884 Chemistry Letters Vol.38, No.9 (2009)

Formation and Structure of Perfluorosulfonated Ionomer Thin Film on a Graphite Surface

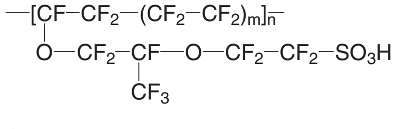
Takuya Masuda,[1,2] Hideo Naohara,[3] Satoru Takakusagi,[1] Pankaj R. Singh,[1] and Kohei Uosaki*[1,2,4]
[1]*Physical Chemistry Laboratory, Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810*
[2]*Network Center for Molecular and System Life Sciences, Graduate School of Science, Hokkaido University, Sapporo 060-0810*
[3]*Fuel Cell System Development Division, Toyota Motor Corporation, Susono 410-1193*
[4]*International Center for Materials Nanoarchitectonics Satellite (MANA),*
National Institute for Materials Science (NIMS), Sapporo 060-0810

(Received June 22, 2009; CL-090587; E-mail: uosaki@pcl.sci.hokudai.ac.jp)

Adsorption process and structure of perfluorosulfonated acid (PFSA) polymer on a highly oriented pyrolytic graphite (HOPG) surface were elucidated by an in situ tapping mode atomic force microscope (AFM). Micellar aggregates of PFSA polymers first randomly adsorbed on a bare HOPG surface, and then the adsorbed aggregates extended under the influence of atomic arrangement of HOPG surface, to form two-dimensionally ordered domains.

Fuel cells, particularly polymer electrolyte membrane fuel cell (PEMFC), have attracted much attention because chemical energy, e.g., hydrogen and methanol, can be directly converted to electrical energy with very high theoretical conversion efficiency. Since PEMFC is composed of a stack of membrane-electrode assemblies (MEAs), which are fabricated by bonding a mixture of ionomer and carbon-supported Pt catalyst layer to both sides of PEM, electron transfer at the catalyst/carbon interface and proton transport through PEM are the key factors for cell performance.

Nafion®, a PFSA polymer as shown in Figure 1, is the most widely used PEM in MEA because of its excellent proton conductivity and chemical durability.[1–4] Understanding of the morphology of bulk Nafion by both theory and experiments has been significantly progressed.[5–10] However, the structure of individual PFSA polymer chains has been studied neither at ionomer/catalyst nor at ionomer/carbon support interfaces, although these structures must have significant impacts on cell performance and durability such as proton conductivity, diffusion of reactants and products, and corrosion of Pt and carbon support. For example, it was reported that densely packed PFSA film showed a very low apparent proton diffusion coefficient, which is one of the predominant factors to determine cell performance because high compactness prevents polymer electrolyte from preferred ion channel formation.[11] In this context, understanding and control of the structure of PFSA at the ionomer/catalyst and at ionomer/carbon support interfaces are essential for further development of PEMFC. Atomic force microscopy (AFM) is known to provide morphological information of adsorbates on solid surfaces in molecular resolution even in solution. Here, adsorption process of PFSA polymer on a HOPG surface was followed by in situ AFM measurement as a model of fabrication process of MEAs, and the structure of PFSA at the interface was observed with molecular resolution after removing the overlayers by rinsing the surface with water.



$$-[\underset{\underset{O-CF_2-\underset{\underset{CF_3}{|}}{CF}-O-CF_2-CF_2-SO_3H}{|}}{CF}-CF_2-(CF_2-CF_2)_m]_n-$$

Figure 1. Chemical structure of Nafion.

Water was purified using a Milli-Q system (Yamato, WQ-500). Nafion® dispersion (DE1020 CS, polymer content: 10–12 wt %, water content: 87–90 wt %) and HOPG were purchased from DuPont and NT-MDT, respectively. The Nafion dispersion was diluted with water so that Nafion content was ca. 100 ppm. Clean HOPG surface was obtained by peeling off the top layers with adhesive tape, and AFM measurements were performed in Acoustic AC mode (Tapping mode) using a 5500 Atomic Force Microscope (Agilent Technologies, USA).

First, the formation of Nafion thin film on an HOPG surface was investigated as a model for MEA processing. Figure 2 shows a series of tapping mode AFM images of an HOPG surface after drops of diluted aqueous Nafion solution were placed on a freshly cleaved surface.[12] Typical step terrace structure of HOPG surface was observed in all images. Immediately after the solution was placed, bright spots, which were higher than the surroundings by 1–2 nm, were observed (Figure 2a), showing that the aggregates of PFSA polymer adsorbed on the HOPG surface. After 1000 s, more aggregates were observed (Figure 2b). Worm-like structures indicated by white arrows were extended from the initial adsorption spots as the adsorption time increased (Figures 2c–2d). Heights of the worm-like structures were less than that of the initially adsorbed colloidal aggregates, suggesting that the formation of PFSA polymer layer at water/HOPG interface involved unfolding/extension process. After further waiting time, only small changes were observed (Figures 2e and 2f). To characterize the nanostructure of the PFSA layer, a region marked by a green square in Figure 2f was imaged with higher resolution as shown in Figure 2g. The entire surface was covered with a fibrous matrix with a width of 5–10 nm. The fibrils seemed to form a two-dimensional structure, although they were not well ordered. Since the AFM measurements were performed in the presence of PFSA polymer solution, adsorption of PFSA polymer was still taking place during the AFM measurements and, therefore, the structure observed in Figure 2g may not be of the first layer of PFSA formed on the graphite surface.

To observe the structure of the first PFSA layer on the graphite surface, AFM measurement was carried out for an HOPG surface covered with a droplet of pure water after a droplet of Nafion solution was kept on the HOPG surface only for ca. 1 h followed by rinsing with pure water so that further adsorption was prevented and excess amount of PFSA polymers had been removed. Two-dimensionally ordered phases composed of uni-

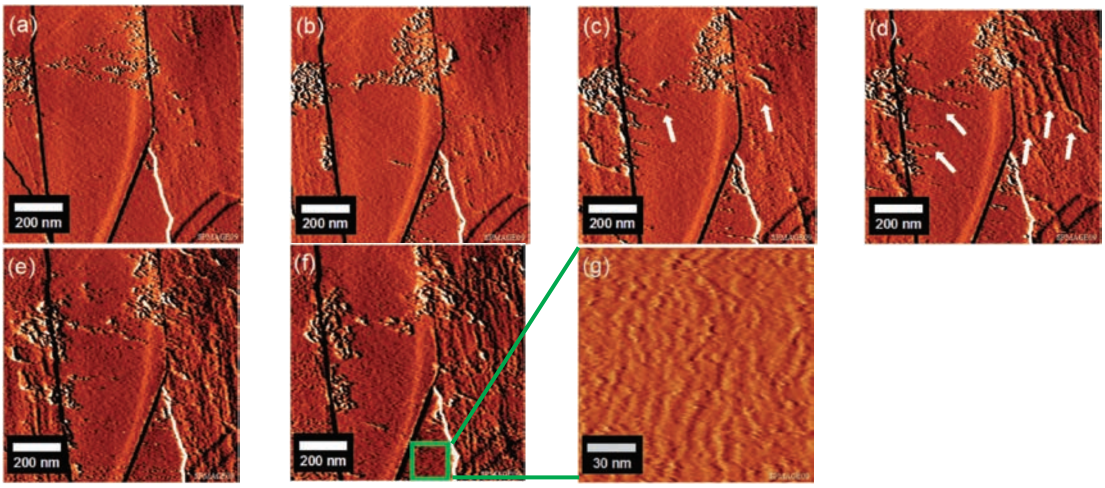


Figure 2. A series of AFM differential images[12] of an HOPG surface captured (a) immediately, (b) 1000, (c) 2000, (d) 3000, (e) 4000, and (f) 5000 s after adding droplets of Nafion solution. A magnified image (g) was obtained after image (f) was obtained.

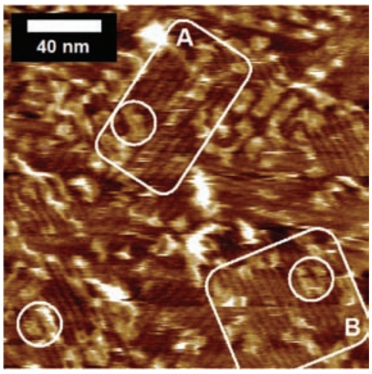


Figure 3. AFM topographic image of the HOPG surface after exchanging Nafion solution with pure water.[14]

directionally aligned ribbon-like wires with a height of 0.3 nm and a width of 5 nm were observed as shown in Figure 3.[14] There are two types of domain in the image indicated as A and B. Each domain is oriented at 60° to each other, showing that the ordered PFSA layer is of threefold symmetry. AFM images obtained under the same conditions but on an amorphous carbon, i.e., glassy carbon, showed no such well-ordered domains on the surface. These results show that the unfolding/extension of the adsorbed PFSA aggregates is influenced by atomic arrangement of the HOPG surface, which is of threefold symmetry. While each wire is much wider than a single strand of fluorocarbon polymer chain, the height is comparable, showing that the wire is neither a fully extended single strand nor a bundle of PFSA polymers. This high aspect ratio can be explained by a folded chain configuration of PFSA copolymer. It was reported that tetrafluoroethylene copolymers with various side groups such as $-CF_3$ and $-OCF_2CF_3$ form planner zig-zag sequences from a single strand of polymer.[15–17] Much higher resolution imaging by STM is required to determine the actual structure of each wire. Relatively large aggregates with a height of 1–2 nm as indicated by white circles were also observed in the middle of a row of the ribbon-like wires. The aggregates should be either PFSA polymer aggregates adsorbed on the two-dimensionally ordered layer or those in the self-assembly process yet to be extended.

In conclusion, micellar aggregates of PFSA polymers first randomly adsorbed on a bare HOPG surface, and then the adsorbed aggregates extended under the influence of atomic arrangement of HOPG surface, to form two-dimensionally ordered domains. Further details of the adsorbed structure using scanning tunneling microscopy (STM) are now under investigation.

The present work is supported by a Grant-in-Aid for Scientific Research (A) (2006–2009, No. 18205016) from JSPS and Global COE Program ("Catalysis as the Basis for Innovation in Material Science"), Promotion of Novel Interdisciplinary Fields Based on Nanotechnology and Materials, and World Premier International Research Center (WPI) Initiative on Materials Nanoarchitectonics from Ministry of Education, Culture, Sports, Science and Technology, Japan.

References and Notes

1 A. Z. Weber, J. Newman, *Chem. Rev.* **2004**, *104*, 4679.
2 C.-Y. Wang, *Chem. Rev.* **2004**, *104*, 4727.
3 K. A. Mauritz, R. B. Moore, *Chem. Rev.* **2004**, *104*, 4535.
4 K. Uosaki, K. Okazaki, H. Kita, *J. Electroanal. Chem.* **1990**, *287*, 163.
5 W. Y. Hsu, T. D. Gierke, *J. Membr. Sci.* **1983**, *13*, 307.
6 M. Fujimura, T. Hashimoto, H. Kawai, *Macromolecules* **1981**, *14*, 1309.
7 G. Gebel, J. Lambard, *Macromolecules* **1997**, *30*, 7914.
8 K. Schmidt-Rohr, Q. Chen, *Nat. Mater.* **2008**, *7*, 75.
9 G. Gebel, *Polymer* **2000**, *41*, 5829.
10 O. Diat, G. Gebel, *Nat. Mater.* **2008**, *7*, 13.
11 L. M. Moretto, T. Kohls, A. Chovin, N. Sojic, P. Ugo, *Langmuir* **2008**, *24*, 6367.
12 For clarification, differential images obtained by WS*x*M are presented.[13]
13 I. Horcas, R. Fernandez, J. M. Gomez-Rodriguez, J. Colchero, *Rev. Sci. Instrum.* **2007**, *78*, 013705.
14 To compare with Figure 2, lower resolution images obtained after capturing Figure 3 are presented as Supporting Information which is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.
15 F. J. Rahl, M. A. Evanco, R. J. Fredericks, A. C. Reimschuessel, *J. Polym. Sci., Part A-2: Polym. Phys.* **1972**, *10*, 1337.
16 E. Giglio, S. Morosetti, A. Palleschi, N. V. Pavel, *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 321.
17 R. Pucciariello, V. Villani, *Colloid Polym. Sci.* **1993**, *271*, 50.

Published on the web (Advance View) August 1, 2009; doi:10.1246/cl.2009.884