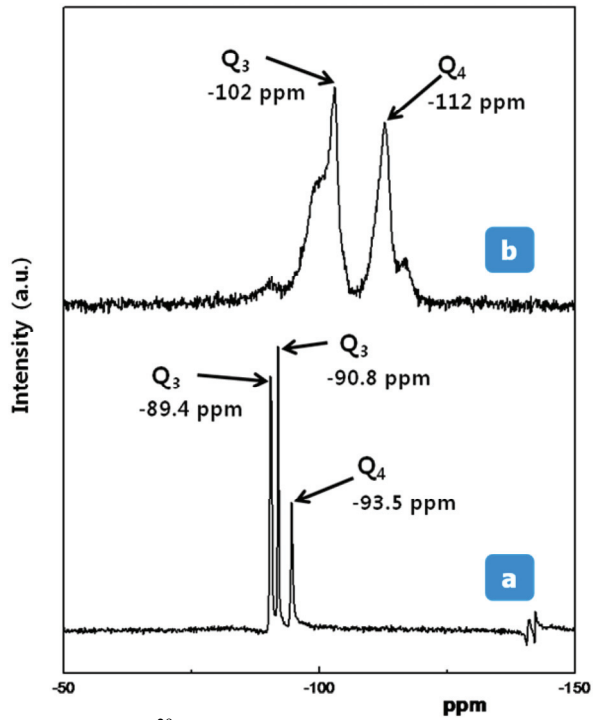

Figure 4: The ^{29}Si MAS NMR spectra of (a) AMH-3, (b) delaminated AMH-3

3.2 Methanol Permeability

Figure 5 shows the methanol permeability of AP series multilayered composite membranes and Nafion 115 at room temperature. From this result, the methanol permeability of AP series multilayered composite membranes decreased with increases LBL cycle numbers. The decrease in the methanol permeability can be explained in terms of AMH-3/PDAC multilayer onto Nafion surface depending on LBL cycle number. That is, methanol molecules have a more tortuous path around the AMH-3/PDAC multilayer. Thus the introduction of AMH-3/PDAC multilayer onto the membrane surface contributes to an increase in their tortuous pathway, thereby resulting in a decrease in their methanol permeability.

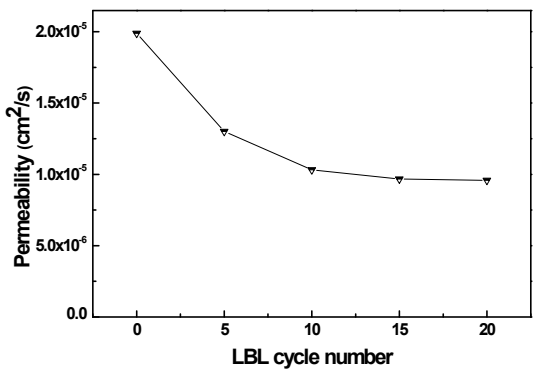

Figure 5: Methanol permeability of AP series multilayered composite membranes

3.3 Proton Conductivity and Selectivity

Figure 6 show the relationship of proton conductivity with the LBL cycle numbers at room temperature. The proton conductivity of multilayered composite membranes showed behavior similar to that observed for their methanol permeability. That is, the proton conductivity decreased with an increase LBL cycle numbers.

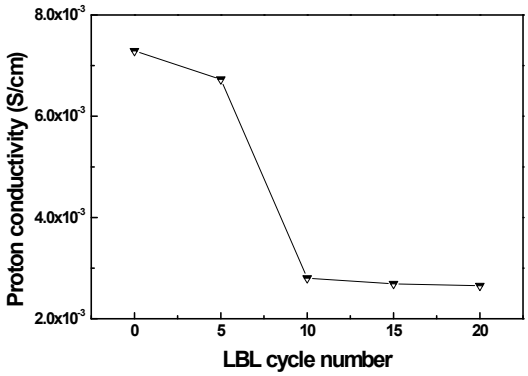

Figure 6: Proton conductivity of AP series multilayered composite membranes

The novel membrane for DMFC should have the highest proton conductivity and the lowest methanol permeability. However, there is trade-off between proton conductivity and methanol permeability. The decrease in methanol permeability accompanies a decrease of proton conductivity. Thus, relationship between proton conductivity and methanol permeability is an important factor in evaluating potential performance of membrane in DMFC. One of the methods used to evaluate the potential performance of DMFC membrane is the selectivity parameter, Φ (S s cm^{-3}). The selectivity is calculated as the ratio of proton conductivity to methanol permeability. Membrane with high selectivity has the potential to show improved DMFC performance. Table 1 lists the selectivity parameters of AP series composite membranes. The maximum selectivity was found at AP5 membrane, implying the novel membrane.

Membrane	Methanol permeability (cm^2 s^{-1})	Proton conductivity (S cm^{-1})	Selectivity parameter (S s cm^{-3})
AP0	1.99×10^{-5}	7.29×10^{-3}	3.66×10^{2}
AP5	1.30×10^{-5}	6.73×10^{-3}	5.18×10^{2}
AP10	1.18×10^{-5}	2.80×10^{-3}	2.37×10^{2}
AP15	9.33×10^{-6}	2.69×10^{-3}	2.88×10^{2}
AP20	9.33×10^{-6}	2.65×10^{-3}	2.84×10^{2}

Table 1: Experimental parameters of AP series multilayered composite membranes

4 CONCLUSIONS

AMH-3 was synthesized by hydrothermal reaction using gels of the following molar compositions; 1 TiO_2: 10 SiO_2: 14 NaOH: 2 $SrCl_2$: 675 H_2O. AMH-3 was successfully delaminated by acid-treatment, and then exfoliated by ultra-sonication. The multilayered composite membranes were prepared by Layer-by-Layer self-assembly with various LBL cycle numbers. The methanol permeability and proton conductivity of multilayered composite membranes decreased with an increase in LBL cycle numbers. To evaluate potential performance of membrane in DMFC, selectivity parameter is introduced which demonstrates to be more effective. The maximum selectivity was found at AP5 membrane, implying the novel membrane.

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