Delamination of microporous layered silicate by acid-hydrothermal treatment and its use for reduction of methanol crossover in DMFC

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1. Introduction

Fuel cells are an attractive electricity generation technology that converts chemical energy directly into electricity with high efficiency and low-pollution emissions. Of the many types of fuel cells, direct methanol fuel cells (DMFCs) have attracted attention for applications in portable electronic devices and transportation because of their high energy densities at low operating temperatures and the ease of their refueling [1]. However, methanol crossover is a significant problem that hinders their commercialization. A high methanol crossover results in the loss of fuel, low efficiency, a mixed potential at the cathode, and a poisoned catalyst. In order to improve the performance of DMFCs, it is necessary to reduce the methanol crossover through the membrane [2–4]. There have been many approaches to this reduction: (1) modify the surface of the membranes to block methanol transport [5–7], (2) introduce organic/inorganic materials into the membrane [8–11], and (3) develop new types of electrolyte polymers [12–14].

Layered silicates are widely used in various fields such as adsorption, catalysis, and the fabrication of nanocomposites [15–17]. Several layered silicates have channel systems or open frameworks within layers, so these silicates can be used as permselective barriers. Therefore, the permselective properties of layered silicates are potentially useful in the reduction of methanol crossover. Of the known layered silicates, AMH-3 is an attractive candidate for preparing permselective barriers due to its 3D microporous framework with an eight-membered ring (8MR) and a high aspect ratio [18,19]. The pore size defined by the 8MR is 3.4 Å, which is smaller than the diameter of methanol and larger than that of water. However, although AMH-3 is a microporous framework material, it has been reported that AMH-3 exhibits almost no porosity when examined with N₂ adsorption and BET analysis [19,20]. The reason for the absence of porosity under these conditions is that cations located in the intralayer and interlayer spaces block the pores [20]. Therefore, these cations must be removed from the AMH-3 interlayer if AMH-3 is to be used as the permselective barrier in a DMFC system. In addition, AMH-3 layers can be swollen or delaminated to increase their aspect ratio, which will provide higher selectivity. However, the removal of cations and the swelling of the interlayer are more difficult than for other layered materials because the Na⁺ and Sr²⁺ cations are strongly bound between the layers. Choi et al. and Kim et al. investigated an interlayer swelling method that uses swelling agents such as dodecylamine and dodecyldiamine [19–21]. However, these swelling agents have hydrophobic alkyl chains, so the resulting swollen AMH-3 is likely to be hydrophobic. The hydrophobic swelling agent is likely to interrupt the transport of water through the
membrane containing the AMH-3, so the proton conductivity of the membrane is expected to be significantly lowered. A Nafion composite membrane with AMH-3 swollen by dodecylamine was investigated [22]. The swollen AMH-3/Nafion composite membrane was found to exhibit lower methanol permeability than neat Nafion. However, its proton conductivity was almost half that of neat Nafion. Further, the ionic cluster region within the Nafion matrix collapses because the size of AMH-3 (20 nanometers) is much larger than that of the ionic clusters (2 nm). Therefore, AMH-3 must be swollen or delaminated without the use of a swelling agent to avoid hydrophobicity, and the surface modification of Nafion should be carried out so as to prevent collapse of the ionic cluster region.

It has been reported that inorganic cations located between the layers of layered materials can be removed and/or exchanged with H+ by using acid treatment [23–25]. This exchange results in variation of the surface charge and leads to the expansion of the interlayers. Therefore, acid treatment could be a candidate for the delamination of AMH-3 without the use of a swelling agent. However, Kim et al. have shown that complete proton exchange results in the collapse of the layered structure of AMH-3 [19]. Therefore, another post-treatment is required to maintain the AMH-3 layered structure. We chose the hydrothermal method to maintain the AMH-3 layered structure after acid treatment.

In this paper, a facile delamination of AMH-3 without the use of a swelling agent will be first discussed. In addition, methanol permeability, proton conductivity and liquid uptake of Nafion membrane coated with a delaminated AMH-3/Nafion nanocomposite layer will be also discussed and compared with those of Nafion.

2. Experimental

2.1. Synthesis of AMH-3

AMH-3 was synthesized by using the hydrothermal reaction of a gel with following molar composition: 1 TiO2: 10 SiO2: 14 NaOH: 2 SrCl2: 675 H2O [18,20]. TiCl3 solution (20 wt.% TiCl3, Kanto), SrCl2 (99 wt.% Junsel), and sodium silicate solution (27 wt.% SiO2, 14 wt.% NaOH, Aldrich) were used as the titanium, strontium, and silicon sources. In a typical synthesis, NaOH was dissolved in deionized water. This solution was heated at 80 °C, then SrCl2·6H2O was added. The solution was stirred for 30 min. After 30 min of stirring, sodium silicate solution was added dropwise and stirred for 30 min. Finally, TiCl3 solution was added dropwise and stirred for another 1 h. The resulting mixture was poured into a Teflon-lined stainless steel autoclave and crystallized at 200 °C for 1 day. The product contains amorphous material that was removed to yield pure AMH-3 as follows. The product was diluted with deionized water and kept for 1 h in an ultrasonic bath, and then the suspension was decanted from the AMH-3 sediment. The AMH-3 sediment was washed with deionized water and kept for 1 h in an ultrasonic bath. This purifying procedure was repeated five times. After purifying, the AMH-3 sediment was dried overnight at 80 °C.

2.2. Delamination and exfoliation of AMH-3

In order to delaminate AMH-3 while maintaining its structure, the acid-hydrothermal treatment at 200 °C was carried out with 1 M HCl solution. These conditions are harsher than those used in the amino acid swelling process [19–21]. To evaluate the effects of the hydrothermal treatment, AMH-3 was immersed in 1 M HCl solution at room temperature. Then, ultrasonication was carried out for 2 h to exfoliate the individual AMH-3 layers mechanically. In this study, acid-treated AMH-3 is denoted A-AMH-3, acid-hydrothermal treated AMH-3 is denoted AH-AMH-3, and acid-hydrothermal treated AMH-3 after ultrasonication is denoted UAH-AMH-3.

2.3. Preparation of Nafion membrane coated with a permselective layer

Nafion membrane coated with a permselective layer was prepared with solution casting method. A 5 wt.% of delaminated and exfoliated AMH-3 was added into Nafion solution (5% Nafion in a mixture of lower aliphatic alcohols and water, Aldrich), then the mixture was stirred at room temperature to yield a well-dispersed coating solution, which was slowly poured into a glass dish containing Nafion 115. The filled glass dish was evaporated at 40 °C for 2 days and then annealed at 120 °C in a convection oven for 2 h. After 2 h, the filled glass dish was cooled in a water bath held at room temperature, and then the membrane was peeled off the glass dish.

2.4. Characterization of the layered silicates

The morphology of the materials was examined with a field-emission scanning electron microscope (JEOL, JSM-6700F) equipped with an energy-dispersive spectroscopy working at 6 kV. Inductively coupled plasma atomic emission spectrometry (ICP-AES) measurements were performed with an Optima-4300 DV (PerkinElmer). The N2 adsorption–desorption isotherms were measured with an ASAP2010 (Micromeritics). The specific surface area of each sample was determined by using the multiple-point Brunauer–Emmett–Teller (BET) method applied to the nitrogen desorption branch of the isotherm. 29Si Magic-Angle Spinning Nuclear Magnetic Resonance (MAS NMR) measurements were performed on a Bruker Avance I4 spectrometer at room temperature. The recycle delay was 15 s, with approximately 500 scans required for a full 7 mm rotor spinning at 7 kHz. Fourier Transform Infrared Spectroscopy (FT-IR) spectra analyses were performed on samples pelletized with KBr powder by using a Thermo Scientific Nicolet 6700 IR spectrophotometer with a resolution of 4 cm−1. Wide-angle X-ray diffraction (WXRD) patterns of the materials were collected at room temperature with a MAC/Sci. MXP 18XHF–22SRA diffractometer equipped with graphite monochromatized Cu-Kα radiation (λ = 1.541 Å, 50 kV, 100 mA) was used as the X-ray source.

2.5. Characterization of the membranes

2.5.1. Methanol permeability and proton conductivity measurements

Methanol permeability measurements were carried out at room temperature by using a home-made methanol permeation measurement cell that consists of two glass compartments separated by a membrane, each of volume 300 mL. The feed compartment was filled with 5 M methanol and the permeate compartment contained deionized water. In order to determine the methanol permeability of a membrane, liquid samples of volume 2 mL were taken from each compartment by using a syringe at prescribed time intervals (30, 60, 90, and 120 min). The samples extracted from the permeate compartment were analyzed with a refractometer (RX-5000α, ATAGO). The methanol permeability was calculated according to Eq. (1):

\[
C_b(t) = \frac{A}{V_b} \times \frac{DK}{L} C_a(t - t_0)
\]

where \(C_a\) and \(C_b\) are the concentrations of methanol in compartments A and B respectively. \(V_b\) is the volume of compartment B. \(A\) is the membrane effective area and \(L\) is the membrane thickness. \(D\) and \(K\) are the methanol diffusivity and the partition coefficient.
between the membrane and the adjacent solution respectively. The methanol permeability \( P \) is defined as the product of the diffusivity and the partition coefficient \( (P = D/K) \).

\[
P = \alpha \times \frac{V}{A} \times \frac{L}{C_A}
\]

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

The measurements of the proton conductivity in 100% RH were carried out with the cell immersed in liquid water at room temperature. The impedance measurements were carried out in the frequency range \( 0.1 - 10^5 \) Hz by using a CH Instruments electrochemical analyzer with ZPlot software. The proton conductivity was calculated by using the following equation:

\[
\sigma = \frac{L}{R \times A}
\]

where \( R \) is the bulk resistance or ohmic resistance of the membrane sample, \( L \) is the distance between the counter electrode and the working electrode, and \( A \) is the cross-sectional area of the membrane.

### 2.5.2. Liquid uptake

The water uptake and methanol–water solution uptake of the membrane samples were determined by measuring the membrane weight difference before and after immersion. Membrane samples were dried under vacuum at 25 °C for 24 h and weighted \( (W_{\text{dry}}) \) before being immersed in deionized water or 5 M methanol–water solution at room temperature for 24 h. The wet membrane was wiped with blotting paper to remove residual water from the surface and weighed \( (W_{\text{wet}}) \). The uptake was calculated by the following equation:

\[
\text{uptake}(\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100
\]

### 3. Results and discussion

#### 3.1. The delaminated and exfoliated AMH-3

Fig. 1 shows FE-SEM images of pristine AMH-3, A-AMH-3, AH-AMH-3, and UAH-AMH-3. In the FE-SEM images of A-AMH-3 and AH-AMH-3 (Fig. 1b and c), it can be seen that the interlayer space of AMH-3 has expanded; these morphologies are better than or similar to those of previously reported proton-exchanged AMH-3 [20]. It is evident that the contents of Na and Sr in each sample are reduced by post-treatment. The cation contents of AH-AMH-3 are smaller than those of A-AMH-3 and proton-exchanged AMH-3. Of these post-treatment methods, the acid-hydrothermal treatment is most effective in the exchange of cations. Table 1 confirms that the cations remaining in AH-AMH-3 are removed mechanically by the ultrasonication procedure used to obtain UAH-AMH-3.

\( ^{29}\)Si MAS NMR spectroscopy was used to characterize the structural changes that occur during the delamination process. An analysis of the \( ^{29}\)Si MAS NMR spectra of pristine AMH-3 and swollen AMH-3 was carried out in a previous study [18–21]. As can be seen in Fig. 3a, the NMR spectrum of pristine AMH-3 contains three peaks located at \(-89\), \(-90\), and \(-93\) ppm, which correspond to \( Q^0 \) and \( Q^1 \) Si species as shown in the figure, with a \( Q^1/Q^0 \) ratio of approximately 3. On the other hand, the spectra of A-AMH-3, AH-AMH-3, and UAH-AMH-3 contain two peaks at \(-102\) ppm \( (Q^0) \) and \(-112\) ppm \( (Q^2) \), resulting in a \( Q^1/Q^2 \) ratio of approximately 1. As reported previously, such changes in peak position and the \( Q^1/Q^2 \) ratio are related to structural changes in the silicate materials. The \( Q^1/Q^2 \) ratio decreases from 3 for pristine AMH-3 to 1 for A-AMH-3, AH-AMH-3, and UAH-AMH-3. This decrease in the \( Q^1/Q^2 \) ratio corresponds to a structural reordering and the increased condensation of the silicate framework. The reason for the decrease in the \( Q^1/Q^2 \) ratio is as follows: since the Na and Sr cations are exchanged by the acid and acid-hydrothermal treatments, negatively charged \( Q^3 \) species on the layer surfaces that are charge balanced with cations become condensed to \( Q^4 \) species. Therefore, the \( Q^3/Q^4 \) ratio changes, which reflects the structural changes that occur during the delamination process. Such structural changes can be explained in terms of intralayer or interlayer condensation [19–21].

On the basis of the BET results obtained in this work, we suggest that in the case of AH-AMH-3, which has a large BET surface area, the \( Q^3 \) species are mainly formed by intralayer condensation of the \( Q^3 \) species in the individual layers in AMH-3 rather than by interlayer condensation between the adjacent layers. On the other hand, the small BET surface area of A-AMH-3 reflects the decreased mesoporosity of AMH-3 that results from interlayer condensation. Thus the hydrothermal treatment leads to intralayer condensation rather than interlayer condensation during the delamination process, which increases the degree of delamination. Kim et al. reported molecular models of the layers of pristine AMH-3 and

\[\text{uptake}(\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\]

where \( R \) is the bulk resistance or ohmic resistance of the membrane sample, \( L \) is the distance between the counter electrode and the working electrode, and \( A \) is the cross-sectional area of the membrane.

### 2.5.2. Liquid uptake

The water uptake and methanol–water solution uptake of the membrane samples were determined by measuring the membrane weight difference before and after immersion. Membrane samples were dried under vacuum at 25 °C for 24 h and weighted \( (W_{\text{dry}}) \) before being immersed in deionized water or 5 M methanol–water solution at room temperature for 24 h. The wet membrane was wiped with blotting paper to remove residual water from the surface and weighed \( (W_{\text{wet}}) \). The uptake was calculated by the following equation:

\[
\text{uptake}(\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100
\]
swollen AMH-3 that were obtained by measuring the \(Q_3/Q_4\) ratios \([19]\). For these models, the molecular model with a \(Q_3/Q_4\) ratio of 1 has a more ordered pore structure. Therefore, after the delamination process AMH-3 has a more ordered pore structure and this ordered pore structure will improve transport of water through the AMH-3 layers.

FT-IR spectroscopy was also used to characterize the structural changes occurring during the delamination process. The FT-IR spectra were assigned on the basis of previous assignments \([19–21]\). The FT-IR spectra of pristine AMH-3, A-AMH-3, AH-AMH-3, and UAH-AMH-3 are displayed in Fig. 4. In the region between 4000 and 2500 cm\(^{-1}\) of Fig. 4, the absorption bands corresponding to the water and hydroxyl groups can be seen. The hydroxyl group bands near 3500 cm\(^{-1}\) appear after the delamination process, and are attributed to the hydroxyl groups from adjacent silicate layers. Hydroxyl groups that are present with water in the interlayer lead to a disordered interlayer structure \([20]\). As mentioned above, negatively charged hydroxyl groups also lead to a variation in the surface charge, which results in an expansion of the interlayer spaces. However, as shown in the FE-SEM images, the hydrogen bonds between the hydroxyl groups and water stabilize the structure. In Fig. 4, the characteristic bands due to the silicate structure can be seen between 400 and 1400 cm\(^{-1}\). The bands in the frequency range 1000–1150 cm\(^{-1}\) due to the \(Q_3\) external linkages are replaced by a single band and broadened for A-AMH-3, AH-AMH-3, and UAH-AMH-3; a new band corresponding to the condensed \(Q_4\) linkages is present near 1300 cm\(^{-1}\). These results are consistent with the \(^{29}\text{Si} \) MAS NMR results, and show that \(Q_3\) species have condensed to \(Q_4\) species during the delamination process. Kim et al. reported that the FT-IR bands in the range between 500 and 750 cm\(^{-1}\) are associated with the crystallinity of the silicate framework and that the disappearance of these bands corresponds to the significant structural disorder that occurs as a result of the swelling process \([19]\). In contrast, in our approach the silicate framework bands are still present after the delamination process, which means that structural disorder does not arise and that the crystallinity of the silicate framework is maintained during delamination. The bands below 500 cm\(^{-1}\) correspond to four-membered rings (4MRs) and are present for all samples, which reflect the preservation of the 4MRs within the layers.

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The WXRD patterns of all samples are shown in Fig. 5. Comparing the WXRD patterns of the samples with that of pristine AMH-3, it can be seen that the WXRD patterns have changed and broadened. WXRD is highly sensitive to the degree of order within

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**Table 1**

Cation contents (wt.\%) of the samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sr</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMH-3 (Theoretical)</td>
<td>21.30</td>
<td>5.59</td>
</tr>
<tr>
<td>Pristine AMH-3</td>
<td>22.52</td>
<td>5.49</td>
</tr>
<tr>
<td>A-AMH-3</td>
<td>2.46</td>
<td>0.10</td>
</tr>
<tr>
<td>AH-AMH-3</td>
<td>0.10</td>
<td>0.04</td>
</tr>
<tr>
<td>UAH-AMH-3</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>Proton-exchanged AMH-3 by amino acid (^a)</td>
<td>3.13</td>
<td>0.72</td>
</tr>
</tbody>
</table>

\(^a\) Previously reported data \([20]\).
silicate layer stacks [28–29]. During the delamination process, the d-spacing distribution becomes broader and the uniformity of layer structure and alignment is decreased due to the coexistence of hydroxyl groups and water in the interlayer spaces and the variation in the surface charge; these effects result in the changing and broadening of the WXRD patterns.

The results in this section confirm that UAH-AMH-3 is the optimal sample. Therefore, we introduced UAH-AMH-3 onto Nafion in order to prepare permselective layer-coated membranes.

3.2. Nafion membrane coated with a permselective layer

As mentioned above, AMH-3 particle size is big enough to cause the disturbance of the formation of ionic cluster in Nafion matrix, which cause proton conductivity drop. In order to minimize the reduction in the proton conductivity of the membrane, a Nafion membrane was coated on one-side with UAH-AMH-3 and it is denoted 'UAC' membrane. Fig. 6a and b show the neat Nafion and UAC membrane surfaces. The surface of neat Nafion is smooth,
that UAH-AMH-3 is well-dispersed within the coating layer. The elemental silicon shown in the figure inset. This image shows that presence of UAH-AMH-3 within the coating layer; the distribution of membrane surface. The EDS elemental mapping confirms the presence of UAH-AMH-3/Nafion nanocomposite layer. It seems that UAH-AMH-3 is more easily coated onto Nafion surface because their opening pore size has smaller than diameter of methanol and bigger than that of water. Thus, UAH-AMH-3 blocks the methanol molecules by tortuous pathway effect, thereby resulting in a reduction of methanol crossover. The proton conductivity of UAC was found to be 1.70 × 10⁻⁶/C²m, which is slightly lower than that of Nafion 115. This result shows that a reduction in methanol crossover can be achieved by a UAH-AMH-3/Nafion nanocomposite layer. UAH-AMH-3 particles in the nanocomposite layer play a role as permselective barrier because their opening pore size has smaller than diameter of methanol and bigger than that of water. Thus, UAH-AMH-3 blocks the methanol molecules by tortuous pathway effect, thereby resulting in a reduction of methanol crossover. The proton conductivity of UAC was found to be 1.70 × 10⁻⁶/C²m, which is slightly lower than that (4.09 × 10⁻²/C²m) of Nafion 115. Proton conductivity drop.

A novel membrane for DMFCs should have low methanol permeability and high proton conductivity. However, there is trade-off between methanol permeability and proton conductivity. Many studies of membranes for DMFCs have observed that a decrease in methanol permeability accompanies a decrease in proton conductivity [5–9]. Thus, the relationship between proton conductivity and methanol permeability is an important consideration in evaluations of the performance of membranes in DMFCs. One parameter used to characterize the performance of DMFC membranes is the selectivity, Φ (S s cm⁻³). The selectivity is calculated as the ratio of proton conductivity to methanol permeability. A membrane with high selectivity has the potential to provide improved DMFC performance. In the case of the UAC membrane, its selectivity is 2.21 × 10⁴ S s cm⁻³, which is an improvement of 31% over that of Nafion 115.

Table 3 lists the water and methanol solution uptakes obtained by soaking the membranes in the respective solutions at room temperature. Liquid uptake is closely related to the basic membrane properties and plays an essential role in the membrane behavior. It is known that layered silicates are excellent traps for water [31], which influences water uptake. UAC membrane exhibited similar water and methanol solution uptake. The differences between the water and methanol solution uptakes of two membranes were not too large, because only one Nafion surface was coated and AMH-3 has water sorption property. These results indicate that UAC membrane properties did not much change from Nafion 115.

4. Conclusions

In this study, we developed a facile and simple delamination process for microporous layered silicate AMH-3 by means of acid and acid-hydrothermal treatments without the use of a swelling agent. Although hydroxyl groups and water within the interlayer space can cause disordering of the interlayer in the absence of a swelling agent, the structure of delaminated AMH-3 can be stabilized by the hydrogen bonds between them. Both post-treatments lead to structural changes due to intralayer and interlayer condensation. Our 29Si MAS NMR and FT-IR results show that the pore structure of delaminated AMH-3 is more ordered and that the crystallinity of individual layers is almost unchanged in contrast to the significant structural disorder that occurs during swelling processes. In addition, our BET analysis showed that the hydrothermal treatment leads to intralayer condensation rather than interlayer condensation.
condensation during the delamination process, which results in an increase of the degree of delamination. The methanol permeability of the UAC membrane was found to decrease while the proton conductivity was nearly unchanged. Water uptake of UAC membrane is almost maintained by addition of AMH-3 particles because of water sorption property. The microporous delaminated and partially exfoliated AMH-3 was applied to the surface of Nafion to provide a better chance of maintaining the proton conductivity and reducing the methanol permeability.

Acknowledgement

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (R11-2005-065).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.micromeso.2012.09.021.

References