

## Effect of Metal Ion Absorption on Structure and Electric Conductivity of Nafion

Takao Mitsui, Masaaki Sugiyama<sup>†</sup>\*, Hiroshi Orihara\*\*, Yong Hona\*\*, Yuji Soejima\*\*\*, Kazuhiro Hara\*\*\*\*, Takashi Sato, Keiji Ito\*, Kazuhiro Mori\* and Toshiharu Fukunaga \*

Department of Mechanical Engineering and Science, Kyoto University, Kyoto 605-8501 Japan

Fax: 81-724-51-2635, e-mail: tmitsui@te05.mbox.media.kyoto-u.ac.jp

Fax: 81-724-51-2635, e-mail: takashisato@t01.mbox.media.kyoto-u.ac.jp

\*Research Reactor Institute, Kyoto University, Osaka 590-0494 Japan

Fax: 81-724-51-2635, e-mail: sugiyama@rri.kyoto-u.ac.jp

Fax: 81-724-51-2635, e-mail: kgito@rri.kyoto-u.ac.jp

Fax: 81-724-51-2635, e-mail: kmori@rri.kyoto-u.ac.jp

Fax: 81-724-51-2635, e-mail: tfuku@rri.kyoto-u.ac.jp

\*\*Division of Applied Physics, Hokkaido University, Hokkaido 060-8628, Japan

Fax: 81-11-706-6639, e-mail: orihara@eng.hokudai.ac.jp

Fax: 81-11-706-6642, e-mail: na@eng.hokudai.ac.jp

\*\*\*Research and Development Center for Higher Education, Kyushu University,

Fukuoka 810-8560, Japan

Fax: 81-92-726-4711, e-mail: okosoe@rche.kyushu-u.ac.jp

\*\*\*\*Department of Applied Quantum Physics and Nuclear Engineering, Kyushu University,

Fukuoka 812-8581, Japan

Fax: 81-92-633-6958, e-mail: haratap@mbox.nc.kyushu-u.ac.jp

Nafion film absorbing metal ions ( $\text{Cu}^{2+}$ ) was investigated by measuring small-angle X-ray scattering modified by an anomalous dispersion effect (ASAXS). ASAXS is a technique for revealing a distribution of a specific atom in nano-scale. When an incident X-ray energy was changed to 8331, 8960, 8970, 8980 and 8990eV in order to observe a distribution of Cu ion (Cu-K absorption edge: 8980eV), the change in the SAXS profiles was observed. After the analysis, it was revealed that the Cu ions gather in a domain of hydrophilic groups when solvent is water. Then, Nafion films with or without metal ions ( $\text{Cu}^{2+}$ ,  $\text{Cu}^{1+}$ ) were soaked in hydrogen peroxide at 70°C for two weeks, and a structural change of these Nafion films was investigated by measuring standard small-angle X-ray scattering (SAXS). By comparing the SAXS profiles of Nafion with Cu ions to that without Cu ion, it was revealed that the structure of Nafion is changed by reaction of metal ions with hydrogen peroxide.

Key words: small-angle X-ray scattering, anomalous dispersion, Nafion, hydrogen peroxide

### 1. INTRODUCTION

Polymer electrolyte fuel cell (PEFC) has attracted a lot of attention as an environment-friendly source of energy. PEFC mainly consists of an anode, a cathode, and polyelectrolyte polymer membrane (PPM). The role of PPM is a separator between the electrodes.

During a long time operation of PEFC, PPM gradually absorbs metal ions from the environment and hydrogen peroxide is produced by catalytic processes in the PEFC operation. As a result, it is considered that Nafion is damaged by radicals created by reaction of the metal ions with hydrogen peroxide (named Phenton reaction)[1,2]. This damage induces some problems such as decrease in electric conductivity and mechanical strength and so on. Especially, the drop of electric conductivity is a serious problem for PEFC to come into wide use. From a nano-scale point of view, it was

supposed that the nano-structure of PPM could be changed by Phenton reaction, which induces the decrease in electric conductivity. Table I shows the electric conductivity of Nafion under various conditions. In the experimental results, it is confirmed that the absorbed metal ions and / or Phenton reaction induce a drop of electric conductivity of Nafion. Therefore, it seems important to know the structural change of Nafion by absorbing the metal ion in order to solve the problems of decrease in the electric conductivity of a Nafion film. In addition, it should be revealed that the location of metal ions and the structural change in PPM by Phenton reaction.

For this purpose, the nano-structure of Nafion film absorbing metal ions ( $\text{Cu}^{2+}$ ) was investigated by measuring small-angle X-ray scattering modified by anomalous dispersion effect (ASAXS) for identifying the location of metal ions in Nafion film.[3,4] In addition, the nano-structure of Nafion films with or

<sup>†</sup>To whom correspondence should be addressed.

without metal ions ( $\text{Cu}^{2+}$ ,  $\text{Cu}^{1+}$ ) soaked in hydrogen peroxide solution were also investigated by observing small-angle X-ray scattering (SAXS).

Table I. Electric conductivity of Nafion under various conditions.

Solution	Electric conductivity (S/cm)
Water	0.0644
Water + Cu ion	0.00509
Cu ion + $\text{H}_2\text{O}_2(70^\circ\text{C})^*$	0.0331

\* Cu ion was removed by washing Nafion film with HCl before measuring the electric conductivity.

## 2. TECHNIQUE

When an incident X-ray energy varies around absorption edge, a form factor of an anomalous atom is drastically changed. Fig. 1 shows form factors of Cu:  $f_0$ ,  $f'$  and  $f''$ .  $f_0$  is proportional to the total number of electrons in the atom and is independent of the incident X-ray energy.  $f'$  and  $f''$  are anomalous dispersion terms, which depend on the incident X-ray energy.

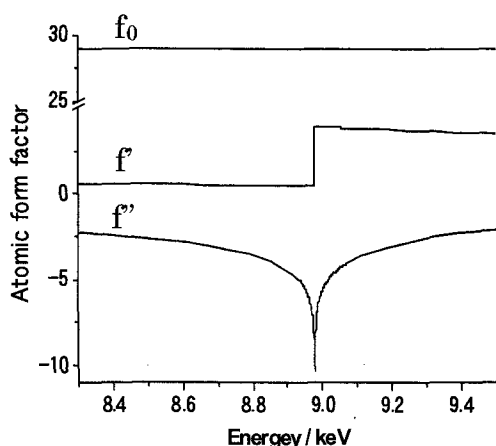


Fig. 1. Form factors of Cu:  $f_0$ ,  $f'$  and  $f''$ . The energy of Cu K absorption edge is 8980eV.  $f'$  and  $f''$  sharply change at Cu K absorption edge.  $f_0$  is independent of the incident X-ray energy. Atomic form factor  $f$  is given as  $f = f_0 + f' + if''$ .

The scattering intensity  $I(q, E)$  of a sample containing normal atoms and anomalous ones is given, as a function of incident X-ray energy  $E$  and momentum transfer  $q$ , as follows;

$$I(\mathbf{q}, E) = \left| \int_V (f_N a_N(\mathbf{r}) + f_A(E) a_A(\mathbf{r})) \exp(i\mathbf{q}\mathbf{r}) d^3\mathbf{r} \right|^2, \quad (1)$$

where  $a_N(\mathbf{r})$  and  $a_A(\mathbf{r})$  are atomic density distribution functions of normal atoms and anomalous ones, respectively.  $f_N$  and  $f_A(E)$  are their atomic form factors;  $f_N$  is nearly independent of the incident energy.  $f_A(E)$  has anomalous dispersion terms:  $f'_A$ ,  $if''_A$ . Therefore,  $f_A(E)$  depends on the incident

energy.  $q$  is given as,

$$q = 4\pi \sin(\theta/2), \quad (2)$$

where  $\theta$  is the scattering angle. Eq. (1) is derived as;

$$I(q, E) = f_N^2 G_{NN}(\mathbf{q}) + |f_A(E)|^2 G_{AA}(\mathbf{q}) + f_N f_A(E) G_{NA}(\mathbf{q}) + f_N f'_A(E) G_{AN}(\mathbf{q}), \quad (3)$$

where  $G_{NN}(\mathbf{q})$ ,  $G_{NA}(\mathbf{q})$ ,  $G_{AN}(\mathbf{q})$  and  $G_{AA}(\mathbf{q})$  are the partial structure factors of correlations between normal atoms, normal and anomalous atoms, anomalous and normal atoms, and anomalous atoms, respectively. Taking into consideration of symmetric property of the sample,

$$G_{NN}(\mathbf{q}) = G_{NN}(q), \quad (4)$$

$$G_{AN}(\mathbf{q}) = G_{NA}(\mathbf{q}) = G_{AN}(q) = G_{NA}(q), \quad (5)$$

$$G_{AA}(\mathbf{q}) = G_{AA}(q). \quad (6)$$

Therefore, Eq. (3) is expressed as;

$$I(q, E) = f_N^2 G_{NN}(q) + |f_A(E)|^2 G_{AA}(q) + 2f_N(f_0 + f'_A(E)) G_{NA}(q). \quad (7)$$

In order to obtain the partial structure factor between the anomalous atoms,  $G_{AA}(\mathbf{q})$ , a SAXS measurement should be carried out at three energies around the absorption edge:  $E_1$ ,  $E_2$ ,  $E_3$ . Here,  $G_{AA}(q)$  is calculated as follows [5];

$$G_{AA}(q) = \left[ \frac{\Delta I(q, E_2, E_1)}{\Delta f'_A(E_2, E_1)} - \frac{\Delta I(q, E_3, E_1)}{\Delta f'_A(E_3, E_1)} \right] \frac{1}{F(E_1, E_2, E_3)}. \quad (8)$$

The functions in Eq. (8) are given as follows,

$$F(E_1, E_2, E_3) = \frac{\Delta f_A^2(E_2, E_1)}{\Delta f'_A(E_2, E_1)} - \frac{\Delta f_A^2(E_3, E_1)}{\Delta f'_A(E_3, E_1)}, \quad (9)$$

$$\Delta I(q, E_m, E_n) = I(q, E_m) - I(q, E_n), \quad (10)$$

$$\Delta f_A(E_m, E_n) = f'_A(E_m) - f'_A(E_n), \quad (11)$$

$$\Delta f_A^2(E_m, E_n) = |f_A(E_m)|^2 - |f_A(E_n)|^2. \quad (12)$$

Therefore, by measuring SAXS intensities at three energies, we can obtain the partial structure factor  $G_{AA}(\mathbf{q})$  by following Eqs. (8)-(12).

## 3. SAMPLE PREPARATION

Nafion 117 film made by du Pont was used. Chemical structure of Nafion is shown in Fig. 2. Nafion has a main chain which consists of Polytetrafluoroethylene (PTFE) and is grafted by a side chain with a sulphate group at the end.

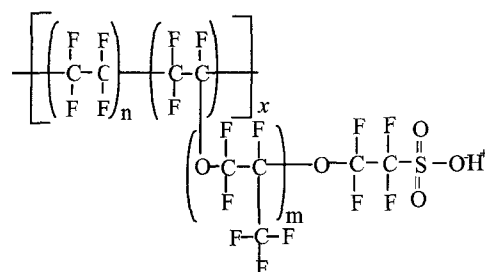


Fig.2. Chemical structure of Nafion.

In order to remove the impurities (mainly metal ions) from purchased Nafion films, all Nafion films were

soaked in HCl (0.1mol/l) and washed by deionized water: we named this procedure as "initialization".

#### Samples A and E

After the initialization, Sample A was soaked into aqueous 0.1M CuCl<sub>2</sub> solution at 25°C for four days and Sample E was soaked into deionized water at 25°C for two weeks. With Sample A, we intended to measure the distribution of Cu ion in Nafion film with ASAXS method and Sample E should be a reference one.

#### Samples B, C, and D

After the initialization, Samples B, C and D were soaked into aqueous 0.1M CuCl solution, aqueous 0.01M CuCl<sub>2</sub> solution and deionized water at 25°C for four days, respectively. Next, these Nafion films were soaked in 30% hydrogen peroxide solution at 70°C for two weeks.

To remove the metal ions from the Nafion films again, Samples B and C were soaked in HCl and washed by deionized water before their SAXS experiments. With Samples B, C and D, we intended to examine the effect of Phenton reaction for the structure in Nafion film.

Table II. Samples.

Code	Salt	Concentration	H <sub>2</sub> O <sub>2</sub> Soaking
A	CuCl <sub>2</sub>	0.1mol/l	×
B	CuCl	0.01mol/l	○
C	CuCl <sub>2</sub>	0.01mol/l	○
D	—	—	○
E	—	—	×

## 4. EXPERIMENTALS

SAXS measurements were performed at BL-10C of Photon Factory in High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. In the standard SAXS measurements, an incident X-ray energy was tuned to be Ni absorption edge (8331eV), where no anomalous dispersion effect occurs by Cu atom. As described in Sec.2, in order to observe structure factor  $G_{AA}(q)$  between Cu, SAXS intensities should be measured at three different energies where atomic form factors of an anomalous atom, Cu, are quite different. Therefore, we observed SAXS intensities of Sample A at 8331, 8960, 8970, 8980eV. Cu absorption edge is 8980eV, as shown in Fig.1. Nano-structures of Samples A, B, C, D and E were also measured by the standard SAXS method. The measurement time was 3000sec. The observed intensity was corrected for the cell scattering and absorption.

## 5. RESULTS AND DISCUSSION

### 5-1 transmission

Fig. 3 shows the transmittance of Sample A at measured X-ray energies. The transmittance steeply drops at Cu K absorption edge with increase in the incident X-ray energy. This result is attributed that the incident X-ray is absorbed by anomalous atoms above Cu K absorption edge, which directly demonstrated that Sample A contained Cu ions.

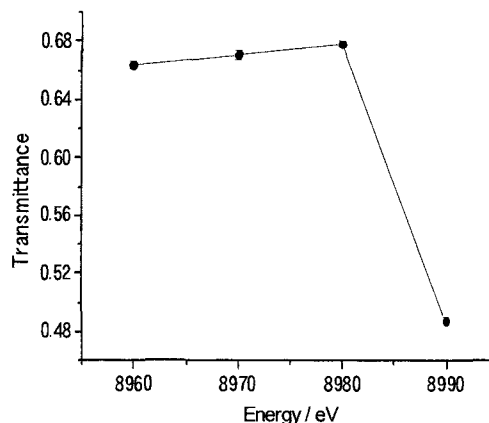


Fig.3. Transmittance of sample A at the measured X-ray energies(8960,8970,8980,8990eV).

### 5-2 Cu ions distribution

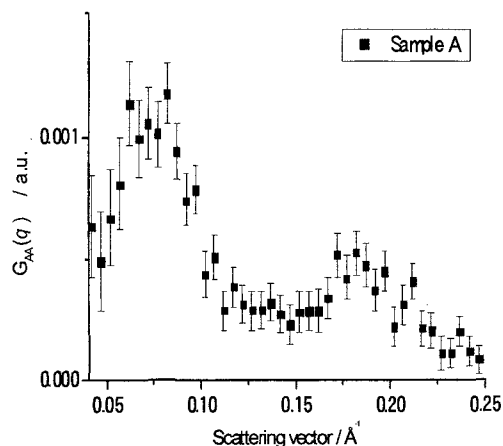


Fig. 4.  $G_{AA}(q)$  profile of sample A.

From the previous work, it is supposed that Nafion film has hierarchical phase separated structure [6]. The higher structure (larger scale structure) consists of two phase separated domains. One is a domain of the main chains (PTFE) and the other is that of the graft chains. The lower structure (smaller scale structure) exists in the domain of the graft chains. The domain of graft chains is separated into the region of hydrophobic block and that of hydrophilic block (sulfate base). In fact, two peaks around 0.05 Å<sup>-1</sup> and 0.18 Å<sup>-1</sup> have been observed in the SAXS profile of Nafion film absorbing water and both peaks have become intensive with increase of the water content in the Nafion film [6]. Taking in consideration of the chemical structure of Nafion (Fig.2), these results are explained as follows. The absorbed water locates in the hydrophilic region in the lower structure and makes contrast higher against the hydrophobic region. Therefore, the second peak intensity becomes higher. In addition, looking at the Nafion film with the larger scale, the contrast between the domain of main chains and that

of graft chain also becomes higher because the absorbed water locates in the domain of the graft chain where the hydrophilic bases gather. Therefore, the first peak also becomes intensive by absorbing water.

Fig. 4 shows a partial structure factor of Cu ion,  $G_{AA}(q)$ , in Sample A.  $G_{AA}(q)$  profile also has the first and second peaks around  $0.06 \text{ \AA}^{-1}$  and  $0.18 \text{ \AA}^{-1}$ , respectively. Therefore, it is reasonable to consider that Cu ions are also distributed in the hydrophilic region same as the water.

### 5-3 Structural change by Phenton reaction

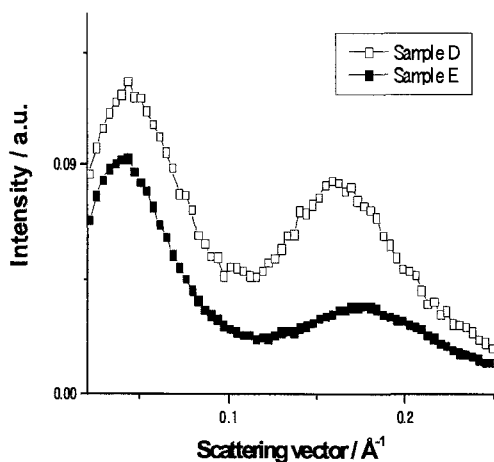


Fig. 5. SAXS profiles of Samples D and E.

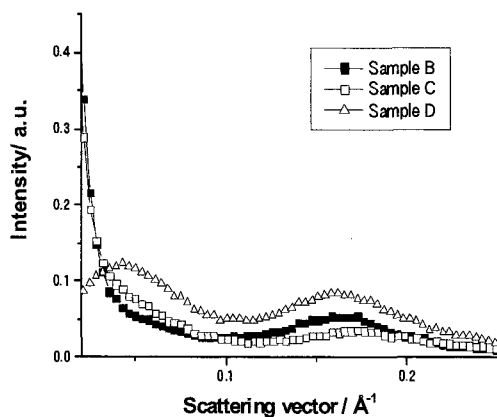


Fig. 6. SAXS profiles of Samples B, C and D.

Figure 5 shows the SAXS profiles of Samples D and E. Both samples show nearly similar SAXS profiles which had the first and second peaks around  $0.04 \text{ \AA}^{-1}$  and  $0.16 \text{ \AA}^{-1}$ , respectively, except for the intensities of the peaks: The peak intensities of Sample D were higher than those of Sample E. The peak intensity is affected by water content in Nafion film [6]. The water content is defined as;

$$\text{watercontent}(\text{wt}\%) = \frac{W_s - W_d}{W_s} \times 100, \quad (14)$$

where  $W_d$  and  $W_s$  are the weights of the dried and swollen Nafion film, respectively. The water content of Sample D was 1wt% higher than that of Sample E. Therefore, it is considered that the structure of Sample D was almost same as that of Sample E even though amount of water in hydrophilic domains was different. It means that hydrogen peroxide does not make structural change.

Figure 6 shows the SAXS profiles of Samples B, C and D. The SAXS profiles of Samples B and C are greatly different from that of Sample D. Particularly, the peak around  $0.04 \text{ \AA}^{-1}$  was disappeared and the intensity in the lowest  $q$  region became remarkably strong in comparison with that of Sample D. The change of the profile means that the radicals produced by Phenton reaction destroyed the higher phase separated structure in Nafion film.

## 6. SUMMARY

ASAXS investigation revealed the location of metal ions in Nafion. When solvent was water, the Cu ion gathered in the domain of hydrophilic groups.

Standard SAXS revealed that the structure of Nafion changed by reaction of metal ions with hydrogen peroxide. The radicals produced by Phenton reaction destroyed the higher phase separated structure in Nafion film.

## ACKNOWLEDGMENT

ASAXS and SAXS experiments were performed at BL10C of PF with the approval of Institute of Materials Structure Science of High Energy Accelerator Research Organization (proposal No.2004G066).

## REFERENCES

- [1] A. Wilkie, R. Thomsen and L. Mittleman, *J. Appl. Polym. Sci.*, **42**, 901-909 (1991)
- [2] T. Kinumoto, M. Inaba, Y. Nakayama, K. Ogata, R. Umehayashi, A. Tasaka, Y. Iriyama, T. Abe and Z. Ogumi, *J. Power. Source*, **158**, 1222-1228 (2006)
- [3] Y. Soejima, S. Kuwajima, M. Sugiyama, M. Annaka, A. Nakamura, N. Hiramatsu and K. Hara, *J. phys. soc. jpn.*, **72**, 2110-2113 (2005).
- [4] M. Sugiyama, S. Soejima, K. Hara, F. Takei, K. Itho, K. Mori and T. Fukunaga, *Trans, the Materials Res Soc of Jpn*, **30**, 855-858 (2005)
- [5] G. Goerick, R. Schweins, K. Huber and M. Ballauff, *Europhys. Lett.*, **66**, 331-337 (2004).
- [6] Y. Akai, M. Sugiyama, K. Itho, K. Mori and T. Fukunaga, *Trans, the Materials Res Soc of Jpn*, **30**, 847-850(2005).

(Received January 1, 2007; Accepted March 31, 2007)