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Reversible/irreversible increase in proton-conductive areas on proton-exchange-membrane surface by applying voltage using current-sensing atomic force microscope

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ABSTRACT

By using a current-sensing atomic force microscope (CS-AFM) under a hydrogen atmosphere, microscopic proton-conductive areas on the membrane surface of sulfonated poly(arylene ether sulfone ketone) block copolymer were investigated. With increasing the bias voltage during the CS-AFM scans, the number and the diameter of proton-conductive spots on the membrane surface continuously increased. Both reversible/irreversible changes in the proton-conductive area on the surface were found. The reversible change indicates that the proton-conductive paths are dynamically rearranged during the power generation in a polymer electrolyte fuel cell. The irreversible change might be related to the enhancement of the performance of the membrane electrode assemblies after being "conditioned" prior to the operation.

1. Introduction

Proton exchange membrane (PEM) is one of the key components that govern the cell performance of a polymer electrolyte fuel cell (PEFC), which is a promising alternative power source for stationary, automotive, and mobile applications due to their advantage of high efficiency and low emission [1,2]. While perfluorosulfonic acid ionomers (PFSA), such as Nafion®, have been most commonly used due to their high proton conductivity and chemical stability, PEMs based on sulfonated aromatic polymers have been extensively studied from the viewpoints of cost, environmental friendliness, and gas impermeability in recent years [2–12]. In our group, a series of sulfonated poly(arylene ether) block copolymer (SPE-bl) membranes have been developed with a unique hydrophilic/hydrophobic phase-separated morphology [13–18]. The performance of cells composed with the SPE-bl membranes has also been reported [16,17,19,20]. The SPE-bl membranes showed high proton conductivity, comparable to that of Nafion due to their phase-separated morphology with well-interconnected proton transport pathways. With using a current-sensing atomic force microscope (CS-AFM), we have elucidated the proton conductive areas on the surface of an SPE-bl membrane, SPE-bl-1 (Fig. 1) [21], under a hydrogen atmosphere at various temperatures and humidities. The size of the proton conducing spots was little changed regardless of the temperature and humidity, whereas the number of the spots increased at higher humidity; accordingly, the total conductive area on the surface increased [21].

Prior to the operation, PEFCs are "conditioned" in general for higher performance. The conditioning processes vary, but normally, a power generation at a high current density for a certain period of time is required [22–25]. One of the major effects of the conditioning is understood as cleaning the membrane electrode assembly (MEA) both in the catalyst layers and in the membrane [22,23] by the reactions on the catalyst surface and water flux through the membrane, respectively. Another factor is believed as the improvement in connectivity of the hydrophilic clusters inside the membrane by the generated water [22]. Sanchez and co-workers reported that the current of proton reduction reaction on the Nafion membrane surface detected by CS-AFM was increased after a cell operation [26]. Furthermore, the improvement in connectivity of the hydrophilic clusters by water vapor is supported by CS-AFM measurements, in which the number of the proton conductive spots on the surface increased as the humidity increased [21,27–32]. Although higher humidity is important for establishing proton paths of the membrane, the effects of the proton flow through the membrane on the membrane performance during the conditioning have not been well understood.

In this study, we investigated the effects of bias voltage on the proton-conductive paths of an SPE-bl-1 membrane using a CS-AFM; the voltage was applied between the tip and the sample both for detecting the current and activating the proton conductive

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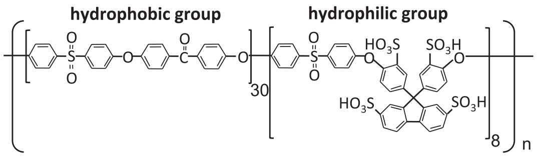

Fig. 1. Chemical structure of SPE-bl-1.

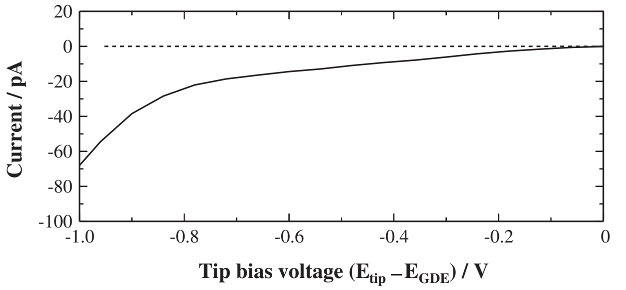

Fig. 2. *I–V* curves of an SPE-bl-1membrane obtained on a Pt-Ir coated AFM tip under dry (dashed line) and 70%-RH (solid line) conditions under 5% H_2 at 30 °C.

paths. At a higher voltage and current density, CS-AFM images clearly showed the increase of proton conductive areas. The change of the proton conductive areas was found both irreversible and reversible. The irreversible process might be related to the conditioning of the MEA, whereas the reversible process to the rearrangement of the proton conductive networks during the power generation as is discussed in the text.

2. Experimental section

An electrolyte membrane sample for the CS-AFM measurement was prepared by hot pressing a Nafion-binder-coated (approximately 2 μm thick) SPE-bl-1 membrane with a gas diffusion electrode (GDE) at 140 °C and 1.0 MPa for 3 min, as described in our previous paper [21]. The SPE-bl-1 membrane with an ion exchange capacity (IEC) = 1.70 mequiv g^{-1} and the repeating unit in hydrophobic and hydrophilic blocks, $X = 30$ and $Y = 8$, respectively, were synthesized in our laboratory [13–17]. The membrane was obtained by casting on a poly(ethylene terephthalate) substrate, and the membrane surface having been attached to the substrate was used for the CS-AFM measurements. GDEs with a three-layer structure, i.e., catalyst layer/microporous layer/wet-proof carbon paper, were prepared as in our previous papers [25,33,34]. The Pt loading of the GDE was 0.5 ± 0.1 mg cm^{-2}. The SPE-bl-1 hot pressed on the GDE was placed on the temperature-controlled sample stage for the AFM measurements.

Morphology and current images were simultaneously recorded using a commercial AFM system (SPM-5500, Agilent) equipped with a homemade environmental chamber and a current sensing circuit between a tip and a sample. A conductive silicon tip coated with Pt–Ir (Nanoworld, tip radius of 10–20 nm) was used as the AFM measurement probe. The CS-AFM observation was carried out in an environmental chamber under a 5%-H_2 (N_2 balance) atmosphere at 30 °C and 70% RH. The flow rate of supplied gas was set at 100 mL min^{-1}. On the CS-AFM measurements, a bias voltage from 0.4 to 0.8 V (negative voltage at the tip) was applied between the AFM tip and the GDE, which may correspond to an overvoltage mainly for the ohmic voltage-loss in proton-conductive paths and in part for the hydrogen evolution at the tip [21], referred to the stable potential for the GDE in an H_2 atmosphere. It took 15 min to obtain a CS-AFM image, and two images (scanned in the downward and upward directions) were recorded at each voltage, the first of which is presented in this paper. During the DC polarization, the oxidation reaction of hydrogen gas (the hydrogen oxidation reaction, HOR) supplied from the environmental chamber took place on the GDE. Then, the protons generated at the GDE were transported through the PEM and reduced to form hydrogen (the hydrogen evolution reaction, HER) at the AFM tip [21]. The measurements were carried out in a contact mode with a contact force of 20 nN.

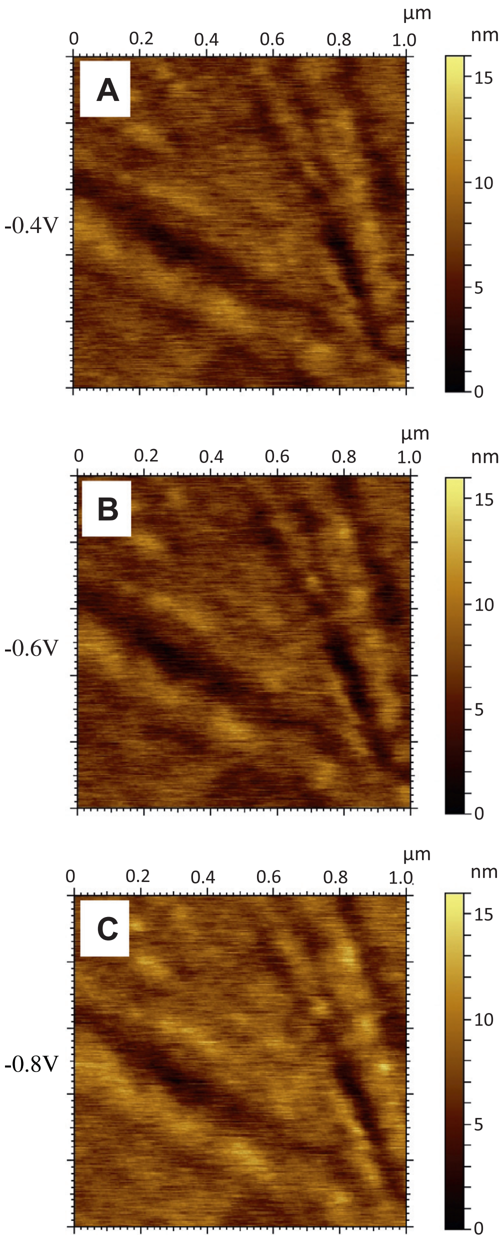

Fig. 3. Morphological images on an SPE-bl-1 surface at various bias voltages under 5% H_2 at 70% RH and 30 °C. Tip bias voltage: (A) −0.4 V, (B) −0.6 V, (C) −0.8 V.

3. Results and discussion

Fig. 2 shows current–voltage (*I–V*) curves between the tip and the GDE measured in an environmental chamber filled with dry and humidified 5%-H_2 gases at 30 °C. The AFM chamber was purged with a feed gas for two hours before the *I–V* measurements. In our setup, the reaction mechanism is similar to that of