Nano-characterization of a nafion thin film in air and in water by atomic force microscopy

Kazuo Umemura,1,2 Tong Wang,3 Masahiko Hara,4 Reiko Kuroda,4,5 On Uchida,1 Masayuki Nagai1

1 Research Center for Energy and Environment Science, Musashi Institute of Technology, 1-28-1 Tamazutsumi, Setagaya, Tokyo 158-8557, Japan
2 Kamoshita Planning, 2-15-1 Shibuya, Shibuya-ku, Tokyo 150-8944, Japan
3 Frontier Research System, RIKEN, 2-1 Hirosawa, Wako-shi, Saitama 351-0198, Japan
4 The University of Tokyo, 3-8-1 Komaba, Muguro-ku, Tokyo 153-8902, Japan
5 Kuroda Chiromorphology Project, ERATO-SORST, 4-7-6 Park Building, Komaba, Meguro-ku, Tokyo 153-0041, Japan

kumemura@sc.musashi-tech.ac.jp

Abstract. Surface structures of nafion films under various conditions were studied using an atomic force microscope (AFM). First, we observed that nanosize pores formed on a nafion film surface when the film was prepared on a glass substrate; however, such pores did not appear on a metal surface. Second, in the case of a hybrid film of nafion and platinum/carbon (Pt/C), the surface morphology in water was different from that of a pure nafion film; however, it was not significantly different from that in air. Third, nanosize cracks appeared when a nafion film was heated at around 100 °C. Last, the effect of hydration on AFM nanolithography in liquids is discussed.

1. Introduction

Nafion is one of the most popular polymers to be used as a solid electrolyte for fuel cells, especially for direct methanol fuel cells (DMFCs).1–4 When used in fuel cells, nafion polymers are attached on an electrode surface as a thin film. The structural study of a nafion film, especially the nanoscopic characterization of the nafion surface by scanning probe microscopy (SPM), has been intensively carried out in the last ten years. This is because the surface structure of films is an important factor for maximizing the energy conversion efficiency of fuel cells.5–12 One of the earliest studies of a nafion film by atomic force microscopy (AFM) was reported by Lehmani et al. in 1998.5 James et al. also observed cluster-like structures of a nafion film by tapping mode AFM in order to examine the humidity effect on a nafion surface.8 Recently, Affoune et al. observed a wet nafion film that was

§ To whom any correspondence should be addressed.

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stored in water and in methanol prior to AFM imaging; however, the imaging itself was carried out in air.\textsuperscript{11,12} They found that a nafion surface exhibits considerably rough structures when it is stored in water and not in methanol. Kanamura \textit{et al.} used scanning probe microscopes (SPMs), instead of the conventional AFM, to observe the ion channels on a nafion surface using a surface potential measurement mode.\textsuperscript{10} They reported the presence of ion channels that were 40 to 100 nm in diameter. The ion channels appeared when a droplet of an electrolyte solution was deposited on the nafion surface in air.

We recently reported the AFM characterization and nanolithography of a nafion film in liquids and air.\textsuperscript{13} During the characterization, we found that a nafion film was much softer in water than in 5% methanol. This was the first report where the mechanical properties of a nafion film in liquids were studied on the nanoscale. We also discovered that a nafion film was softened in liquids, especially in water. It is known that nafion polymers expand in water because of hydration.\textsuperscript{14–16} It can be speculated that nafion polymers soften as a result of hydration. In the AFM nanolithography, we successfully fabricated nanopatterns on a nafion surface in liquids and not in air. Further, we suggested that the hydration of a nafion film might be a key point for the AFM lithography in liquids.

In this paper, we have focused on studying the nanostructures of a nafion surface under several different conditions. In our previous paper, we mainly studied the surface properties and carried out AFM lithography.\textsuperscript{13} Further, the effect of substrates, heating, and mixing carbons on nanostructures of a nafion film surface have been examined. In addition, AFM nanolithography in liquids, which was effective on a nafion surface, was examined on another polymer surface.

2. Materials and Methods

Nafion 117 (5 w/v in 2-propanol) manufactured by DuPont (Wilmington, DE) was purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO). Pt/C powder was purchased from Tanaka Kikinzoku (Tokyo, Japan). Poly-L-lactic acid film (PL), called ecologie, was provided by Mitsubishi Plastics Inc. (Tokyo, Japan).

Fifty \( \mu l \) of a nafion solution or a mixed suspension of nafion and Pt/C was dropped on a metal disc or a glass surface and dried in air at room temperature. The metal and glass surfaces were washed with ethanol prior to the experiments. The diameter of the nafion film formed was around 1 cm. Further, 1 \( \text{cm}^2 \) of the poly-L-lactic acid film was cut and attached onto a metal surface.

Commercially available AFMs—NanoScopeIIIa (Veeco Inc., Santa Barbara, CA) and PicoPlus (Molecular Imaging Co., Tempe, AZ)—were employed for imaging and nanolithography. A silicon cantilever was used for the tapping mode in air. A silicon nitride cantilever was used for the contact mode in air and the tapping mode in liquid. Spring constants of the silicon and silicon nitride cantilevers were 20-40 and 0.1 N/m, respectively. For imaging and nanolithography in liquid, a sample was set to an AFM liquid cell, and more than 100 \( \mu l \) of pure water was injected into the lipid cell. A PicoPlus temperature controller was used to heat the sample in air. The temperature was measured at the back of the sample.

AFM nanolithography was carried out in water. A 1 \( \mu m^2 \) area was scanned five times in the contact mode, and then a larger area was imaged by the tapping mode. For the experiments, a silicon nitride cantilever (0.1 N/m) was employed. In most cases, the scratching force was usually 80 nN. In the control experiments, scratching forces of 40 and 160 nN were also applied. The force values for imaging and scratching were estimated from the force curve measurements.\textsuperscript{17}

3. Results and Discussion

Figure 1 shows the AFM images of a nafion film prepared on a glass surface. Many pores were observed on the glass surface. The pore sizes fluctuated between 100 nm and 1 \( \mu m \) in width, although the nafion films were always prepared by a similar procedure at room temperature. The depth of the pores also fluctuated between 50 nm and 150 nm. On the other hand, uniform thin films were obtained without pores on a metal surface. This suggests that the surface structures of a nafion film is easily affected by the type of substrate and other minute environmental differences, such as temperature or
humidity, during the process of drying the nafion solution on a glass surface. To minimize the unknown factors in the experiments, we used a metal disc as a substrate in the following sample preparation process.

We examined the surface structures of nafion films containing platinum/carbon (Pt/C) because Pt/C powder is frequently mixed with nafion polymers in actual fuel cell applications. We have already reported the AFM images of a film surface, which was prepared with a pure nafion solution. In this paper, a mixture of nafion and Pt/C was examined for the first time.

For the images taken in air, no significant difference between a pure nafion film (Fig.2A), 0.1% Pt/C mixture (Fig.2B), and 1% Pt/C mixture (Fig.2C) was found. On the other hand, in water, the surface morphology changed gradually with an increase in Pt/C. It has been found by macroscopic studies that nafion polymers expand in water because the molecule has both hydrophobic and hydrophilic sites. If a sample surface was constructed with pure nafion molecules, it should expand uniformly. However, the Pt/C portion, if Pt/C is present on the surface, must not expand. For this reason, we think that the morphological difference between a pure nafion film and a hybrid film in water was reasonable.

We also prepared 25% and 50% Pt/C samples; however, it was difficult to fabricate a uniform thin film because of the high viscosity of the suspension. It therefore became very difficult to carry out AFM observations. We think that this fact is a typical problem with regard to combining nanotechnology with fuel cell technology. However, further developments in the sample preparation process are necessary to prepare a precisely controlled thin nafion film that contains a large amount of Pt/C.

It is known that the efficiency of a fuel cell that includes nafion polymers decreases significantly when the temperature is increased to around 100 °C. The characterization of a nafion film at such a high temperature from the viewpoint of structural study could probably be valuable. Figure 3 shows the AFM images of a nafion film observed in air at room temperature (Fig.3A) and at 120 °C (Fig.3B), respectively. The temperature was measured at the back of the sample. Therefore, we speculated that temperature on the sample surface was roughly around 100 to 120 °C. Although the imaged area was not entirely the same, the images were taken on the same sample. The AFM images clearly show that many cracks appeared at 120 °C (see arrows in Fig.3B). The shape of the cracks was not sharp; in fact, the cracks appeared as depressions. The wide size of the cracks was in the range of several hundred nm. However, the imaging of the same sample at 80 °C did not reveal any cracks (data not shown). From these results, we can at least notice that the surface structures of a nafion film changes at around 100 °C, although the relationship between the structural change and the efficiency decrease is still unclear.

Figure 4 shows the results of the AFM nanolithography on a nafion film (Fig.4A) and on another polymer (poly-L-lactic acid, Fig.4B), both of which were processed in water. The central area was scratched using an AFM tip in the contact mode, and then, a larger area was scanned using the same tip in the tapping mode. In the case of the nafion surface, square-shape nanostructures could be successfully fabricated, which was previously reported by us. The lithography is possible in liquids such as water and 5% methanol; however, it was impossible to conduct it in air. We have discussed that AFM nanolithography was possible in liquids because the polymer molecules were softened by hydration. The fabricated structures were stable when the surfaces were continuously imaged many times by the tapping mode.

On the other hand, in the case of the poly-L-lactic acid film, which is a typical biodegradable polymer film, it was not possible to fabricate square holes, although the process was similar to that for the nafion film. Wave-like structures increased in size with the scratching force (see squares in Fig.4B). The wave structures are typical results of a scratching polymer in air, as described previously. These results support our speculation that the hydration of nafion is a key factor for fabricating holes on a nafion film. In other words, AFM lithography in liquids might be possible for hydrated polymers.
4. Conclusion
Our results suggest that the surface structures of a nafion thin film changed according to the substrate, temperature, and the ratio of Pt/C. Additional information on the mechanism of the AFM nanolithography in liquids was also obtained by the comparison of two polymers.

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FIGURE CAPTIONS
Figure 1 AFM images of nafion films prepared on a glass surface. Imaging was carried out in air in the tapping mode. Image size is 20 μm (A and B) and 30 μm (C). Cross sections are indicated below the topographs in (A) and (B).

Figure 2 AFM images of mixture of nafion and Pt/C. Fifty μl of the mixed solution was dropped on a metal substrate and dried. Image size is 1 μm for the all images. (A) and (D): control (pure nafion film). (B) and (E): 0.1% Pt/C. (C) and (F): 1% Pt/C. (A) to (C): observed in air. (D) to (F): observed in water.

Figure 3 AFM images of a nafion film observed at different temperatures. Image size is 2 μm. (A) at room temperature. (B) at 120 °C.

Figure 4 AFM nanolithography in water. (A) nafion surface. (B) poly-L-lactic acid (ecologe) surface. Image sizes are 20 μm and 10 μm for (A) and (B), respectively.
