Surface Morphology and Proton Conduction Imaging of Nafion Membrane

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AC-mode atomic force microscopy (AFM) and electrochemical methods were used to identify the proton conducting regions of Nafion membrane. It was found that the surface of Nafion membrane was constructed of small hydrophobic granular domains and that protons passed through the hydrophilic regions formed in the interstices between those domains.

Polymer electrolyte membranes are one of the most important components for polymer electrolyte fuel cell (PEFC) systems, which are considered to be a promising alternative power generator for the vehicle and stationary use. To improve the properties of polymer electrolyte membrane and maximize the fuel cell performance, it is necessary to explicate the mechanism of proton conduction. Even in Nafion, one of the most popular polymer electrolyte membrane, the proton conduction mechanism still remains unclear parts despite large numbers of studies.[1] The nanostructure of Nafion membrane is found to be an inhomogeneous, hydrophilic–hydrophobic phase-separated structure on the basis of small angle X-ray scattering (SAXS) studies.[2] This finding led to a proposed model called "ionic cluster network," and it has been widely accepted for fundamental understanding and explanations of the proton conduction mechanism of Nafion. However, it is not confirmed whether this model agrees with the actual surface and internal structure. Thus, a number of attempts that observe the surface structure including ionic cluster networks of Nafion by using atomic force microscopy (AFM) have been conducted.[3] Recently, several groups independently reported the results that distinguish the active proton channels of the membrane surface using a combination of contact-mode AFM and electrochemical techniques.[4–6] In those studies, although mapping of proton conduction was obtained, the correlation between the surface structure and the active ion path was not explained. In this paper, simultaneous observations of proton conduction and surface structure by using AC-mode AFM are presented. This technique achieves much higher resolution, enough to distinguish the electrochemically active regions; thus the relationship between the membrane morphology and the active proton path becomes apparent.

Nafion membrane NE-1135 and Nafion dispersion DE2020 were purchased from DuPont (Wilmington, DE). NE-1135 is a membrane of 1100 equiv wt polymer and 88-μm (3.5 mil) thickness. DE2020 is 20 wt % dispersion in water/alcohol mixture of 1000 equiv wt polymer. Membrane and dispersion samples were used as received. A diagrammatic sketch of the AFM equipment is shown in Figure 1. A commercial AFM apparatus (JSPM-5400, Nihon Denshi (JEOL)) and Pt-coated conductive cantilever (Budgetsensors), with a resonance frequency of 300 kHz and a spring constant of $40\,N\,m^{-1}$, were used. A

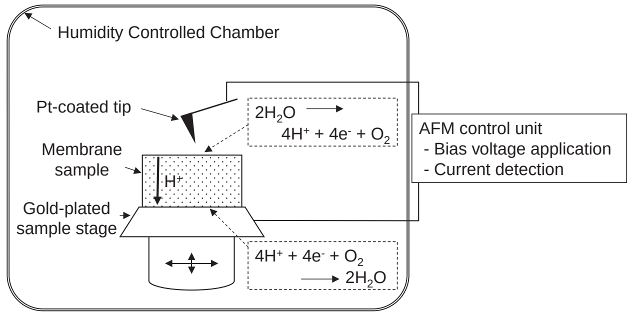

Figure 1. Diagrammatic sketch of AFM equipment.

humidifier unit was connected to control the inside humidity of the AFM chamber. A Nafion membrane sample was placed on the gold-plated conductive stage with Nafion dispersion as adhesives. During the observation, a bias voltage was applied to the sample stage. If a current is detected, it means the tip comes in contact with some water that exists on an active ion path. When the tip contacts the water, protons are provided through electrolysis. They are transported to the opposite side through the membrane and react with the oxygen dissolved into the membrane at the interface of membrane and sample stage. Even if the tip contacts to some water on an inactive region, no current is detected. The mapping of these currents gives the images of proton-conducting regions.

Figure 2 depicts (a) topography, (b) phase, and (c) current images of an NE-1135 surface exposed to the air of 90% relative humidity.[7] All the images are simultaneously collected; therefore, they are exactly the same area. The proton conducting spots were homogeneously dispersed on the surface regardless of the roughness of the topography. There seems to be no simple correlation between the topography and current image as other groups have mentioned.[4–6] On the other hand, the phase images have correlation with the current image compared with the topography. The proton-conducting areas represented as bright spots in the current images were observed at roughly the same positions as the dark spots which correspond to hydrophilic regions in the phase images. More detailed observation at smaller areas provides important information about the surface morphology and the proton conduction. The topography and phase images displayed in Figures 3a and 3b, respectively, show that the surface of a Nafion membrane is composed of small particles which correspond to the hydrophobic regions.[8] They might imply coagulation of backbone-rich units, and the size range is 10–20 nm. The hydrophilic regions, which are recognized as dark areas in the phase image, exist in the interstices between the hydrophobic particles, and the shapes are not circular. In

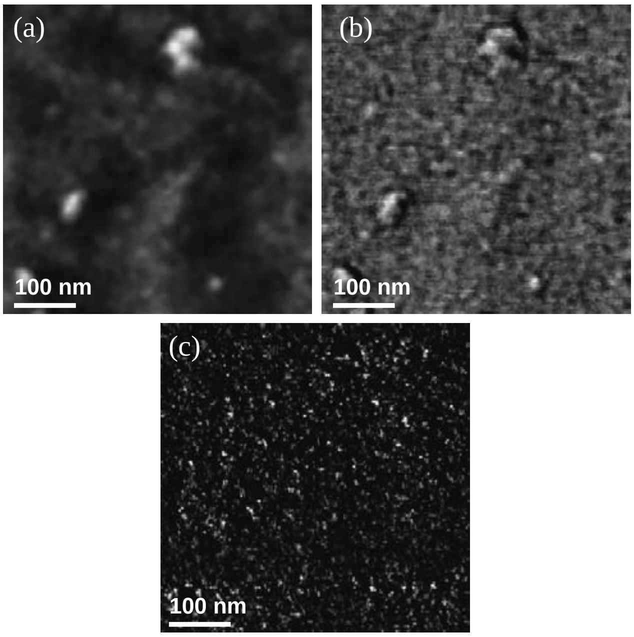

Figure 2. High-resolution AC-mode AFM images of Nafion NE-1135 membrane sample: (a) Topography (z-scale maximum 10 nm), (b) phase image (z scale 15°), and (c) current image (z-scale maximum 30 pA represented in white). Scan size: 500 nm × 500 nm. Scan rate: 2 Hz. Applied bias voltage: −1.5 V.

the current mapping image (Figure 3c), the proton conduction is observed only at the hydrophilic regions. Interestingly, each of the conductive domains is not one spot, but gathering of a number of spots over a several nm scale as shown in Figure 3d. Numerical analysis of the current value indicates that each domain has different activity which might reflect the tortuosity and connectivity of the network through the membrane. In fact, not every hydrophilic region conducts the same current value, and some domains are inactive, which means no current was detected. These results provide an assumption about the origin of the well-known water cluster network of Nafion. The proton conduction areas seem to be formed by the agglomeration of polymer particles, which have hydrophobic cores and hydrophilic shells.

In conclusion, the simultaneous observations of surface morphology and current imagings were performed by using of AC-mode AFM under humidified conditions. The results revealed a relationship between the surface structure and proton conduction of Nafion. The surface was composed of hydrophobic particles, and well-known ionic-cluster networks existed in hydrophilic domains filled in the interstices between the polymer particles. This new method to obtain the morphology and the current images simultaneously is useful for not only the clarification regarding the proton-conducting mechanism for polymer electrolytes but also for the development of new electrolyte materials. Especially, this method needs no membrane–electrode assemblies, so damages on the surface are avoided, and the amount of membrane required for the evaluation is very small. It will be a powerful tool to accelerate the development of polymer electrolyte membranes.

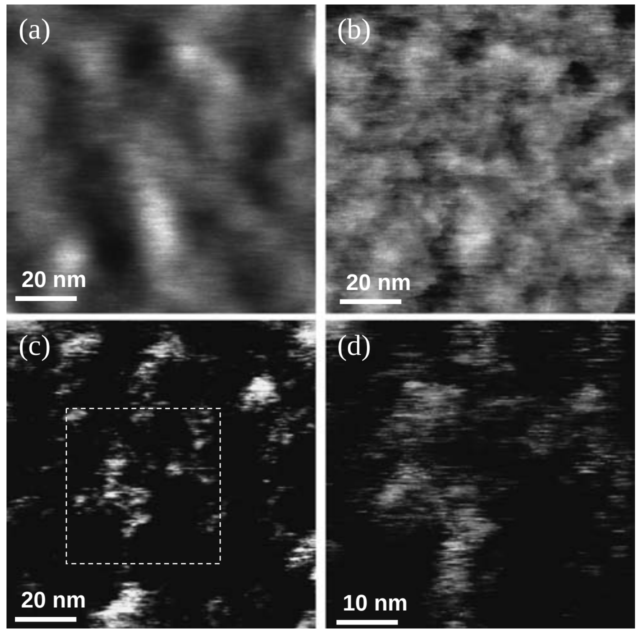

Figure 3. High-resolution AC-mode AFM images of Nafion NE-1135 membrane sample: (a) Topography (z-scale maximum 4 nm), (b) phase image (z scale 15°), (c) current image (z-scale maximum 30 pA), and (d) current image of the area enclosed with dashed lines in c (collected independently). Scan size: 100 nm × 100 nm (a,b, and c) and 50 nm × 50 nm (d). Scan rate: 2 Hz. Applied bias voltage: −1.5 V.

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7 In order to avoid the other possibilities of interpretation for the obtained images, many control experiments were conducted. As a result, no current is detected without Pt-coated cantilever, humidified condition, bias voltage, and electrical connection between sample stage and membrane. This indicates that the detected current is attributed to electrochemical reactions, thus they reflect the proton conduction of the membrane. The influence of the applied bias voltage upon both the topographic and the phase images is also checked and found to be negligible.

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