In-situ observation of dynamic water behavior in polymer electrolyte fuel cell by combined method of Small-Angle Neutron Scattering and Neutron Radiography

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Abstract. In-situ observation was conducted on an operating polymer electrolyte fuel cell with a combined method of small-angle neutron scattering (SANS) and neutron radiography (NR). The combined measurement system has been recently developed to visualize water in a wide length scale from nano- to millimeter and successfully detected a spatial distribution of the water generated in individual cell elements; NR macroscopically detected the water in a gas diffusion layer and a flow-field, whereas SANS microscopically did in a membrane electrode assembly. In particular SANS was found to be a strong tool to make a rather precise analysis on the water content inside of ion conducting channels of polymer electrolyte membrane.

1. Introduction

A Fuel cell has attracted a lot of interests as a next-generation power supply. Particularly a polymer electrolyte fuel cell (PEFC) is promising replacement for conventional power sources because it exhibits efficient energy conversion without the chemical pollution associated with fuel combustion. The cell has an operating temperature near 80 °C, removing the need for thermal shielding and allowing for instant start-up. Additionally, the direct conversion of chemical energy to electrical energy side steps the inefficient intermediate conversion to heat and can thus result in efficiencies as high as 90%. As a result the PEFC has promising application in transportation and consumer electronic and considerable amount of research funding is being directed towards improving the efficiency, reliability, and cost effectiveness of a PEFC system¹.

Efficient water management has become increasingly important in the effort to optimize fuel cell energy production²,³. During an operation of PEFC, water is generated in individual cell elements (a polymer electrolyte membrane (PEM), catalysts, gas diffusion layers (GDL), and flow fields) as a result of electrochemical reaction, transportation and exclusion of water. Because the proton
conductivity of the PEM is highly dependent upon its internal water content, the cell must balance water production and removal to create equilibrium where the PEM is highly saturated without flooding either of the electrodes. A deficiency of water in the flow channel can potentially dry out the membrane, reducing conductivity and efficiency. However, flooding the channels with water impedes gas flow and also reduces efficiency. Therefore, it is crucial to determine simultaneously and in-situ the distribution and diffusion of the water appeared in the individual cell elements belonging to a given single fuel cell under operation.

In order to evaluate the effectiveness of water management schemes, a method capable of looking inside an operational fuel cell and visualize movement of water dynamic could be very useful. So far, many of in situ observations on the water in an operating PEFC have been attempted by several methods \(^\text{4-15}\), however scientist are still developing the best way to visualize the water generated inside an operating PEFC in a wide length scale from nanometer (microscopic scale) to millimeter (macroscopic scale). In fact it is an ambitious attempt to cover the whole length scale from nano to millimetre at once. Nevertheless, any difficulties can be overcome by taxing one’s ingenuity. Here in order to attain our purpose, utilization of neutron beam as a probe for water seems a promising solution. For example, in the microscopic scale, Small-angle X-ray scattering (SAXS) \(^\text{4}\) and small-angle neutron scattering (SANS) \(^\text{5,12}\) have successfully observed a scattering maximum, the so-called “ionomer peak” \(^\text{5-16}\), due to the ion-cluster swollen by water \(^\text{4,5,16,17}\) in the PEM. While the measurement of ionomer peak of PEM under the operating condition of PEFC is hardly achieved by SAXS since X-ray has small magnitudes in the scattering lengths, \(b\), for the “light” elements such as C, H, O and the scattering from those elements is easily overwhelmed by that from the other metallic elements. Contrarily, neutron is endowed with potential for in-situ observation of the materials consisting of light elements by following points; (i) neutron has no charge and interacts not with electrons but with nuclei of the atoms through nuclear forces (ii) the energy level of neutron (an order of 10meV) is much lower than that of X-ray (an order of keV) when they are compared with at the similar wavelength of Å order. Because of the character (i), neutron shows generally high penetration and complementary scattering properties as compared with those of X-ray. That is, neutron can pass through some kind of metal, e.g., aluminium, nearly 100\% (when its thickness is around 1cm), while neutron is fairly scattered by the materials composed of light elements, like water. Another merit of neutron given by character (ii) is that during the irradiation neutron makes nearly no damages on the specimen, such as degradation through bond breaking and following generation of radicals. Furthermore, owing to the complexity of nucleus-neutron interaction \(b\) can be greatly changed even between isotopes of the same element and in particular the difference in \(b\) between hydrogen (H) and deuterium (D) corresponds to an outstanding case. With all those merits of neutron are taken into account, in this study we conducted an in-situ observation of operating PEFC by using SANS technique. As will be described in detail in the experimental section, the accessible length scales by SANS are from micrometer to several micrometers, and thus, crucial information regarding to the water distribution within PEM and catalyst layers is well-detectable by this technique. Meanwhile, the water distribution in the flow field as well as in GDL is related to an issue of macroscopic scale and beyond the scope of SANS. However, neutron has already established the other solution to observe those macroscopic scales larger than several tens of microns, that is, a real-space imaging technique, neutron radiography (NR). Here it should be stressed again that the character (i) effectively enhances the value of NR in observation of operating PEFC. As neutron can completely pass the outer metallic parts and is highly sensitive to hydrogen, NR is one of the best methods to visualize the water distribution inside of PEFEC in the macroscopic length scale \(^\text{7,11,13-15}\).

Naturally, SANS and NR, have been developed independently to investigate static or dynamic structural properties of materials in micro- and macro-scales, respectively. From now on, it certainly gives great advantage to make both of two measurements be conducted in the same instrument and to acquire the data from micro- to macro-scales at once. To realize this idea, a neutron imaging system is installed between the sample position and detector chamber of the SANS spectrometer \(^\text{38}\). Though this
contrivable method itself is already described elsewhere\textsuperscript{18}, here we introduce typical SANS data obtained from operating PEFC giving the significance of comparison with the simultaneous NR data.

2. Experimental section

2.1. Combined SANS and NR set-up

Figure 1 shows a schematic illustration for the concept of combined measurement of SANS with NR in one instrument. As shown in figure 1a the basic instrument is the focusing and polarized neutron ultra-small-angle scattering spectrometer (SANS-J-II) at research reactor (JRR-3) at Japan Atomic Energy Agency (JAEA), Tokai, Japan\textsuperscript{19}. The total length of the spectrometer from the 1st aperture, which is located at just behind the velocity selector, to detector is 20m, and the sample position is located at the centre between the 1st aperture and detector. Thus, both of the distances from 1st aperture to sample and from sample to detector are equal to 10m and such long distances make an advantage of high spatial resolution for both SANS and NR measurements. The other detailed specifications of SANS-J-II spectrometer are described elsewhere\textsuperscript{18,19} and here we mention the typical collimations employed in measurements. The incident neutron was usually monochromatized by using a velocity selector to the wavelength of $\lambda = 6.5 \text{ Å}$ and $\Delta\lambda/\lambda = 0.13$. With utilizing the conventional pinhole collimation (i.e., $D_1$ and $D_2$, which denote the sizes of 1st and 2nd apertures, respectively, are set to $D_1 = 20 \times 20 \text{ mm}^2$ and $D_2 = 8 \text{ mm} \phi$) and the $^3$He main position sensitive detector (PSD), whose diameter and spatial resolution were 0.58 m and 5 mm, respectively, and the camera length was changed from 10m to 2.5m, we can cover the $q$-range from $q = 3 \times 10^{-3}$ to 0.2 Å$^{-1}$, where $q$ is magnitude of wave vector given by $q = (4\pi\lambda \sin(\theta)/\lambda)$ with $2\theta$ being the scattering angle. Furthermore, a high-resolution position sensitive scintillation detector (5 inch in size with 0.5 mm spatial resolution) was utilized for focusing ultra-small-angle neutron scattering (focusing USANS), to access the range of $q = 3 \times 10^{-4} \sim 3 \times 10^{-3}$ Å$^{-1}$. In all, by employing both pinhole SANS and focusing USANS, a wide range of $q$ from $3 \times 10^{-4}$ to 0.2 Å$^{-1}$, corresponding to from several micrometers to nanometers in real space, can be measured on SANS-J-II instrument.

Figure 1. Schematic diagram of a focusing and polarized neutron ultra-small-angle scattering spectrometer (SANS-J-II) (a), and illustration of a combined method of neutron radiography (b) and small-angle neutron scattering (c) installed at the SANS-J-II spectrometer at research reactor (JRR-3) Japan Atomic Energy Agency (JAEA), Tokai, Japan.
To combine SANS with NR, we installed a neutron imaging system just behind the sample position of SANS-J-II (cf. figure 1). Figure 1b and 1c schematically show our switching mode of NR and SANS measurements, respectively. The imaging system was composed of a sheet of ZnS/LiF scintillator (0.2 mm thickness), two optical mirrors, optical lens (MicroNikkor, 55 mm, Nikon Co.), and a full frame transfer type CCD camera (C4880, Hamamatsu Photonics Co. Ltd.), respectively. The CCD camera was placed far from a direct neutron beam to protect from radiation damage. The scintillator and first optical mirror were mounted on a vertical elevating bench. For NR measurements, we selected $D_1 = 20 \times 20$ and $D_2 = 50 \times 50$ mm$^2$, and $L = 10000$ mm, giving $L/D_1 = 500$ which was matched with the spatial resolution of the imaging system of 184 $\mu$m. When we observed SANS from PEFC, a scintillator sheet and the first optical mirror (defined as a NR set), were removed out from a beam line, and SANS were acquired by a 2D detector (figure. 1c).

2.2. Fuel Cell set-up
In this study we have made the following modifications on the standard single fuel cell provided by Japan Automobile Research Institute (JARI) to optimize it for the measurements of SANS and NR. On a JARI standard single fuel cell, an active area of MEA was originally 50 x 50 mm$^2$ and a flow channel for H$_2$ and air gases was a single parallel serpentine, the width, depth and pitch of which were 1mm, each. Figure 2 shows a front view of JARI cell on which the shaded square corresponds to the 50 x 50 mm$^2$ of active area of MEA as well as the area irradiated by neutron when NR measurement was conducted. While the circles with numbers correspond to the spot size of 10mmφ and indicate the irradiated area of each SANS measurement performed at different nine positions. As will be discussed later, the position dependence of SANS profile should be related to the distribution of water at microscopic scale. With each standard dimension of the JARI cell being kept, we replaced some of cell elements to enhance the transmission of neutron. Graphite flow field plates and cupper current collectors, which cause strong small-angle scattering for neutron, were replaced with those made of aluminum and further coated with a gold thin layer (1$\mu$m thickness) to achieve chemical stability and low electric resistance. Clamping plates were also made of thinner aluminum. Rubber sheet heaters were placed not to cover a MEA area of 50x50 mm$^2$. Transmission of the modified cell with those replacements described above was dramatically improved from 0.01 to 0.86 for a cold neutron $\lambda = 6.5$ Å. As will be discussed later a current-voltage curve was compared between the original standard JARI cell and the modified one and confirmed that it was well reproduced through the modification.

![Figure 2. Single fuel cell designed by Japan Automobile Research Institute, JARI is modified as suitable for SANS and NR measurements.](image)

A membrane electrode assembly (MEA) element consisted of a Nafion 212 (DuPont) sandwiched with carbon-supported catalysts of Pt (0.5 mg/cm$^2$) and PtRu (0.5 mg/cm$^2$) for the cathode and anode,
respectively was prepared by Eiwa Co. Ltd. Japan. Carbon papers were used as the GDL (190 μm thickness) for both anode and cathode. Hydrogen gas (99.99 \%) was supplied from a hydrogen generator (OPGU-2200, HORIBA STEC Co., Ltd. Japan) and air was supplied from a common gas bomb. The other description related to PEFC operating system is elsewhere.\[^{18}\]

2.3. *In-situ observation of dynamic water by combined SANS and NR method*

In this study, the fuel cell temperature was controlled at 80 °C, and dew-points of the anode and the cathode at 80°C, respectively. The flow rates of hydrogen for the anode and these of air for the cathode were set at 180 ml/min and 800 ml/min, respectively. The current density was increased step-wisely from 0 to 640 mA/cm\(^2\) with duration of 5 min at each current density. Before starting PEFC in operation, PEFC was purged with dry nitrogen for 15 min, and it was confirmed by NR that the no water was left inside the PEFC.

NR observation of operating PEFC was done for every increased current density from 0 to 640 mA/cm\(^2\). Exposure time was 210 s for each observation. After subtracting a dark image, the all images were normalized by these of the dried cell obtained before operation. Other specifications for the measurement are described in sec. 2.1.

SANS measurements were also performed on the same operating PEFC at each current density from 0 to 640 mA/cm\(^2\) alternately with NR ones. Furthermore, at each current density SANS profiles were measured for nine times at the different positions as described in sec. 2.2 (cf. figure. 2) to get the information about the distribution of water in microscopic level. The measuring time spent for each profiles was 80 s. Other detailed conditions for the SANS measurement are described in sec. 2.1, or elsewhere.\[^{18}\] The obtained data were analyzed by SANS-J-II data analysis and IGOR-Pro version 5.02 program. A scattering profile from each measurement was subtracted by the scattering profile of operating PEFC without MEA.

3. *Results and discussion*

In figure 3 the polarization curves obtained from a standard (JARI) cell and from a modified one are shown. On the same figure, the distance between ion channels, \(L_{\text{ion}}\), which is determined by SANS measurement and thus obtained from a center part of modified cell (i.e., position 5 in figure 2), is also plotted as a function of the current density. This \(L_{\text{ion}}\)-current density curve facilitates understanding of relationship between the electrochemical performance of PEFC and the water distribution at microscopic scale in PEM. Note that a more detailed explanation of \(L_{\text{ion}}\) will be described later when we illustrate a general feature of SANS profile obtained for operating PEFC system (cf. figure 5).

According to the polarization curves in figure 3, performance of the modified cell is slightly better than that of the standard cell, i.e., at the intermediate range of current density (300-400 mA/cm\(^2\)), the cell voltage (\(V_{\text{cell}}\)) of modified cell is slightly higher (by ca. 0.03-0.05 V) than that of standard cell. However, both of polarization curves of standard and modified cells exhibit basically the same behavior and can be divided into following three stage: (1) A rapid initial fall in \(V_{\text{cell}}\) occurred at the initial increment of current density from 0 mA/cm\(^2\). At the same time \(L_{\text{ion}}\) did also abruptly decrease by ca. 1.5 Å (from 39.5 to 38 Å), however, for the moment we cannot judge if there is a significant correlation between those decrement in \(V_{\text{cell}}\) and \(L_{\text{ion}}\). (2) After the first rapid fall, the \(V_{\text{cell}}\) behaved rather stable and gradually reduced from ca. 0.8 to 0.65V during the increment of current density from 50 to 450 mA/cm\(^2\). In the same stage, \(L_{\text{ion}}\) also exhibited an interesting behavior; at the smaller range of current density (from 50 to 150 mA/cm\(^2\)) \(L_{\text{ion}}\) was stable at 38 Å. While in the range of current density between 150 and 450 mA/cm\(^2\), \(L_{\text{ion}}\) certainly increased from 38 to 44 Å. It seems to exist an explainable correlation between the behaviors of \(V_{\text{cell}}\) and \(L_{\text{ion}}\) in this stage. A gradual decrement in \(V_{\text{cell}}\) with increasing current density can be attributed to the sight increments of activation over voltage as well as resistance over voltage but hardly to the increment of concentration over voltage. The ground for excluding the concentration over voltage here is the observed increment in \(L_{\text{ion}}\) at the same region. In fact, \(L_{\text{ion}}\) lends upward when the ion channels are swollen by water (cf. the symbols of dry and swollen MEA, □ and ■, in figure 3). Therefore a constant increment of \(L_{\text{ion}}\) in the range of current
density from 150 to 450 mA/cm² well reflects the increment of water content in ion channels. Such an increment is, on one hand, resulted from the enhancement in reaction rate of water production, and on the other hand, leading to an enhancement in transportation rate of protons, instead of causing a concentration over voltage. (3) In contrast, when the current density became over 500 mA/cm², the behaviors of both the \(V_{\text{cell}}\) and \(L_{\text{ion}}\) were completely changed from those observed in stage 2. Namely, \(V_{\text{cell}}\) rapidly fell down with increasing the current density and eventually PEFC stopped to operate at the current density of 640 mA/cm². While \(L_{\text{ion}}\) kept nearly constant at around 44 Å, suggesting a saturation of swelling of ion channel with water or some equilibrium swelling of ion channel attained by the balance between the inflow and outflow of water. In any case, the rapid decrement of \(V_{\text{cell}}\) observed on this stage tends to be attributed mainly to the concentration over voltage and to be connected with a curious correlation of \(L_{\text{ion}}\) behavior. Flooding of water occurred inside of the cell is, for instance, a well-known cause to impede smooth supply of reactant stuff, and one of the probable scenario to bring about both of a drop of \(V_{\text{cell}}\) and a saturation of \(L_{\text{ion}}\) simultaneously. However, to make sure such an interpretation, getting further information about water distribution by NR seems indispensable.

Figure 3. Cell voltage of PEFC before and after replacement of cell element for the combined method of SANS and NR, and inter ionic domain distance as function of current density at position 5.

Figure 4 shows NR images obtained for the modified cell operated at current densities from 0 to 640 mA/cm². Note that the inlets of anode (H₂) and cathode (air) gasses were at lower and upper right corners of the images and, their outlets were at upper and lower left corner of the images, respectively. After subtracting a dark image, the all images are normalized by these of the dried cell obtained before operation. When the current density was lower than 190 mA/cm², all of the observable area through the NR measurement is almost transparent, indicating that macroscopically water does not appear in the flow field plates. On the other hand, when the current density was ranging from 240 to 390 mA/cm², water started to appear as a shadow in the image at the upper right portion, near to the air inlet, the. The dark shadow was clearly observed along the single parallel serpentine. When the current density further increased and came to 440 mA/cm², the water started to accumulate widely from upper to middle parts of the NR image, and at 640 mA/cm², almost all area in the flow field-plates was fully filled with water. In particular, darker and more shadowed area was observed mainly on the portions of right and left edges in NR image where 90° turn regions of serpentine route exists, indicating a lot of water droplets generated in the flow fields. In contrast, the entire area irradiated by neutron becomes slightly dark, which originate from the accumulated water distributed in MEA or GDL. After acquisition of the above knowledge on the macroscopic distribution of water, the above interpretation as to the behaviors of \(V_{\text{cell}}\) and \(L_{\text{ion}}\) in figure 3 becomes more convincing. Namely, a rapid decrement in \(V_{\text{cell}}\) or a constant \(L_{\text{ion}}\) observed in stage 3 is most likely caused by the flooding of water occurred in the major part of flow field and GDL, as is clearly captured by the NR images of bottom row in figure...
4. Such a comprehensive understanding concerning the water distribution should be a great merit of combined measurements of SANS and NR and will be further discussed later (cf. figure 6 and 7). However, before making a comparison of SANS and NR data, it is necessary to illustrate the overall SANS profile obtained for the modified cell under operating condition.

Figure 4. Neutron radiography images (50 x 50 mm$^2$) obtained for PEFC with single parallel serpentine flow field at operated current densities of 0 to 640 mA/cm$^2$. Anodic inlet and outlet for H$_2$, and cathodic inlet and outlet for air supplies are shown by arrows.

Figure 5 shows SANS profiles obtained at position 5 of modified cell (cf. figure 2) and with increasing current density from 0 to 640 mA/cm$^2$, where the profiles taken at various current density from (1) 0 mA/cm$^2$ to (2) 640 mA/cm$^2$ are superposed. According to the difference in power-law behavior as well as in the change of profile with increasing current density, the scattering profiles can be divided into two regions; (i) One possesses a power-law index of ca. -4 and is appeared in the $q$ region of 0.003 $\sim$ 0.02 Å$^{-1}$, which is attributed to the carbon-supported catalysts packed in MEA. Within this region, the scattering intensity was slightly decreased with increasing current density (cf. a thick gray arrow indicating downward at $q=0.005$ Å$^{-1}$). (ii) The other possesses a power-law index of -2 and dominate the $q$ region of 0.035 $\sim$ 0.2 Å$^{-1}$, which is reflecting the structure of Nafion membrane in MEA. The scattering peak appeared at around $q = 0.15$ Å$^{-1}$ corresponds to “ionomer peak” and this peak intensity was increased with increasing current density due to the swelling of ion-cluster by water.

Assuming that the Nafion membrane, which is under the PEFC operation and swollen by water, is separated into the following two phase; (i) crystalline domains, which consists of polytetrafluoroethylene (PTFE) backbone and strongly expels water, and (ii) ion conducting channel, which is induced by and composed of the water surrounded by the sulfonic acid side chains of Nafion. Then, the scattering intensity in the second region (Nafion membrane) can be formulated as follow:

$$I(q) = I_{cr}q^{-\alpha} + I_{ion}\exp[-C(q-q_m)^2] \quad (C > 0)$$

where $I_{cr}q^{-\alpha}$ is scattering intensity of crystalline domain phase with slope, $\alpha = 2$, and $I_{ion}\exp[C(q-q_m)^2]$ is scattering peak due to the spatial distribution of the ion conducting channel of Nafion approximated by a Gaussian function.

From the scattering intensity of ion conducting channel, $I_{ion}$ peak-height is related to the magnitude in scattering length difference between water in the ion channel and matrix phase of the Nafion.
membrane. High peak indicated large contrast and therefore large amount of water is expected to be included in the ion channel. The $I_{ion}$ can be calculated as follow:

$$I_{ion} = \Delta b_{ion}^2 \, \varphi (1 - \varphi)$$  \hspace{1cm} (2)

where $\varphi$ is the volume fraction occupied by ion channel in the membrane, and $\Delta b_{ion}$ is the difference in the scattering length density between the ion channel (here approximately consists of only water) and the matrix phase of Nafion membrane as given by following eq. 3.

$$\Delta b_{ion} = \varphi \, b_{D_2O} + (1 - \varphi) \, b_{H_2O} - b_{Nafion}$$  \hspace{1cm} (3)

The coherent scattering length of $j$-th molecule, $b_j$ ($j = D_2O, H_2O$ and Nafion), is calculated by $b_j = \left[ N_A \rho_j \sum n_i b_i \right] / M_{w,j}$, where $N_A$ is Avogadro’s number, $\rho_j$ is the mass density (g/cm$^3$) of $j$-th molecule, $n_i$ is number of atomic species $i$ in $j$-th molecule, $b_i$ is the bound scattering length of atomic species $i$, and $M_{w,j}$ is the molar mass (g/mol) of $j$-th molecule. $\varphi$ is the fraction of deuterated water (D$_2$O) in the ion channel when D$_2$O and H$_2$O coexist in the system. In this study $\varphi = 0$ due to only H$_2$O produced in the experiment. The $b_{H_2O} = 5.6 \times 10^{-7}$ Å$^2$, and $b_{Nafion} = 4.11 \times 10^{-6}$ Å$^2$. Meanwhile, $C$, which controls the peak-width, is related to inhomogeneity of the interdomain distance of ion channel. Wider peak indicated large inhomogeneity in interdomain distance. And, $q_{m}$, peak-position, where the maximum intensity of the peak is located, is related to $L_{ion}$, i.e., the magnitude of interdomain distance between ion channels itself, as has already been introduced in figure 3. $L_{ion}$ is determined from $q_{m}$ by $L_{ion} = 2\pi / q_{m}$. Shift of the peak to the lower $q$ indicates increase in $L_{ion}$ and as a consequence suggesting the accumulation of water in ion channel. In summary, as the current density increases we found the following features on SANS profile: the scattering intensity at $q= 0.005$ Å$^{-1}$ slightly decreases; whereas the scattering peak at around $q = 0.15$ Å$^{-1}$ systematically increases, and its $q$-value shifts to a lower value. These findings are attributed to appearance of the water in MEA in nanometer scale.

![Figure 5. SANS profiles obtained for an operating PEFC at steady state at position 5 with increasing a current density from 0 to 640 mA/cm$^2$.](image-url)

Next we will show the advantages of the combined NR and SANS method to visualize water in operating PEFC. As shown in figure 4 that at the current densities of 0 to 190 mA/cm$^2$, the NR images...
in all observable area is almost transparent, indicating that water does not appear macroscopically in the flow field plates. However, when these range of current densities was applied, actually the water already appeared in the MEA, which was detected by SANS as shown in figure 6. This figure shows $L_{ion}$ determined by SANS measurement at each position from 1 to 9 (cf. those positions for SANS measurement have been assigned in figure 2) as a function of current density. As we discern in the figure 6, even no current density was applied in the operating PEFC, $L_{ion}$ at any positions is bigger than that of in dried MEA (35 Å). This indicates that the water still remained in the ion channel after purging process of residual water from inside of PEFC with nitrogen gas. At low current densities (smaller than 190 mA/cm$^2$), the accumulation of water at upper positions of MEA (position 1, 2, and 3) was higher than that of other positions as indicated by higher $L_{ion}$ values. Further, by increasing the current density up to 390 mA/cm$^2$, distribution of water in the ion channel increased rapidly indicated by drastic increase in $L_{ion}$. Especially, at the position 1, 2 and 3, water appeared not only microscopically in MEA, but also macroscopically in the flow field as recorded by NR (cf figure 4). At higher current density (above 390 mA/cm$^2$), there was no change in $L_{ion}$ at the position 1, 2 and 3 indicating that saturation as to swelling of ion channel with water was reached in those positions. Excess of water seemed to flow over to the flow-field plates and dropped to the lower flow field until reached the water outlet of the operating PEFC. At the same time, at the lower positions of SANS measurements, the distribution of water in ion channel increased rapidly to reach the maximum of $L_{ion}$, and the excess of water also distributed to the flow field. In such a way, by applying combined SANS and NR method, we can make a seamless visualization of water inside of PEFC in wide range scale from nano- to millimeter order.

Moreover as has been partly argued in figure 3, due to the in-situ observation by SANS, we can estimate the relationship between microscopic water distribution during the operating of PEFC and electrical properties of the MEA. In figure 7, $V_{cell}$ is plotted as a function of $L_{ion}$, of which data is estimated from the SANS profile taken at position 5, as an attempt to visualize the relationship between these two parameters more directly. Note that the curve of figure 7 is hereafter denoted as “$L_{ion}$- $V_{cell}$” curve for simplicity. In this figure an increase in $L_{ion}$ from 38 Å to about 44 Å, indicating an accumulation process of water in ion conducting channel, is clearly recognized as nearly horizontal part of $L_{ion}$-$V_{cell}$ curve. In this stage, where current densities being higher than 190 mA/cm$^2$ and up to 440 mA/cm$^2$, the performance of the MEA did not show any significance changed which was showed
by small decrease in the cell voltage (0.8 to 0.71 V). However, at current densities higher than 440 mA/cm², an abrupt decrease in \( V_{\text{cell}} \), indicating that the performance of the PEFC lowered, is observed in \( L_{\text{ion}} - V_{\text{cell}} \) curve at the position of \( L_{\text{ion}} \approx 44 \, \text{Å} \) where inter ionic distance was still smaller than that of swollen MEA (46 Å). In summing up those observed information, it may be speculated that the cause of lowering of the performance in this PEFC system was not the limitation of proton conductivity of Nafion membrane but the limitation of reaction rate at catalyst layer or the limitation of the rate of discharging water in flow field as well as GDL.

4. Conclusion

In-situ observation was successfully conducted on the operating PEFC system with applying the combined measurement system of SANS and NR, which has been recently developed. Due to a complementary combination in accessible length scale between SANS and NR, nearly seamless observation was possible as to water widely distributed from nano- to millimetre scale. In particular, SANS was found to be a powerful tool to estimate the amount of water in swollen state of PEM as well as that in catalyst layer. Through this study it was well confirmed that microscopic distribution of water (obtained by SANS) as well as macroscopic one (obtained by NR) are strongly correlated to the electrochemical performance of PEFC system.

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