

Vibrational Sum Frequency Generation Study of Ionomers on Platinum Surfaces

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In polymer electrolyte fuel cells (PEFCs), perfluorosulfonated polymers such as Nafion are usually utilized as electrolyte membrane and ionomers in catalyst layers. Recently, molecular structure and ion-conducting mechanism in the ultrathin ionomer films covering catalysts' surfaces have been interested and various measurements at ultrathin Nafion films were carried out by means of electrochemical methods,[1-3] *in situ* vibrational spectroscopy,[3,4] and DFT calculations. However, the evaluation of the molecular conformation and orientation of perfluorosulfonated polymers are very difficult, since the molecular weights of these molecules are much larger and the vibrations of C-F bonds included in both the backbone and side-chains overlap with those of sulfonic acid groups, which can provide useful information to speculate the orientation of side-chains. In addition, even the assignments of C-F stretching vibrations of fluorinated molecules are not well defined.

Recently, we have performed homodyne vibrational sum frequency generation (VSFG) spectroscopic measurements at Nafion-covered Pt surfaces. By comparing the VSFG spectra and ATR-IRRAS spectra of the same samples, where the thicknesses of Nafion film were controlled, VSFG spectroscopy selectively detect the vibrational bands, especially the stretching band of sulfonate terminal in Nafion at the Pt/Nafion or Nafion/air interface. Since the relative hydrophobicity was confirmed at the top most layer of the samples, sulfonate groups were considered not to be adsorbed at Nafion/air interface. However, the picture is just a speculation from the indirect experimental results.

In the present study, heterodyne VSFG spectroscopic measurements[5,6] are applied to directly determine the direction of the transition dipole of the sulfonate terminals. To confirm the direction of sulfonate group, sulfonate-terminated self-assembled monolayers (SAMs) were also prepared on Pt and Au surfaces and characterized by both heterodyne VSFG spectroscopy and electrochemical measurements.

Acknowledgement

This work was supported by New Energy, Industrial Technology Development Organization (NEDO), Fuel Cell Promotion Office of the Agency of Natural Resources and Energy, Ministry of Economy, Trade and Industry (METI).

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