



Effects of hot liquid-water treatment on local proton conductivity at surfaces of sulfonated poly(arylene ketone) block copolymer membrane for fuel cells studied by current-sensing atomic force microscopy



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ABSTRACT

Microscopic proton conductivity at surfaces of a hydrocarbon-type polymer electrolyte membrane of sulfonated poly(arylene ketone) block copolymers (SPK-bl-1) was investigated by current-sensing atomic force microscopy (CS-AFM) under a hydrogen atmosphere. The distributions of proton-conductive regions on the SPK-bl-1 membrane surfaces were different on two surface sides of the membrane: the substrate side and the air side after being cast on a poly(ethylene terephthalate) substrate. After a liquid-water treatment of the membrane at 60 °C, the surface morphology of both sides changed. The proton-conductive area and the “pseudo current density” increased especially on the substrate side, and the difference between two sides of the membrane became very small. The scanning transmission electron microscopy inside the membrane showed no structural change after the hot-water treatment, and the water uptake and conductivity of the membrane were also unchanged. This hot liquid-water treatment activating the membrane surfaces should be related to the conditioning processes of the membrane-electrode assemblies of polymer electrolyte fuel cells.

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1. Introduction

Proton exchange membrane (PEM) is one of the key components that govern the cell performance of a polymer electrolyte fuel cell (PEFC) [1,2]. While perfluorosulfonic acid (PFSA) ionomers, such as Nafion[®], have been commonly used for their high proton conductivity and chemical stability, PEMs based on sulfonated aromatic polymers are also extensively studied from the viewpoints of cost, environmental friendliness, and gas impermeability [2–11]. In our group, a series of sulfonated aromatic hydrocarbon block copolymer membranes, such as sulfonated poly(arylene ether) block copolymers (SPE-bl) [12–17] and sulfonated poly(arylene

ketone) block copolymers (SPK-bl) [18] membranes, have been developed with their unique hydrophilic/hydrophobic phase-separated morphologies. The SPK-bl membranes showed higher proton conductivity than that of Nafion or SPE-bl under a wide range of humidity due to their phase-separated morphology with well-interconnected proton transport pathways as well as high water uptake. The performance of cells composed with the SPK-bl membranes was also high [18]. In order to investigate the proton conductive areas on MEAs, current-sensing atomic force microscopy (CS-AFM) [19–35] is widely used. By CS-AFM, we have elucidated proton-conductive areas on the surfaces of SPE-bl-1 [19,20] and SPK-bl-1 [21] membranes under a hydrogen atmosphere controlling the temperature and humidity; the total conductive areas and the currents on the surfaces were found to increase mainly with raising the relative humidity.

In general, membrane electrode assemblies (MEAs) for PEFCs, either using PFSA membranes or hydrocarbon-type membrane, are treated by on-line and/or off-line “conditioning processes” (or cell break-in procedure) prior to the cell operation, which are essential

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for higher and stable performance [36–42]. For on-line conditioning, a power generation at a high current density is generally performed for a certain period of time, to clean the MEA, both in the catalyst layers by the reactions on the catalyst surface and in the membrane by water flux through the membrane. The water flux also improves the development and the connectivity of the hydrophilic clusters inside the membrane [36,37]. As an off-line conditioning for an electrolyte membrane, thermal and/or chemical treatments are applied before and after assembling an MEA, e.g. boiling in hot water and/or immersing in acid solution [36,40–42]. The changes in proton-conduction areas [28,29], as well as morphologies [43], on membranes surfaces after thermal treatment have been observed by CS-AFM. From CS-AFM studies, the current detected on proton-conductive areas on PEMs surface was also reported to increase after cell operation or applying high bias voltage [20,27]. Swelling the membrane with water was also found to change the surface morphology and the local proton conductivity on PFSA membranes [34,35]. Although the changes in surface morphology and conductivity were reported by CS-AFM [34,35,44,45], influences of the membrane treatments on the bulk morphology and conductivity are not clear.

In our previous papers, we have reported that a high bias voltage applied between an AFM tip and a hydrocarbon-type membrane increased proton conductive areas, as well as the proton current at each conductive spot [20,21]. This phenomenon should be related to the on-line conditioning during the power generation. In this study, we investigated the influence of hot liquid water on the SPK-bl-1 membrane surfaces by CS-AFM. The hot liquid-water treatment irreversibly increased the proton-conductive areas on the surface accompanied by the surface morphology change. On the other hand, the bulk morphology and conductivity were unchanged after the hot-water treatment.

2. Experimental

2.1. Sample treatment

SPK-bl-1 (Fig. 1) with an ion exchange capacity (IEC) = 2.53 mequiv g^{-1} and the average repeating unit in hydrophobic and hydrophilic blocks, X = 10 and Y = 3–5 respectively, was synthesized in our group as reported previously [18]. The membrane was obtained by casting a dimethyl sulfoxide solution containing SPK-bl-1 on a poly(ethylene terephthalate) (PET) substrate. Membrane surfaces having been attached to the substrate (substrate side) and exposed to air (air side) during the formation of the membrane were both used for the CS-AFM measurements. For a hot liquid-water treatment, SPK-bl-1 membranes were immersed and gently stirred in Milli-Q® water at 60 °C for 90 min while the water was changed six times. After the hot liquid-water treatment, the membranes were dried up in air at room temperature. Gas diffusion electrodes (GDEs) with a three-layer structure, i.e. catalyst layer/microporous layer/wet-proof carbon paper, were prepared as in our previous papers [39,46,47]. Pt loading of the GDE was 0.5 ± 0.1 mg cm^{-2} . The SPK-bl-1 membrane was hot pressed with a Nafion-binder-coated (approximately 2 μm thick) GDE at 140 °C and 1.0 MPa for 3 min [19–21]. The SPK-bl-1 specimen hot pressed on the GDE was placed on the temperature-controlled sample stage for the AFM measurement.

2.2. Surface analysis: CS-AFM

Morphology and current images were simultaneously obtained using a commercial AFM system (SPM-5500, Agilent) equipped with a homemade environmental chamber and a current-sensing circuit between a conductive silicon tip coated with Pt-Ir (Nanoworld) and a sample [19–21]. The CS-AFM observation was carried out in an environmental chamber at 50 °C purged with a 5%-H₂ (Ar balance) gas at 40% RH supplied at 100 mL min^{-1} . During the CS-AFM measurements, a sample voltage of 0.4–0.8 V (positive voltage at the GDE) was applied between the AFM tip and the GDE. 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 molecules (by the hydrogen evolution reaction, HER) at the AFM tip. The measurements were carried out in a contact mode with a contact force of 20 nN. The threshold value was set at 0.4 pA, a background current, for analyzing proton-conductive areas.

2.3. Bulk analyses: STEM, water uptake, and proton conductivity

For the observations by scanning transmission electron microscopy (STEM), the membranes were stained with lead ions by ion exchange of the sulfonic acid groups in 0.5 M lead acetate aqueous solution, rinsed with deionized water, and dried in vacuum oven for 12 h. The stained membranes were embedded in epoxy resin, sectioned to 90 nm thickness with Leica microtome Ultracut UCT, and placed on copper grids. Images were taken on a Hitachi H-9500 transmission electron microscope with an accelerating voltage of 200 kV. Water uptake and proton conductivity of the membrane at 80 °C before and after the hot-water treatment were measured with a solid electrolyte analyzer system (MSBAD-V-FC, Bel Japan Co.) equipped with a temperature and humidity controllable chamber. Weight of the membranes was measured by magnetic suspension balance at given humidity, and then water uptake ((weight of hydrated membrane - weight of dry membrane)/weight of dry membrane \times 100%) was calculated. Vacuum drying for 3 h at 80 °C gave the weight of dry membranes and exposure to a given humidity for at least 2 h gave the weight of hydrated membranes. Proton conductivity was measured using four-probe conductivity cell attached with impedance spectroscopy (Solartron 1255B and 1287, Solartron Inc.) simultaneously in the same chamber. Ion conducting resistances (R) were determined from the impedance plot obtained in the frequency range from 1 to 10⁵ Hz. The proton conductivity (σ) was calculated from the equation $\sigma = l/(A \times R)$, where A and l are the conducting area and the membrane thickness, respectively.

3. Results and discussion

3.1. Surface morphology and conductivity

Fig. 2(a-1) and 2(b-1) show AFM morphological images on the substrate side and the air side, respectively, on a pristine SPK-bl-1 membrane surface in 1 $\mu m \times 1 \mu m$ at 50 °C and 40% RH under 5% H₂. The surfaces of both sides were very flat, with the maximum

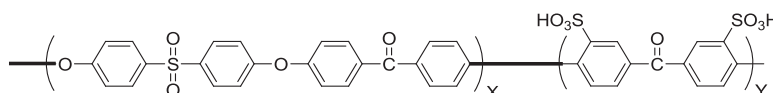


Fig. 1. Chemical structure of SPK-bl-1.

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