

Observation of Interface between Pt electrode and Nafion® Membrane

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Polymer electrolyte fuel cells (PEFC) have been developed as power sources for electric vehicles, because of an acceptance of a high discharge current at 80 °C. This is due to an excellent catalytic activity of Pt deposited on carbon materials and an activation of electrochemical reaction site by an ion-exchange membrane. Therefore, a design of the interface between Pt/carbon electrode and ion exchange membrane is very important. In this study, the interfacial behavior in PEFC was investigated with Atomic Force Microscopy (AFM) combined with surface potential measurement (SPoM) and *in situ* FTIR technique.

Figure 1 shows the AFM-SPoM system used in this study. Using this equipment, topology and surface potential on an ion exchange membrane can be measured. From these results, a hydrophobic part of Nafion® can be distinct from a hydrophilic one. The former part corresponds to an agglomerate of fluorocarbon chains and the later part corresponds to ion channel in Nafion® membrane. Figure 2 shows AFM and SPoM images for Nafion® membrane. From the AFM image, both parts cannot be distinguished, but ion channels can be observed in the SPoM image. White spots correspond to the hydrophilic part of Nafion® membrane. A density of these spots is 10~15 spots in 5 $\mu\text{m} \times 5 \mu\text{m}$ square area. If only these parts worked as an electrochemical reaction site, a high current density of PEFC would not be achieved. Probably, the SPoM image obtained under dry atmosphere may not represent the interfacial situation between Pt and Nafion® membrane.

Figure 3 shows the differential FTIR spectra for the interface between Pt and Nafion® membrane after an introduction of LiClO₄ aqueous electrolyte in the cell. These spectra were measured by internal reflection type *in situ* FTIR electrochemical cell with p-polarized IR beam. Some upward and downward peaks were observed in the spectrum just after the introduction of electrolyte. These peaks were assigned to CF₃, -CF₂-, SO₃⁻, and OH, respectively. The observed upward peaks indicate that chemical bonds corresponding to the wavenumber are disappeared from the interface between Pt and Nafion®. On the other hand, the downward peaks show that chemical bonds corresponding to the wavenumber were increased at the interface between Pt and Nafion®. Therefore, from the spectrum in Figure 3, it can be seen that fluorocarbon chain related chemical bonds are decreased and OH group is increased by the introduction of electrolyte. The interface between Pt electrode and Nafion® membrane is not static, but is dynamic corresponding to circumstance of PEFC.

From the AFM-SPoM and FTIR measurements, it can be concluded that the closed ion channel in a dry state is opened with increasing humidity around PEFC. This change should be controlled in order to minimize an amount of Pt catalyst.

In addition, the electrode potential also influences on the interface between Pt electrode and Nafion® membrane. This behavior was also examined with *in situ* FTIR spectra. Figure 4 shows the differential spectra obtained from two reflectance spectra before and after potential

step experiments. The potential step conditions were indicated in this figure. Several upward and downward peaks were observed according to the potential region. In the potential region of oxygen reduction, the interface became more hydrophobic. On the other hand, the potential region of hydrogen oxidation, the interface became more hydrophilic.

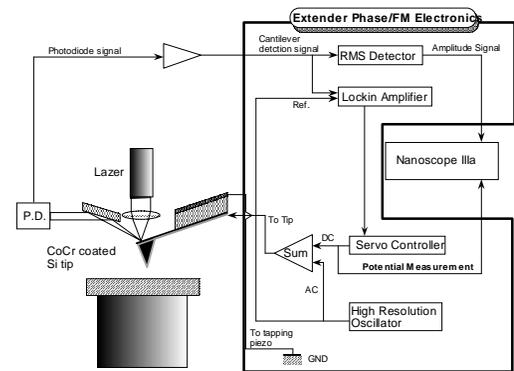


Figure 1 Schematic illustration for AFM-SPoM measurement.

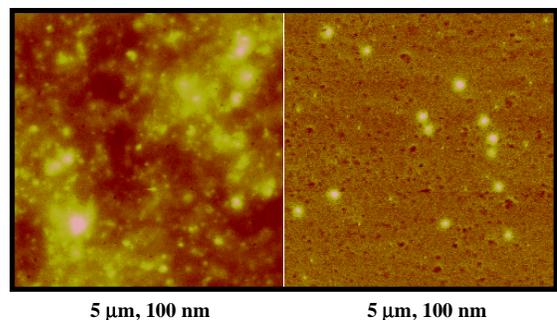


Figure 2 AFM and SPoM images for Nafion® membrane in a dry state.

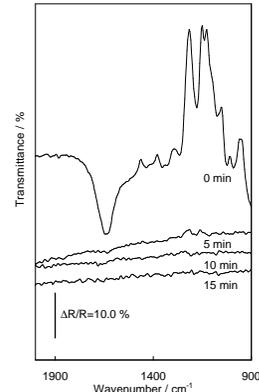


Figure 3 Differential FTIR spectra after introduction of electrolyte in the cell.

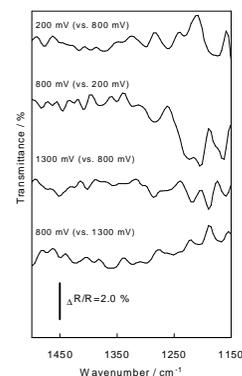


Figure 4 Differential FTIR spectra for various potential step experiments.