

## *In situ* observations of fuel cell electrodes by ambient-pressure hard X-ray photoelectron spectroscopy

The polymer electrolyte fuel cell (PEFC) is a promising technology as a highly-efficient clean energy source for automobiles. Many issues, however, remain to be solved, such as the improvement of power generation performance and the reduction in the usage of expensive platinum catalysts in the cathode. The development of next-generation high-efficiency fuel cells requires that the oxygen reduction reaction mechanism, which occurs at the cathode catalysts, to be well understood (Fig. 1). Direct observations of the electronic states in the catalyst materials under fuel-cell conditions should help realize a highly active catalyst in membrane electrode assemblies (MEAs) under fuel-cell reaction conditions.

X-ray photoelectron spectroscopy (XPS) is a powerful technique to investigate electronic states, but the application of XPS at elevated pressures is complicated due to two factors. One is the necessity of low pressures in the electron energy analyzer to avoid discharges on the electrostatic lens elements and the detectors. The other is attenuation of photoelectrons through the gases in the measurement chamber due to the strong photoelectron interactions with gaseous molecules at energies typically used in XPS. The first factor was overcome by long differential pumping system with a small aperture to reduce the molecular flows into the analyzer, whereas the latter was resolved through a shorter working distance between the sample surface and the aperture. Recently, the development of photoelectron spectrometers and the use of intense X-rays from synchrotron radiation sources have allowed XPS spectra to be measured under near ambient pressure conditions. This technique is known as ambient pressure X-ray photoelectron spectroscopy (AP-XPS) [1].

Meanwhile, XPS using hard X-rays (HAXPES) was developed during the last decade to observe buried samples [2]. One of the advantages of HAXPES is a long mean free path of photoelectrons when their kinetic energy is increased. If a beam energy in the hard X-ray region is used in AP-XPS, then spectra can be obtained under higher pressures than those in the case of soft X-rays. Moreover, it becomes possible to observe liquid/solid interfaces in heterogeneous catalysts and buried nanoparticles in a polymer electrolyte membrane because the inelastic mean free path of electrons within a solid, which has a kinetic energy of 8 keV, is 5–50 nm. A system that combines AP-XPS and HAXPES, i.e., ambient pressure hard X-ray photoelectron spectroscopy (AP-HAXPES),



Fig. 1. Schematic drawing of PEFC.

should facilitate the observation of the electronic states of catalysts at buried interfaces under reaction conditions.

We developed a near ambient pressure photoelectron spectroscopy instrument that is used with hard X-rays at beamline **BL36XU** (Catalytic Reaction Dynamics for Fuel Cells) [3]. The experiments were conducted using a commercial differentialpumping type analyzer (R4000 HiPP-2, VG Scienta) [4]. The equipment consists of a pre-lens in the differential pumping chamber evacuated with several vacuum pumps and a standard hemispherical electron energy analyzer. Using the front cone with a 300- $\mu$ m aperture diameter, the pressure of the measurement chamber can be increased up to 3,000 Pa during operation.

The Au 4*f* spectra obtained at an incident photon energy of 7.94 keV at various nitrogen gas (N<sub>2</sub>) pressures are shown in Fig. 2. The intensity of the spectra is almost constant under the conditions from the high-vacuum ( $2 \times 10^{-5}$  Pa) to 100 Pa, but decreased rapidly as the N<sub>2</sub> pressure is increased to 3,000 Pa due to photoelectrons scattering by gaseous molecules. The signal attenuation from the signal level in the high vacuum is, however, only 46% at 3,000 Pa, which indicates that the apparatus allows AP-HAXPES measurements to be performed at the saturation vapor pressure of water at room temperature.

We performed *in situ* AP-HAXPES measurements of the Pt/C cathode of the PEFC [5]. To observe the modified electronic states of Pt atoms in Pt/C cathode catalysts during operations, the Pt  $3d_{5/2}$  peaks were recorded at an incident X-ray beam energy of 7.94 keV (Fig. 3). We performed curve fitting analysis for these peaks with three components at 2122.0, 2123.3, and 2125.2 eV. The lowest energy peak is assigned to Pt metal (Pt<sup>0</sup>) and the highest one to Pt<sup>2+</sup> species such as PtO. The peak at 2123.3 eV is attributed to Pt<sup>1+</sup> species such as PtOH.

When the cathode is exposed to H<sub>2</sub>O and hydrogen gas flowed in the anode side under the open circuit condition, a voltage of 0.12 V is generated between the electrodes. The spectrum shows a major metallic Pt peak at 2122.0 eV, along with small peaks at 2123.3 eV from the surface Pt atoms with contaminants (Fig. 3(a)). When the applied voltage is maintained at 1.3 V, the higherenergy peak at 2125.2 eV for PtO was observed, in addition to the peak 2123.3 eV (Fig. 3(b)). In contrast, the peak at 2125.2 eV almost disappears when the applied voltage is decreased to 0.1 V (Fig. 3(c)). The Pt nanoparticles at the cathode are oxidized and reduced when the applied voltage between the electrodes was increased to greater than 0.8 V and decreased to less than 0.7 V, respectively. The observed peaks reflect oxidized Pt nanoparticles with different valences on the MEA electrode, depending on the applied voltage. Consequently, the AP-HAXPES



Fig. 2. Au 4f spectra of Au foil recorded with a 7.94 keV photon energy under different pressures of N<sub>2</sub>.

apparatus allows the oxidization/reduction reactions of the electrodes to be observed during the operation of a fuel cell, promoting the development of fuel cell electrodes and catalyst materials.



Fig. 3. In situ AP-HAXPES Pt  $3d_{5/2}$  spectra of the Pt/C catalyst in the cathode.

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