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Structural Analysis of Polyelectrolyte Film Absorbing Metal Ion by SAXS Utilizing with X-ray Anomalous Dispersion Effect[†]

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A distribution of Cu ions in polyelectrolyte film (Nafion) is directly observed with a small-angle X-ray scattering (SAXS) method utilizing an X-ray anomalous dispersion effect. A partial structure factor of the Cu ions, $G_{AA}(q)$, can be derived from the SAXS profiles obtained by scanning the incident X-ray energy around the Cu K absorption edge. $G_{AA}(q)$ has two peaks, indicating that the Cu ions hierarchically distribute in Nafion film. In addition, a standard SAXS also shows that Nafion film has a hierarchical structure. These results mean that the Cu ions locate in the domain where the hydrophilic bases aggregate.

1. Introduction

In recent years, as raising awareness for global warming, low emission energy generation devices have gotten a lot of attention. One of the most expected devices is polymer electrolyte fuel cell (PEFC). PEFC is being used for a power source of electric devices, electric mobiles, and so on. PEFC mainly consists of three parts: an anode, a cathode, and several sheets of polymer electrolyte membrane.¹ The roles of the membrane are a separator between the electrodes and a conductor of protons.

Nafion film is used for the membrane of PEFC because it has superior resistance to corrosion and thermodynamical stability. As shown in Figure 1, Nafion consists of main chains (polytetrafluorocarbon, PTFE) and graft chains with a sulfate group at the end. Because of this chemical structure, it has been supposed that Nafion film could make micro phase separation in nanoscale: the domains of graft chains with nano size distribute in the PTFE matrix.^{2–6} In addition, it has been also supposed that a proton could propagate in the domains of the graft chains, which include many ionic groups. In other words, the connection of the domain of graft chains could create the pathway for electric conductivity.⁷ This structure model means that the nanostructure is greatly related to the electrostatic features of Nafion film. For example, if the pathway is blocked off for any reason, the electric conductivity of Nafion film deteriorates.

There are still some problems in PEFC for widely practical use. One of the problems is that PEFC starts to lose an electrical output in a long time operation. There are several reasons for the deterioration of the electrical output, such as catalyst degradation at the electrodes, degradation of electric conductivity

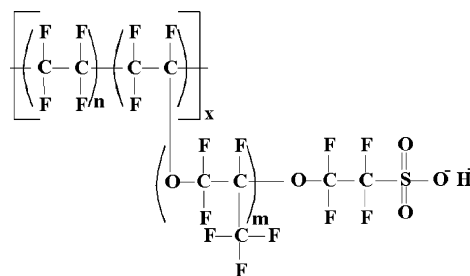


Figure 1. Chemical structure of Nafion.

of the membrane (Nafion film), and so on. Concerning the degradation of electric conductivity, it is deduced that Nafion film could absorb metal ions from the environment, and then the accumulated metal ions make its electric conductivity decrease by blocking the electric pathway as described before. Therefore, it is very important to elucidate the relation between the structure of pathway and the distribution of the absorbed metal ions. In addition, it is expected that the elucidation reveals the mechanism of the degradation of the electric conductivity and also leads to improvement of the electrostatic property of the Nafion film for PEFC.

Small-angle X-ray scattering (SAXS) is one of the most powerful tools to investigate a nanoscale structure. SAXS measurement gives us information of a spatial fluctuation of electron density. From the information, a nanostructure model of Nafion film can be built up by taking into account the difference between the electron density of ion-rich domains and that of PTFE matrix. However, because of the low spatial resolution, the standard SAXS cannot reveal the origin of the fluctuation of the electron density: the fluctuation of the atomic densities or that by heterogeneous distribution of constituent atoms. In other words, the standard SAXS can distinguish high or low electric density domains but cannot tell if many atoms or heavier atoms aggregate in the high electric density domain. It means that we cannot know the distribution of a particular atom only by standard SAXS; we have to clarify the distribution of absorbed metal ions in Nafion film.

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Recently, utilization of an X-ray anomalous dispersion effect was proposed as one answer for clarification of the distribution of a particular atom. Up to now, the X-ray anomalous dispersion effect has been usually utilized to solve a phase problem in an X-ray crystal structure analysis for a large molecule, such as a protein: the method is called "MAD" (multiwavelength anomalous diffraction).^{8,9} Because an atomic form factor of a marked atom drastically changed around its absorption edge, it should be observed that the SAXS intensity coming from the marked atom could also change by scanning the energy of the incident X-ray energy. Following this idea, Fuoss et al. applied the X-ray anomalous dispersion effect in SAXS method (ASAXS) to reveal the distributions of anomalous atoms in a metal alloy.¹⁰ Moreover, Ballauff et al. also applied the ASAXS method to a colloid particle.^{11–13} On the other hand, we have made an attempt to utilize the ASAXS method to reveal the distributions of anomalous atoms in a gel and a liquid crystal.^{14,15}

In this paper, we examine the ASAXS method as the technique to clarify the distribution of particular atom, the absorbed metal ions, in Nafion film.

2. Theory

SAXS intensity of a sample with an anomalous atom is given around the absorption edge as follows,

$$I(\mathbf{q}, E) = |\int_V \{\rho_N(\mathbf{r}) + \rho_A(\mathbf{r}, E)\} \exp(i\mathbf{q}\mathbf{r}) d^3\mathbf{r}|^2 \quad (1)$$

where, $\rho_N(\mathbf{r})$ and $\rho_A(\mathbf{r})$ are scattering powers of normal atoms and an anomalous one, respectively. Here, to separate the energy-dependent term from the independent terms, $\rho_N(\mathbf{r})$ and $\rho_A(\mathbf{r}, E)$ are rewritten as follows,

$$\rho_N(\mathbf{r}) = f_N a_N(\mathbf{r}) \quad (2)$$

$$\rho_A(\mathbf{r}, E) = f_A(E) a_A(\mathbf{r}) \quad (3)$$

where $a_N(\mathbf{r})$ and $a_A(\mathbf{r})$ are atomic density distribution functions of normal atoms and an anomalous one, respectively, and f_N and $f_A(E)$ are their atomic form factors. The energy-dependent term, $f_A(E)$, is expressed by

$$f_A(E) = f_{0A} + f'_A(E) + if''_A(E) \quad (4)$$

where $f'_A(E)$ and $f''_A(E)$ are anomalous dispersion terms that drastically change around the absorption edge.^{14,15} Here, we introduce atomic correlation functions for normal and anomalous atom density distributions.

$$g_{NN}(\mathbf{R}) = \int_V a_N(\mathbf{r}) a_N(\mathbf{r} + \mathbf{R}) d^3\mathbf{r} \quad (5)$$

$$g_{NA}(\mathbf{R}) = \int_V a_N(\mathbf{r}) a_A(\mathbf{r} + \mathbf{R}) d^3\mathbf{r} \quad (6)$$

$$g_{AN}(\mathbf{R}) = \int_V a_A(\mathbf{r}) a_N(\mathbf{r} + \mathbf{R}) d^3\mathbf{r} = g_{NA}(-\mathbf{R}) \quad (7)$$

$$g_{AA}(\mathbf{R}) = \int_V a_A(\mathbf{r}) a_A(\mathbf{r} + \mathbf{R}) d^3\mathbf{r} \quad (8)$$

Their Fourier transforms are expressed by

$$G_{NN}(\mathbf{q}) = \int_V g_{NN}(\mathbf{R}) \exp(i\mathbf{q}\mathbf{R}) d^3\mathbf{R} \quad (9)$$

$$G_{NA}(\mathbf{q}) = \int_V g_{NA}(\mathbf{R}) \exp(i\mathbf{q}\mathbf{R}) d^3\mathbf{R} \quad (10)$$

$$G_{AN}(\mathbf{q}) = \int_V g_{AN}(\mathbf{R}) \exp(i\mathbf{q}\mathbf{R}) d^3\mathbf{R} \quad (11)$$

$$G_{AA}(\mathbf{q}) = \int_V g_{AA}(\mathbf{R}) \exp(i\mathbf{q}\mathbf{R}) d^3\mathbf{R} \quad (12)$$

SAXS intensity is expressed by substituting eqs 2–12 into eq 1.

$$I(\mathbf{q}, E) = f_N^2 G_{NN}(\mathbf{q}) + |f_A(E)|^2 G_{AA}(\mathbf{q}) + f_N f_A(E) G_{NA}(\mathbf{q}) + f_N f_A(E) G_{AN}(\mathbf{q}) \quad (13)$$

Here, we assume that the atomic density fluctuation could be isotropic in our samples. Under this assumption, the average correlation functions do not have angular dependence as follows,

$$\bar{g}_{NN}(R) = g_{NN}(\mathbf{R}) \quad (14)$$

$$\bar{g}_{NA}(R) = g_{AN}(\mathbf{R}) = g_{NA}(\mathbf{R}) = g_{AN}(-\mathbf{R}) \quad (15)$$

$$\bar{g}_{AA}(R) = g_{AA}(\mathbf{R}) \quad (16)$$

and their Fourier transforms become

$$G_{NN}(q) = \int_V 4\pi R^2 \bar{g}_{NN}(R) \frac{\sin(qR)}{qR} dR \quad (17)$$

$$G_{NA}(q) = G_{AN}(q) = \int_V 4\pi R^2 \bar{g}_{NA}(R) \frac{\sin(qR)}{qR} dR \quad (18)$$

$$G_{AA}(q) = \int_V 4\pi R^2 \bar{g}_{AA}(R) \frac{\sin(qR)}{qR} dR \quad (19)$$

By substituting eqs 4 and 17–19 into eq 13, SAXS intensity is expressed by

$$I(q, E) = f_N^2 G_{NN}(q) + |f_A(E)|^2 G_{AA}(q) + 2f_N(f_{0A} + f'_A(E)) G_{NA}(q) \quad (20)$$

We are interested in a partial structure factor, $G_{AA}(q)$; distribution of an anomalous atom, which should be a metal ion absorbed in Nafion film. In order to derive $G_{AA}(q)$ from an experimental $I(q, E)$, SAXS measurement should be carried out at three energies around the absorption edge: E_1 , E_2 , and E_3 . We can eliminate $G_{NN}(q)$ by making the difference between SAXS intensities observed at two different energies.

$$\begin{aligned} \Delta I(q, E_2, E_1) &= I(q, E_2) - I(q, E_1) \\ &= \Delta f_A^2(E_2, E_1) G_{AA}(q) + 2f_N \Delta f'_A(E_2, E_1) G_{NA}(q) \end{aligned} \quad (21)$$

$$\begin{aligned} \Delta I(q, E_3, E_1) &= I(q, E_3) - I(q, E_1) \\ &= \Delta f_A^2(E_3, E_1) G_{AA}(q) + 2f_N \Delta f'_A(E_3, E_1) G_{NA}(q) \end{aligned} \quad (22)$$

where $\Delta f'_A(E_m, E_n) = f'_A(E_m) - f'_A(E_n)$ and $\Delta f_A^2(E_m, E_n) = |f_A(E_m)|^2 - |f_A(E_n)|^2$. With eqs 21 and 22, $G_{NA}(q)$ could be

TABLE 1: Characteristics of Samples

code	solution	R	σ_1 [S/cm]	σ_2 [S/cm]
A			$<10^{-5}$	$<10^{-5}$
B	deionized water	0.159	0.0511	0.2977
C	0.1 M CuCl ₂	0.254	0.0033	0.0075

eliminated, and $G_{AA}(q)$ is given as follows:

$$G_{AA}(q) = \left\{ \frac{\Delta I(q, E_2, E_1)}{\Delta f_A(E_2, E_1)} - \frac{\Delta I(q, E_3, E_1)}{\Delta f_A(E_3, E_1)} \right\} \cdot \left\{ \frac{\Delta f_A^2(E_2, E_1)}{\Delta f_A(E_2, E_1)} - \frac{\Delta f_A^2(E_3, E_1)}{\Delta f_A(E_3, E_1)} \right\}^{-1} \quad (23)$$

With experimental data, $I(q, E_1)$, $I(q, E_2)$ and $I(q, E_3)$, and eq 23, we can obtain the partial structure factor of the anomalous atom, $G_{AA}(q)$.

3. Experiment

3.1. Sample. Nafion 117 film, purchased from DuPont, was used. Structural parameters of Nafion 117 are $x = m = 1$ and $n = 6.5$ as shown in Figure 1 (EW = 1100 g/equiv), and its thickness is 175 μm in a dry state. At first, Nafion film was washed with 1 N HCl and then rinsed with deionized water to remove residual metal ions. Next, the Nafion film was dried at 80 $^{\circ}\text{C}$ for 30 min to remove the water. The above-mentioned procedure was named “initialization”: the structure of the initialized sample (sample A) was measured with a standard SAXS method. One sheet of the initialized Nafion film was soaked in deionized water (sample B) at 25 $^{\circ}\text{C}$ for 2 weeks, which is the usual state as a membrane of PEFC. The other sheet was soaked in 0.1 M CuCl₂ solution at 25 $^{\circ}\text{C}$ for 2 weeks (sample C, expecting that sample C absorbed not only water but also Cu ions from the solution. Therefore, we were interested in the Cu ion distribution in sample C. All samples are sealed into cells with kapton windows.

The weight of Nafion film was measured before every experiment. The increase in the weight ratio was defined by

$$R = \frac{M_s - M_i}{M_s} \quad (24)$$

where M_s is the weight of Nafion film after soaking in deionized water or CuCl₂ solution and M_i is the weight of initialized Nafion film. In addition, the electric conductivity of the Nafion film was also measured using an AC four-terminal method (Impedance meter: HIOKI 3532-80). Table 1 describes the characteristics of the samples.

3.2 Small-angle X-ray Scattering. A synchrotron light (SL) is a suitable X-ray source for our SAXS experiment with energy sweep because a SL provides intensive X-rays in a wide wavelength range. The used SAXS apparatus was SAXES-installed at BL10C of the Photon Factory in the Institute of Materials Structure Science (IMSS), High-Energy Accelerator Research Organization (KEK), Tsukuba, Japan. The energy of the incident X-ray was tuned with a double Si monochromator with a resolution $\Delta E/E \approx 10^{-4}$, and the scattered X-ray was detected with a one-dimensional detector. The magnitude of the observed scattering vector ranged from 2.5×10^{-2} to $2.8 \times 10^{-1} \text{ \AA}^{-1}$.

SAXS intensities were measured at three energies (8970, 8980, and 8990 eV) around the Cu K absorption edge (8980 eV) and at the Ni K absorption (8331 eV). Since it was not expected that the anomalous dispersion effect of Cu in the

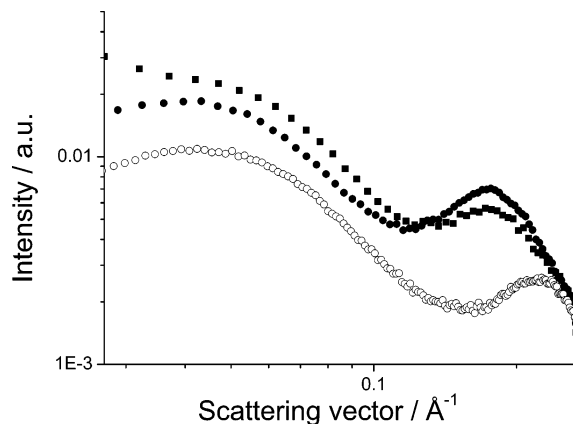


Figure 2. SAXS profiles of samples without any anomalous dispersion effect. Open circles, closed circles, and closed squares denote the SAXS profiles of samples A, B, and C, respectively.

sample could be a major component in the SAXS intensity, the scattered X-ray should be accumulated for a relatively long time, 3600 s, to observe the change in the SAXS intensity around the absorption edge. The observed SAXS intensity was normalized for the amount of the incident X-ray and corrected for the cell scattering and absorption by the kapton window taking into account the transmission.

4. Results and Discussion

4.1. Standard SAXS. Figure 2 shows standard SAXS profiles of samples A, B, and C at 8331 eV (Ni K absorption edge), where no anomalous dispersion effect is expected. As a beginning, we will examine the structure of Nafion film. Two peaks were observed in all the SAXS profiles. This result means that Nafion film does not have a simple phase-separated structure. Comparing the SAXS profiles of samples soaked in solution (samples B and C) with those of the initialized sample (sample A), the second peak position was shifted to $q \approx 0.18 \text{ \AA}^{-1}$ (samples B and C) from $q \approx 0.22 \text{ \AA}^{-1}$ (sample A). In addition, it was also observed in another experiment that the second peak position was shifted to a smaller q -position with an increase in the amount of water.¹⁸ Therefore, the second peak corresponds to the phase-separated structure between the aggregates of the hydrophobic block and those of the hydrophilic block in which the absorbed water is located because the scale of the phase separation is enlarged by the absorption of water. On the other hand, the first peak position ($q \approx 0.05 \text{ \AA}^{-1}$) did not move as a result of the absorption of water. Considering these results, we propose that Nafion film could have a hierarchical phase-separated structure, as shown in Figure 3. The superstructure, the larger phase-separated structure, is a bicontinuous phase separation between the domain of the main chains (PTFE matrix) and that of the grafted ones, of which the scale is around 150 $\text{\AA}$. The substructure, the smaller structure, is located in the domain of the graft chains where there is also a bicontinuous phase separation between the region of the hydrophobic blocks and that of the hydrophilic ones (sulfate groups) in the graft chain. The water was selectively absorbed in the hydrophilic region, and the scale is enlarged from 28 $\text{\AA}$ to 35 $\text{\AA}$ by the water absorption. However, the decrease in the volume of the hydrophobic region could compensate for the increase in the volume of the hydrophilic region because the hydrophobic block in the graft chain could be more flexible than the main chain. Therefore, the scale of the substructure becomes larger with the increase in water content, whereas that of the superstructure is almost independent of the water content.¹⁸

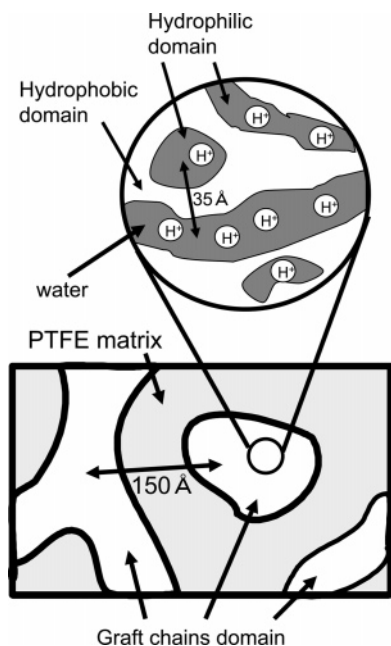


Figure 3. Schematic drawing of the hierarchical structure of Nafion film. In the superstructure, the light gray and white zones represent the domains of PTFE matrix and the aggregates of the graft chains, respectively. In the substructure, the white zone and diagonal line show the regions of hydrophobic and hydrophilic chains in the graft chains, respectively.

4.2. Anomalous Dispersion Effect around the Cu K Absorption Edge. 4.2.1. *Transmission.* Figure 4 shows X-ray transmission of the Nafion film with deionized water (sample B) and that of the Nafion film absorbing Cu ions (sample C) in the energy range between 8331 eV (Ni K absorption edge) and 8990 eV; the Cu K absorption edge is 8980 eV. The transmission of sample B monotonically increased with the incident X-ray energy due to energy dependence of no anomalous atoms, H, C, O, F, S, and Cl, in this energy range. On the other hand, that of sample C drastically dropped at the Cu K absorption edge. This clearly indicated that sample C included Cu atoms.

Here, the density of the Cu atom, d_A , can be found with the transmission data as follows,

$$d_A = \frac{1}{(\sigma_2 - \sigma_1) \cdot t} \ln \frac{T_1}{T_2} \quad (25)$$

where T_1 and T_2 are transmission at the energies across an absorption edge, σ_1 and σ_2 are their absorption coefficients, and t is the thickness of the sample. Following eq 25, the Cu density, d_A , was found to be 7.51×10^{-2} g/cm³ in sample C; $T_1 = 0.679$ (at $E = 8980$ eV), $T_2 = 0.488$ (at $E = 8990$ eV), $\sigma_1 = 35.8$ cm²/g, $\sigma_2 = 287$ cm²/g, and $t = 1.75 \times 10^{-2}$ cm. This means that the weight of CuCl₂ corresponded to 8% in the increase weight ratio, $R = 25\%$, of sample C (see Table 1). Therefore, sample C absorbed almost the same amount of water as sample B ($R = 19\%$). In addition, an area density of Cu ion ($s_A = d_A t$) in sample C was also found to be 2.06×10^{-5} mol/cm² from eq 25, whereas that of the ionic group is 3.27×10^{-5} mol/cm² in Nafion 117 (EW = 1100 and $s_{\text{Nafion117}} = 3.6 \times 10^{-2}$ g/cm²). It was supposed that the charge of the ionic group in sample C could be screened by the Cu ion if the Cu ion is located around the ionic group.

4.2.2. Distribution of Cu Ion. Figure 5 shows the energy dependence of SAXS profiles of sample C around the Cu K absorption edge. At $E = 8990$ eV, the intensity of the

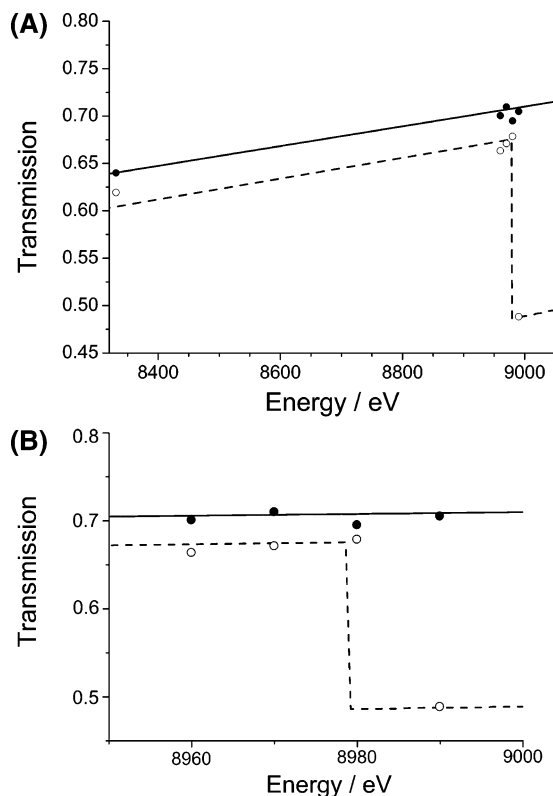


Figure 4. (A) Energy dependence of observed transmission of samples. Closed circles denote the transmission of the Nafion film without Cu ions (sample B). The solid line also shows the least-squares fitting of those data. Open circles denote the transmission of the Nafion film with Cu ions (sample C). Dashed line shows the convolution of the transmission of Cu ion, and the solid line: the density of Cu ion that was calculated with equation 25. (B) The magnified one around the Cu K absorption edge.

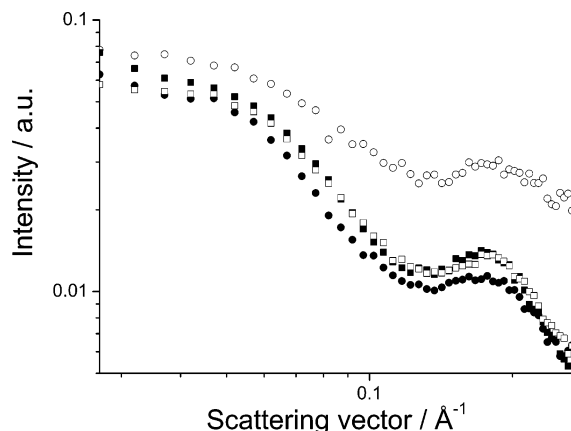


Figure 5. Energy dependence of SAXS profiles of sample C around the Cu K absorption edge. Closed squares, closed circles, open squares, and open circles denote the SAXS profiles at $E = 8331$ eV, $E = 8970$ eV, $E = 8980$ eV and $E = 8990$ eV, respectively. At $E = 8990$ eV, the background intensity became stronger due to fluorescence X-ray.

background scattering became stronger due to fluorescence X-ray from the Cu atoms. This is more clear evidence that sample C included Cu ions. However, it is difficult to estimate the amount of fluorescence X-ray in the background scattering. Therefore, we have chosen three SAXS profiles at the energies below the absorption edge, $E_1 = 8331$ eV, $E_2 = 8970$ eV, and $E_3 = 8980$ eV, to derive the partial structure factor, $G_{AA}(q)$, corresponding to the distribution of Cu ions in the Nafion film. For calculation of $G_{AA}(q)$ following eq 23, the adopted values

TABLE 2: Anomalous Dispersion Terms of Atomic Form Factors

energy [eV]	f'	f''
8831	-2.35	0.550
8970	-6.64	0.484
8980	-10.34	0.483

of the anomalous dispersion terms in the atomic form factor at these energies are listed in Table 2.

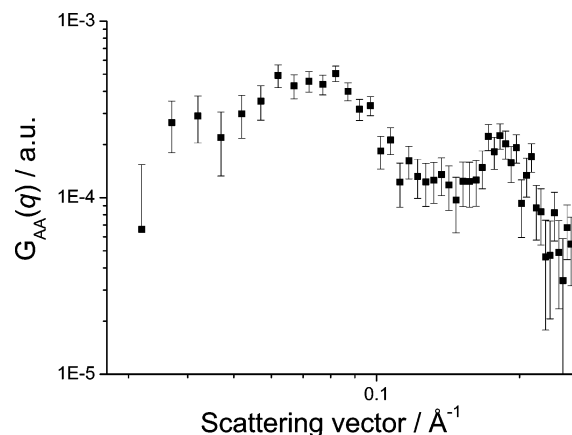
As shown in Figure 6, the partial structure factor of Cu atoms, $G_{AA}(q)$, in sample C was successfully derived from the observed three SAXS intensities. Two clear peaks are found in Figure 6, similar to the standard SAXS profile shown in Figure 2, suggesting the hierarchical distribution of Cu ions. The position of the second peak at $q = 0.18 \text{ \AA}^{-1}$ is almost the same position as that of the second peak of sample B ($q = 0.17 \text{ \AA}^{-1}$, Figure 2). This clearly indicates that the Cu ion in the Nafion film is located in the hydrophilic region consisting of water and sulfate groups. Supposing that Nafion film keeps a hierarchical structure after absorbing the Cu ions and the Cu ion is located in the region of hydrophilic groups, the distribution of Cu ions should also be hierarchical. It means that the structure factor of the Cu ions, $G_{AA}(q)$, should have the peak corresponding to the superstructure. Therefore, the first peak at $q = 0.07 \text{ \AA}^{-1}$ in $G_{AA}(q)$ could be the peak corresponding to this superstructure.

Here, we look back to the result of sample C by the standard SAXS measurement. When we compared the standard SAXS profile of sample C with the obtained $G_{AA}(q)$, we found that the positions of two peaks in $G_{AA}(q)$ are almost overlapping with those of the standard SAXS profile of sample C. This also means that the Cu ions are located in the hydrophilic region, which distributes hierarchically.

In terms of the relation between the structure and the electric property, the connectivity among the hydrophilic regions becomes higher with the an increase in the water content in Nafion film, and then the electric conductivity also becomes higher, as indicated in Table 1. When Nafion film absorbs Cu ions, it also absorbs water, and the connectivity among the hydrophilic regions increases. However, the Cu ion is replaced with a proton as a counterion of a sulfate group, and it creates the degradation of the electric conductivity on the Nafion film, as indicated in Table 1.

5. Conclusions and Remarks

We can successfully derive a distribution of Cu ions in Nafion film from small-angle X-ray scattering intensities by utilizing the anomalous dispersion effect. The Cu ion is distributed in a region where hydrophilic bases (sulfate bases) gather. This is consistent with the structural model based on the result of standard SAXS experiments. In addition, we can show how to be able to find the density of an anomalous atom in a sample

**Figure 6.** Partial structure factor of Cu ion $G_{AA}(q)$ in sample C.

from the difference in transmission below and above the absorption edge, as described in Section 4.2.1. These results indicate that we can obtain various information of a material with an anomalous atom by utilizing the anomalous dispersion effect.

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