

Proton Conductive Areas on Hydrocarbon-Based Electrolyte Membranes Analyzed by Current Sensing Atomic Force Microscopy under a Controlled Hydrogen Atmosphere

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Polymer electrolyte membrane is an important component of PEFCs. Recently, membranes of hydrocarbon-based multiblock copolymers with phase-separated morphology have been extensively studied as an alternative to Nafion[®] from the viewpoints of cost, environmental friendliness, and low gas permeability. The surface morphology and proton conductive regions on Nafion and hydrocarbon-based membranes have been investigated using an AFM in air.¹⁻³ In those cases, protons were generated by the electrolysis of water molecules at relatively high voltages (>1.5 V). The temperature and the humidity were usually not well controlled. In this study, hydrocarbon-based membranes of sulfonated poly ether and sulfonated poly(arylene ketone) multiblock copolymers, SPE-bl-1⁴ and SPK-bl-1⁵, were studied under a hydrogen atmosphere with controlling temperature and relative humidity (RH).

A current sensing-AFM equipped with a homemade environment-control chamber was used in this study.⁶ A schematic illustration of the principle of the current sensing-AFM measurements, carried out in the environment-control chamber, is presented in Fig. 1. A Pt-coated cantilever was employed as a probe for detecting protons. A bias voltage (approx. 0.6 V) was applied between the AFM tip and the gas diffusion electrode (GDE) surface. During the dc polarization, an H₂ gas was supplied to the environmental chamber and oxidized to protons on the GDE. The protons generated at the GDE are transported through the membrane and reduced to form hydrogen at the AFM tip.

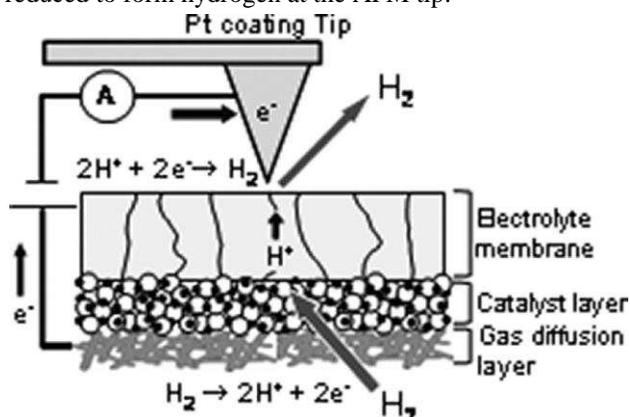


Fig.1 Schematic illustration of the principle of the current-sensing AFM measurement under hydrogen atmosphere.

SPE-bl-1⁴ (IEC=1.70meq/g) and SPK-bl-1⁵ (IEC=2.33meq/g) were synthesized in our laboratory and cast on a polyethylene terephthalate sheet. Those membranes have the same hydrophobic groups but different hydrophilic groups. The membranes were hot-

pressed on the GDE with catalyst layers composed of Pt/C and Nafion binder, and were placed on the temperature-control sample stage. The gases were humidified by a bubbler. The images of the proton conducting currents were obtained under a 5%-H₂ (Ar balance) atmosphere at temperatures between 30 and 70 °C and humidities between 0 and 70% RH. The morphological and current images were obtained at the contact mode with the contact force of 20 nN.

The topographic images were obtained under all conditions. Under dry conditions, the proton-conductive areas were not observable on either membrane, indicating that the conductive paths were not efficient under the dry atmosphere. As the humidity increased, the proton conductive areas were clearly visualized. Figs. 2 (a) and 2 (b) show the current images obtained on SPE-bl-1 and SPK-bl-1, respectively, at 50 °C and 70% RH. The proton conductive areas were detected as bright spots. In Fig. 2 (a), the spots were observed to be 8 - 10 nm in diameter. At the brightest area, the current was detected as 1 pA. Dark areas with current less than 0.2 pA were commonly seen. On the other hand on SPK-bl-1 (Fig. 2 (b)), the proton conductive paths were detected as bright spots of 10 - 12 nm in diameter. At the brightest area, the current was detected as 10 - 20 pA, an order larger than on SPE-bl-1.

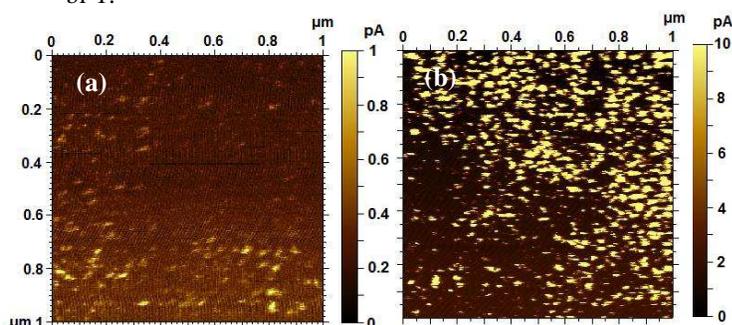


Fig.2 Current images on SPE-bl-1(a) and SPK-bl-1 (b) at 50 °C and 70% RH

On SPE-bl-1, the surface coverage of the proton conductive regions, where the hydrophilic regions are effectively connected through the bulk of the membrane, was 5-10%, whereas that on SPK-bl-1 was approx. 50%. On both surfaces, the coverage was found to be strongly dependent on humidity, but less on temperature. The proton conductivities measured by impedance spectroscopy were also very sensitive to humidity. The larger proton conductive areas, as well as the larger proton current, microscopically obtained on the SPK-bl-1 surface should be related to the bulk proton conductivity, which is twice larger than that of SPE-bl-1 at a similar condition. The differences between the membranes under different conditions will be discussed in detail.

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