High Proton-Conducting Nafion/Calcium Hydroxyphosphate (CHP) Composite Membranes

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High proton conducting Nafion/Calcium hydroxyphosphate (CHP) composite membranes were prepared using homogeneous dispersive homogenizing and solvent casting process for fuel cell applications. Crystallinity from decomposed X-ray diffractograms, increased whereas crystalline sizes gradually decreased in composite membranes with the CHP amounts. In X-ray profiles, new crystalline peaks were found in the original amorphous region of Nafion in composite membranes. It suggests that the incorporated CHP forms the crystalline structure within Nafion. It may allow composite membrane to have better thermal and mechanical stability by the virtue of a kind of nucleating agent in its crystallization process. In the analysis of water bending vibration at 1673 cm$^{-1}$ by FT-IR, composite membranes showed lower water uptakes than in cast Nafion. It is also noteworthy that the disappearance of hydrated proton bending vibration at 1731 cm$^{-1}$ might explain that less water is required for proton to transport in composite membranes. In FIB micrographs many holes, considering as clusters and channels in the surface of the all membranes, were shown. It is likely that these channels are connected three-dimensionally. The 5% composite membrane has not only higher conductivity but also lower activation energy than in the cast Nafion. We conclude that the structural modification in crystalline and cluster regions as well as the improvement of proton transport through three dimensional channels may cause higher conductivity and lower activation energy in composite membranes.

Key Words : Nafion, Calcium Hydroxy Phosphate, Crystallinity, Proton Conductivity, FT-IR, Fuel Cell

1 Introduction

Nafion$^3$, perfluorosulfonate ionomer (PFSI) developed by E. I. Du Pont de Nemours, has been widely used in the various electrochemical applications.$^1$–$^3$ It is well known that hydrophilic sulfonate ion groups, linked with the per-fluorinated vinyl ethers, aggregate to form ionic clusters$^4$ or ionic domains. Its ion conductivity is affected by the formation of ionic clusters in hydrated state.$^5$

However, there are two considerable problems in Nafion. The first problem is called “methanol crossover”$^6$ where methanol, supplied as a fuel, passes through the Nafion membrane from an anode to a cathode, resulting in the oxidation in the cathode. It produces fuel consumption and efficiency loss in fuel cell. Secondly, “dehydration phenomena” at high temperatures may cause a decrease in proton conductivity considerably.$^7$ Recently several methods have been performed to suppress methanol crossover, to improve heat resistance, and to increase proton selectivity for Nafion membrane. For instance, a plasma treatment was utilized onto the surface of Nafion to suppress methanol crossover for modifying a surface morphology.$^8$–$^9$ On the other hand composite membranes were manufactured to increase proton conductivity using organic$^{10}$ polymer and inorganic materials.$^{11}$–$^{12}$

In this study, we firstly used inorganic calcium hydroxy phosphate (CHP) with Nafion ionomer in order to prepare nano-composite proton conducting membranes. This CHP was chosen because of its distinguished properties such as the proton conductivity via hydroxyl ion channels,$^{13}$–$^{14}$ the high heat stability up to 1,000°C, the high crystallinity more than 95%, a high porosity and low apparent density, and the good compatibility with various polymers.$^{15}$–$^{16}$

2 Experimental

2.1 Materials and Preparation of composite membranes

The commercially available CHP powder and Nafion perfluorinated ion exchange 5% solution (EW-1100), in a mixture of lower aliphatic alcohols and water, were purchased from Aldrich. The CHP particles were put into Nafion solution to form mixed suspension at the various concentrations. An ultra-sonicator and a magnetic stirrer were used for well-dispersed mixed solution at room temperature for 30 min. This preparation method using ultrasonicator has been also used in the fabrication of Nafion/SiO$_2$ composite membrane.$^{17}$

During solvent casting process, Nafion solution (Aldrich) or pre-dispersed CHP/Nafion solution was spread into a glass container equipped with the four-edged dam and the flat glass plate. Next, solvents were naturally dried at 25°C for 4 days and further dried on the heater plate at 60°C for 40 min to remove the residual solvents. Then, dried cast film was detached from the
flat glass surface by dripping some drops of distilled water. Finally detached membrane was boiled in the distilled water at 100°C for one hour and subsequently reserved in distilled water at 25°C prior to being tested.

2. Observation of CHP and composite membranes by TEM, SEM and Focused ion beam (FIB)

The morphology and the state of distribution of CHP particles in Nafion/CHP composite membrane were observed using SEM, TEM and FIB. The SEM image of CHP powders was obtained using JEOL 1500 microscope when the powders were scattered onto the copper plate and sputter-coated with carbon.

The interfacial adhesion state between Nafion and CHP particle was characterized by transmission electron microscopy (TEM). It is noteworthy that specimen of TEM was prepared by means of solvent casting method instead of conventionally used micro-cutting method using a diamond knife and the solvent staining.18,19 We could obtain very thin films being enough to observe directly without staining process when a drop of homogenized Nafion/CHP suspension was dropped onto the flat Cu grid, and then carbon was sputtered on the surface of membrane after drying in the vacuum for 1 h.20 This preparation method was effective to observe the interfacial adhesion state between CHP fine particles and Nafion without damage to specimen.

The FIB micrographs using positively charged Ga ion beam were obtained by FB-2000A FIB system (Hitachi) that was operated in a similar fashion to a scanning electron microscope (SEM). High beam current was used during a digging process while low beam current during imaging process.

2. 3 Crystallinity variation by WAXD

The partially dehydrated specimens for X-ray study were prepared by room-temperature drying process in a desiccator for one week. The X-ray diffractograms were recorded with Rigaku 1200 diffractometer and RINT 2000 goniometer using nickel filtered copper radiation (λ = 0.1542 nm). The X-ray system was operated at 40 kV and 20 mA. Angular scanning was continued in the range of 10° < 2θ < 50° at a rate of 2°/min. We separated original diffractogram into two decomposed peaks, crystalline and amorphous, using by Gaussian function. Subsequently the crystallinity index was obtained by the ratio of the area under the decomposed crystalline curve to the sum of under the decomposed amorphous and crystalline area. On the other hand crystalline sizes were calculated by using Scherrer equation in cast Nafion and composite membranes using Eq. (1).

\[
\text{Crystallite Size} = \frac{K \times L}{FW \times \cos q} \quad (1)
\]

where K is the shape factor of the average crystallite (generally 0.9), L is the wavelength (usually 0.1542 nm for Cu Kα), FW is the full width at half maximum, and q is the peak position.

Another specific feature in this study is that PTFE (poly tetrafluoroethylene) was chosen as a reference material for confirming accuracy of crystallinity which is obtained by four data-processing methods using: (a) a original diffractogram, (b) a base line correction, (c) a background subtraction, and (d) a background/base line correction.

2. 4 Water uptake amounts by FT-IR

Various hydrated states of cast Nafion and 5% composite membrane were examined by using Shimazu 8700 Fourier transform infrared spectroscopy at a resolution of 4 cm⁻¹ in the range 400-4,000 cm⁻¹. Fully hydrated membrane was prepared with each membrane submerging in distilled water at 25°C for 4 day. We used firstly in this study that the various hydration states in membrane could be obtained continually by controlling infrared scan numbers in the range 10-250 scans at intervals of 10 scans. This is different from conventional method that uses a kind of saturated salt solutions pertaining each characteristic vapor pressure to obtain different hydrated states.21

Water bending vibration at 1639 cm⁻¹ was used to compare water uptake amount of cast Nafion with composite membrane. On the other hand the peak at 1731 cm⁻¹ assigning to bending vibration of hydrated water was utilized to understand the form of hydrated proton in cast Nafion and composite membrane.

2. 5 Proton conductivity measurement by AC Impedance technique

Proton conductivity was measured by using ac impedance method. Blackened Pt was prepared as a working electrode that is connected to AC impedance measuring system (Hokudo Denko). To prepare blackened Pt, two pure Pt foils (Tanaka kikinzoku, 10 μm/thickness) were cut to 1.3 cm in width and 5 cm in length. Platinum wire was connected to Pt foil by a small hole. Platinum paste (Tanaka kikinzoku) was pasted and then heat-treated in electric furnace at 1,200°C for 1 h. The repetitive oxidation-reduction reaction of pure platinum metal was performed in an electrolytic solution, consisting of three components: hydrogen hexachloro platinate hexahydrate, lead acetate trihydrate, and water. Prior to the measurement, each membrane was pre-treated with 2% H₂O₂ solution and 1 M HCl solution for 3 day at 25°C. The proton conductivities were measured in lateral-transverse direction from 50°C to 99°C. Specially designed conductivity cell21 was machined by two Teflon blocks. Each block was made with a well 1.3 cm in depth, 2.54 cm in width and 2 cm in length. The distance between two electrodes was 0.5 cm. Test membrane was placed between the upper and under part of the blackened platinum. Four sets of Teflon bolts and nuts were machined at four edges to assemble cell firmly. The test cell was set up in humidity chamber where relative humidity was always fixed to 100% at each temperature maintaining for over 7 h to obtain an equilibrium state. The applied voltage was fixed to 200 mV and the frequency 100 kHz-1 Hz. The ohmic resistance was measured in the Cole-Cole plot where a linear line was extrapolated to the zero capacitance in real impedance axis, which is similar to DuPont’s method.22 Activation energy was also obtained by Arrhenius law.24
3 Results and Discussion
3.1 Microstructure of composite membrane by SEM, TEM and FIB

Figure 1 shows the microstructure of 5% CHP/Nafion composite membrane. The SEM image of CHP particles is given in Fig. 1(a). It is clear from the figure that CHP is an agglomerated particle with a diameter from submicron to over 20 \( \mu m \) in a spherical shape. It seems that these agglomerates are very fragile, and thus easily ground into small fragments by homogenizing process, performed by ultra-sonicator. In Fig. 1(b), the close-up view of the dispersed state of CHP particles in Nafion matrix is shown in the TEM image of 5% CHP composite membrane. A bunch of branch-like aggregates in the range 150-300 nm and particles under 100 nm are shown. Each aggregate seems to be consisted of many chopped fiber-like fragments. Adhesion state, in the interface region between CHP particle and Nafion, seems to be strong, indicating high interfacial adhesion strength and good compatibility. In FIB micrographs in Fig. 1 (c) and (d), many holes and channels, ranging from sub-micron to 10 \( \mu m \) in internal region, are shown. These channels are well arranged perpendicularly in the surface I as well as inner surface II. However, these hollow-fiber like channels were not seen at the first stage. It is clear that during a digging process, thermally weaker matter or physio-chemical bonding such as water and amorphous region would be easily removed by the temperature increase due to a collision with massive Ga ion. Considering the network structure model of Nafion, the small holes in the range 70-100 nm, shown in the surface, seem to be cluster regions, consisting of some sulfonic acids and some water, i.e. weaker bonding than fluorocarbon crystalline region. These channels, shown in surface II, are thought to be connected three-dimensionally. It is likely that these well-built channels can allow membrane to get high proton conductivity. In the preparation of membrane, we used the solvent casting method in which volatile solvents in gas such as alcohol and water flow vertically mostly from the heated glass bottom place to the surface, contacted with the air. It is probable that this vertical flow may form vertically arranged channel. In the section area (Fig. 1(d)), small holes are also seen, which is thought to be due to the existence of hydroxyapatite. Consequently these distributed three-dimensional network channels may contribute to high proton conductivity by the virtue of diverse proton paths.

3.2 Crystallinity study of composite membranes by Wide-angle X-ray diffraction (WAXD)

Figure 2 shows the characteristic X-ray diffractograms for PTFE, cast Nafion and composite membranes. PTFE was used as a standard material for evaluating crystallinity. The characteristic peak at 18.2° in PTFE shifts to the left lower angle in the cast Nafion and composite membranes as the CHP increases. In the composite membranes, new crystalline peaks (●) appear in the amorphous region in range 10°-16° of 2θ, and in the tiny crystalline region in the range 25°-50° of 2θ of Nafion. It

Fig. 1 Microstructure of CHP/Nafion composite membrane. (a) Scanning Electron Microscopy of CHP powders, (b) Transmission Electron Microscope for 5% composite membrane, (c) and (d) Focused Ion Beam microscopes of 5% CHP/Nafion composite membrane.
The crystallinity of Nafton is in agreement with the other results.\(^3\) The crystallinity in composite membranes, however, increases gradually with an increase in CHP contents. It suggests that some new crystals are created in the amorphous region of Nafton due to a change in crystalline kinetics.

Crystalline size was obtained by using full width at half maximum and peak position (see Eq. 1). As a result crystalline size of cast Nafton is 4.7 nm while 4.0, 3.7, and 3.6 nm for 2.5%, 5%, and 7.5% CHP composite membranes. It is certain that the crystalline size decreases with the CHP contents in composite membranes. Considering the change in crystalline size, it is probable that there are some changes even in crystalline region as well as amorphous region in composite membrane, compared to cast Nafton.

We may conclude tentatively that the CHP modify the amorphous and crystalline regions of Nafton structure by performing as a kind of nucleating agent in terms of higher crystallinity and smaller crystalline size. We are expecting that high crystallinity may improve the methanol crossover problem.

3.3 The molecular vibration by Fourier transform infrared spectrum (FT-IR)

In Fig. 4(a), two bending vibration peaks are shown in partially dehydrated states in cast Nafton. The peak at 1639 cm\(^{-1}\) can be assigned to water bending vibration in solvation layer while the peak at 1731 cm\(^{-1}\) corresponds to hydrated protons in internal and external region.\(^{20}\) However the latter peak at 1731 cm\(^{-1}\) is not shown in composite membrane in Fig. 4(b). It indicates that there are some variations in the hydration state in the form of hydrated proton in cluster region between cast Nafton and composite membrane. It is likely that less hydrated protons do exist in composite membrane. It implies that there is an important change in the hydrated proton form in a cluster. As it were, less water may be required for the proton to transport through clusters for the composite membrane.

Figure 5 shows the peak absorbance variation of water.
It is shown that ohmic resistance in real axis decrease because of lower water uptake due to a composite membranes. It takes of composite membranes are lower than that of cast Nafion. To sum up the above results, the composite membrane can have higher proton conductivity despite lower uptake contents than cast Nafion.

According to the study by R. Buzzoni et al., water bending vibration band at 1639 cm<sup>-1</sup> is related to the methanol absorption because this peak absorbance increase when the methanol dosage increase. At last we expect that methanol crossover decrease in the composite membranes because of lower water uptake due to a crystallinity increase.

### 3.4 Proton conductivity

Figure 6(a) shows the Nyquist Cole-Cole plot for 5% composite membrane from 50 to 90°C by using AC impedance method with specially designed conductivity cell. It is shown that ohmic resistance in real axis decrease gradually with increasing temperature. In Fig. 6(b), it can be seen that the proton conductivity in 5% composite membrane is higher while 7.5% composite membrane is lower than that in cast Nafion. The higher conductivity in 5% composite membrane is thought to be due to three-dimensional proton transport paths in FIB microscope in Sec. 3.1) and less water necessity for proton to transport (as explained in Sec. 3.3). The lower conductivity in 7.5% composite membranes is thought to be due to lower water uptake. From the results of water uptake test at 25°C, the water uptake content of cast Nafion was 30%, while 20% for 5% and 15% for 7.5% composite membranes. The conductivity in cast Nafion increases from 50-80°C, but starts to decline at 85°C. As explained in the introduction part, this phenomenon might be caused by water dehyadratation at high temperature and the decrease of unassociated sulfonic groups due to fluoro backbone deformation. This phenomenon was also shown in this study.

It is note worthy that the conductivities in composite membranes increased gradually from 50°C to 99°C without a decrease shown in cast Nafion. The conductivity increase at high temperature seems to be related to high thermal stability. This assumption can lead us to the tentative conclusion that the crystalline deformation such as high crystallinity and small crystalline size in composite membranes may either increase thermal stability in main backbone resulting in the hindrance from unassociated sulfonic group to associated sulfonic group formation or decrease in cluster size to obstruct the dehydration of water at high temperature. We will further study on this study by water sorption study.

On the other hand the activation energy for cast...
Nafion from 50°C to 80°C was 13.2 kJ/mol while 11.7 and 7.7 KJ/mole for 5% and 7.5% composite membranes in the range 50°C to 99°C. Lower activation energies in composite membranes are considered to be due to lots of transport paths, based on the assumption on three-dimensional channels.

4 Conclusion

In the composite membranes, it was found that the structural modification such as an increase crystallinity and a decrease in crystalline size by X-ray study. It may allow the composite membranes to have high thermal stability, which contributes higher conductivity at high temperature without a decrease in conductivity shown at the cast Nafton. It is believed that the structure modification around clusters was constituted in composite membranes, verifying by the elimination of hydrated proton bending vibration at 1731 cm⁻¹ in FT-IR spectrogram which was present in cast Nafion. It suggests that less water is necessary for proton to transport in composite membranes. Also three-dimensional conducting channels were shown in the FIB micrograph. Higher conductivity and lower activation energy in composite membrane are likely to be due to these reasons in spite of its lower water uptake. We also expect lower water uptake may improve methanol crossover in composite membranes.

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