

Investigation on Nano-Structure of Nafion Film with Metal Ion

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Nano-structure of Nafion membranes with H₂O and metal ions (Cu²⁺, Na⁺) was investigated by small-angle X-ray scattering (SAXS). The Nafion membrane brings about phase separation between ion-rich domains and fluorocarbon matrix. After soaking the membrane to water, the membrane absorbs the water and then the ion-rich domain expands. On the other hand, after soaking the membrane to a metal ion solution, the metal ion absorbed in the ion-rich domain block the expansion of the domain by making chelate with sulfate group. As a result, the membrane with the metal ion absorbs less water than that without the metal ion.

Key words : Nafion, fuel cell, small-angle X-ray scattering, absorption edge

1 INTRODUCTION

Recently, fuel cells have gotten a lot of attention in various fields as a low emission energy generation device. In fact, polymer electrolyte fuel cell (PEFC) is being used for a power source of electric devices, mobiles and so on. The PEFC mainly consists of an anode, a cathode and polymer electrolyte membranes.¹⁾ The roles of the membranes are a separator between the electrodes and a conductor of proton. Nafion, of which a chemical structure is shown in Fig. 1, is used for the membrane of PEFC because it has superior resistance for causticity and stability on thermalchemistry.

A number of small-angle X-ray and neutron scattering (SAXS and SANS) experiments have been carried out to reveal the nano-structure of Nafion membrane. It has been proposed that the Nafion membrane could make phase separation between ion-rich domains where graft chains are gathered and fluorocarbon matrix in a nano-scale.²⁻⁶⁾ It has been also supposed that the proton could propagate in the ion-rich domains and then the Nafion membrane could work as an electric conductor.⁷⁾ This means that the nano-structure deeply relates with the electrostatic features of Nafion membrane. However, the structure relating with the electroconductivity has not been clarified in detail.

In a long time operation, PEFC loses an electrical output. We deduced that the Nafion membrane could change in nano-structural scale due to absorption of water and/or metal ions. In other words, the degree of the propagation of proton could be degraded by the change in the nano-structure of the membrane. Following this line, we performed SAXS experiments in order to clarify the change in the nano-structure of Nafion by the absorption of water and metal ions. Moreover, our final goal is to improve the stability

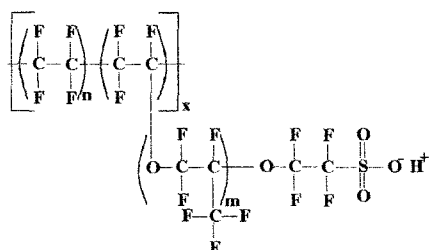


Fig. 1. Nafion chemical structure.

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Table 1. Samples.

Code	Salt	Concentration (mol/l)	Temperature (°C)	R (%)
A	Untreated	-	-	-
B	H ₂ O	-	60	14.9
C	CuCl ₂	1.00	60	16.4
D	CuCl ₂	5.00	60	13.4
E	NaCl	1.00	60	8.87
F	NaCl	5.00	60	5.82

R is the increase weight ratio of Nafion membrane after soaking in a solution(see text).

of proton conductivity by control of the nano-structure.

2 EXPERIMENTS

Nafion 117 membrane used was purchased from du Pont. Its equivalent weight and thickness were 1100 g/equiv and 175 μm in a dry state, respectively. In order to make the Nafion membrane absorption of water and metal ions, five mother solutions with different species of ions and their concentrations were prepared; H₂O (no ion), 1 mol/l CuCl₂, 5 mol/l CuCl₂, 1 mol/l NaCl and 5 mol/l NaCl. The Nafion membranes were soaked in the solutions at 60 °C for 10 days. The prepared samples are listed in Table 1. Here, increase weight ratio R of a membrane is defined by

$$R = \frac{M_b - M_a}{M_a}, \quad (1)$$

where M_a and M_b are the weights of membranes before and after soaking in the solution, respectively. Sample A is a membrane which is not soaked in any mother solution.

The SAXS experiments were carried out with a SAXS camera (SAXES) at BL10C of Photon Factory in High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. The observed scattering vector ($q = (4\pi/\lambda) \sin(\theta/2)$) was ranged from 1.6×10^{-2} to $4.5 \times 10^{-1} \text{ \AA}^{-1}$, where λ is the wavelength and θ is the scattering angle. The scattered X-ray was accumulated with a one-dimensional detector for 300 sec. The scattered intensity was normalized with an incident X-ray intensity and corrected for cell scattering and absorption. In addition, X-ray transmissions of samples C and D were observed around a Cu absorption edge. In these experiments, the energy of the incident X-ray were changed from

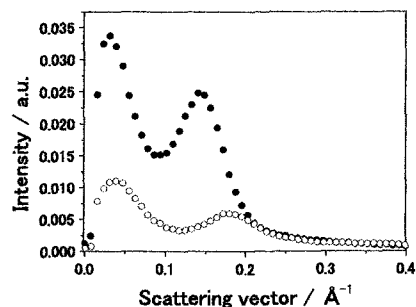


Fig. 2. SAXS profiles of Nafion membranes: Open and closed circles indicate SAXS profiles of samples A and B (untreated Nafion membrane and that soaked in H₂O), respectively.

8.89 to 9.02 keV.

3 RESULTS AND DISCUSSION

Figure 2 shows SAXS profiles of samples A and B (untreated Nafion membrane and that soaked in H₂O). There are two peaks in the SAXS profiles of samples A and B. It indicates that both samples make micro-phase separation between the ion-rich domain and the fluorocarbon matrix. However, their peak position and intensity make difference. The second peak intensity and position are more affected by the absorption of water than those of the first peak. From now on, we, therefore, concentrate on the second peak.

After soaking the Nafion membrane in H₂O, the peak position shifts to the lower q region. This means that the water penetrating to the Nafion membrane is gathered in the ion-rich domain and then the ion-rich domain is expanded. It is reasonable that the ion-rich domain absorbs the water because the fluorocarbon matrix is highly hydrophobic.

The peak intensity of sample B is more intensive than sample A. This means that the contrast for X-ray between the ion-rich domain *with* the water and the fluorocarbon matrix become more distinct than that between the ion-rich domain *without* the water and the fluorocarbon matrix.

Next, let us consider nano-structures of Nafion membranes soaked in metal ion solutions. Figure 3 shows SAXS profiles of the Nafion membranes soaked in the metal ion solutions. The peaks of membranes soaked in the metal ion solution ($q \simeq 0.15 \text{ \AA}^{-1}$) located between those of samples A and B ($q=0.144$

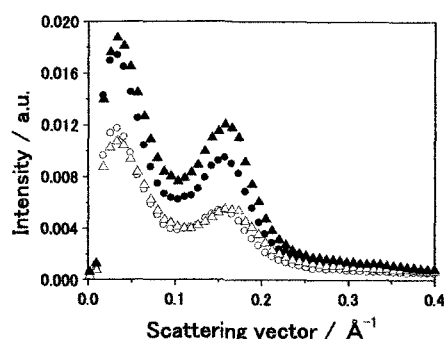


Fig. 3. SAXS profiles of Nafion membranes: Closed and open circles indicate SAXS profiles of samples C and D (Nafion membranes soaked in 1 mol/l and 5 mol/l CuCl_2 solutions), respectively. Closed and open triangles indicate SAXS profiles of samples E and F (Nafion membranes soaked in 1 mol/l and 5 mol/l NaCl solution), respectively.

and 0.183 \AA^{-1}). This means that the ion-rich domain also expands when the membrane is soaked in the metal ion solution. However, its size is smaller than that of the membrane soaked into H_2O . The peak intensity of membrane soaked in the metal ion solution is lower than that soaked in H_2O but higher than untreated one. Taking account that the water penetrating to the ion-rich domain makes the contrast for X-ray distinct, this result means that the membrane soaked in the metal ion solution absorbs less water than that soaked in the pure water does. Then it can be deduced that an electrostatic interaction between the metal ion and the sulfate group in the ion-rich domain disturbs to expand the domain and, as a result, the membrane with the metal ion absorbs less water than that without the metal ion.

Figure 4 shows the second peak position and intensity after soaking in the several metal ion solutions. The second peak of samples D and F (the membranes soaked in the 5 mol/l CuCl_2 and NaCl solutions) is less intensive than samples C and E (the membranes soaked in the 1 mol/l CuCl_2 and NaCl solutions). Considering the relation between the peak intensity and the amount of the water in the ion-rich domain, the ion-rich domains in samples C and E absorb more water than those in samples D and F. This result also suggests that a lot of metal ions could disturb water absorption into

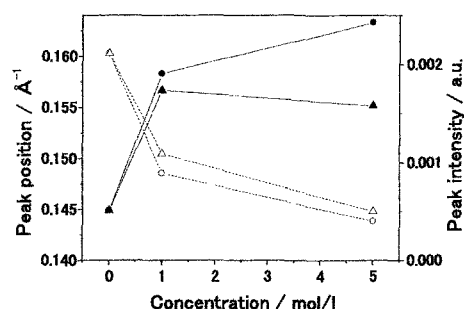


Fig. 4. The position and intensity of the second peaks of the Nafion membranes after soaking in the several metal ion solutions: Open triangle and circle indicate the peak intensities of Nafion membranes soaked in CuCl_2 and NaCl solutions, respectively. Closed triangle and circle indicate the peak positions of Nafion membranes soaked in CuCl_2 and NaCl solutions, respectively.

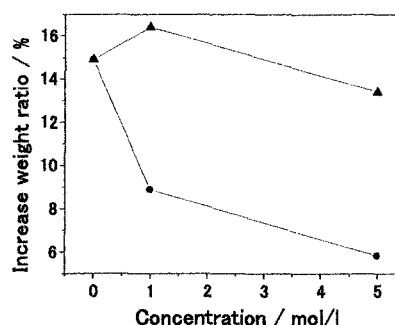


Fig. 5. Increase weight ratio of membrane with metal ion concentration: Closed triangle and circle are increase weight ratios of membranes soaked in CuCl_2 and NaCl solutions, respectively.

the ion-rich domain.

Here, going to the macroscopic view, we examine the weight change of the membrane before and after soaking. As shown in Fig. 5, the increase weight ratios of samples C and E (membranes soaked in the lower concentration solution) are larger than those of samples D and F (membranes soaked in the higher concentration solution). From the analysis of the peak intensity, it is supposed that Nafion membrane soaked in the higher concentration solution could absorb less water than that soaked in the lower concentration solution. The results of the measurement of the increase weight ratio also support this idea. In addition, we also deduced that a metal ion in

Nafion membrane disturbs the water absorption. Therefore, compared the Nafion membrane with the less water (samples D and F) to that with more water (samples C and E), the former could have more the metal ion. However, the amount of the absorbed metal ion into Nafion membrane can not be clarified by measurements of the increase weight ratio.

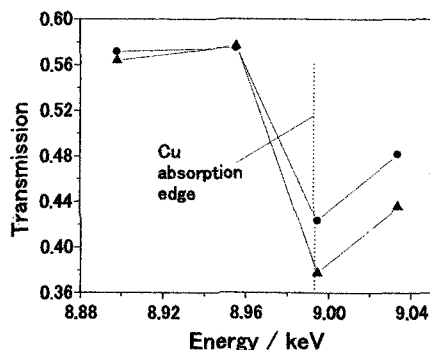


Fig. 6. Transmission of X-ray around the Cu absorption edge: Closed and open circles indicate transmissions of X-ray through samples C and D (Nafion membranes soaked in 1 mol/l and 5 mol/l CuCl_2 concentrations), respectively.

In order to clarify the amount of Cu^{2+} , X-ray transmissions were measured around the Cu absorption edge. Figure 6 shows the transmission of membrane around the Cu absorption edge. The transmissions of samples C and D are almost same in the energy region lower than the Cu absorption edge. On the other hand, in the energy region higher than the Cu absorption edge, the transmissions show clear difference: the transmission of sample D is lower than that of sample C. Taking account for X-ray absorption power around an absorption edge, the more the amount of Cu^{2+} in Nafion membrane is, the lower the transmission should be in the energy region higher than the Cu absorption edge. Therefore, sample D absorbs more Cu^{2+} than sample C. As mentioned in the previous sections, the membrane soaked in the higher concentration solution absorbs less water than that soaked in the lower concentration solution. Therefore, this result support our idea that the metal ion disturbs the water absorption because metal ions make chelate with sulfate groups.

4 CONCLUSIONS

We investigated the change of nano-structure of Nafion membranes by absorbing water and metal ion. The results of SAXS experiments are summarized as follows. Nafion membrane causes phase separation between the ion-rich domain and the fluorocarbon matrix in a nano-scale. When Nafion membrane is soaked in H_2O , the ion-rich domain absorbs water and then the ion-rich domain expanded. On the other hand, when Nafion membranes are soaked in metal ion solutions, the ion-rich domain also expands but its size is smaller than that of membrane soaked in H_2O . The metal ion in the ion-rich domain could make a chelate with sulfate group and could disturb to expand the domain. As a result, the ion-rich domain *with* metal ions could not absorb more water than that *without* them. This idea is also supported with the results of measurements of increase weight ratio after soaking and X-ray transmission around the Cu absorption edge.

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