

In Situ Applications of X-ray Absorption Fine Structure to the Characterization of Electrode Surfaces

전극표면의 특성연구를 위한 X-선 흡수미세구조의 *In Situ* 응용

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Characterization of electrode surfaces, particularly when modified by foreign species, has been the subject of extensive studies because they often offer sites for electrocatalytic reactions of technological importance. Techniques solely based on electrochemical measurements have limitations for providing information as to structural and electronic aspects in an atomic or molecular level. The advent of intense and continuous X-ray beam generated from synchrotron radiation has opened a new way of looking at electrochemical interfaces. This tunable and high energy X-ray source made it possible to investigate spectroscopic properties of a specific element.

The *in situ* application of XAFS to electrochemistry has been confronted with many technical difficulties: i) the small number of species confined on the surface causes worse S/N ratio. ii) the presence of electrolyte scatters X-ray which put limits on the thickness of a cell. In this presentation we place our emphasis not only on the technical aspects of experiments in which the detailed description of a cell was made, but on the structural and electronic aspects of electrocatalysts on electrode surfaces as a function of externally applied potential.

XAFS spectra were acquired at line 3C1 of Pohang Light Source and 7C of Photon Factory, operating at an energy of 2.05 and 2.5 GeV with a ring current of 100-200 and 200-400 mA, respectively. The beam was monochromatized by a Si(111) double crystal with an exit slit adjusted to $1 \times 5 \text{ mm}^2$. The monochromator was detuned by 40 % to reject higher harmonics. All the *in situ* measurements were carried out in a fluorescence mode using a Lytle-type detector purged with Ar gas with a Mn filter of 3-absorption length.

Iron phthalocyanine-related systems are investigated which include i) FePc-adsorbed electrodes, ii) sol-gel derived composite electrodes containing FePc, and iii) FePc-catalyzed nitric oxide reduction. FePc has been known to catalyze many technologically and environmentally important reactions such as dioxygen and nitrite reduction. FePc showed great structural changes upon the oxidation state change. Polarization of the electrode at +0.2 V showed a $1s \rightarrow 4p_z$ transition at 7118.0 eV as a shoulder to the main absorption edge and a weak $1s \rightarrow 3d$ pre-edge peak. Due to the oxidation of iron and structural distortion, the absorption edge position was shifted from 7121.8 eV to 7124.8 eV and the $1s \rightarrow 3d$ transition was enhanced by polarizing at +0.7 V. XANES obtained with reduction of Fe(II)Pc(-2) at 0.20 V was very similar to that of Fe(II)Pc(-2) except that the white line became more intense and $1s \rightarrow 4p_z$ transition almost disappeared. This was explained by the reduction of the Pc ring to form [Fe(II)Pc(-3)]-. The transferred electron is considered to be delocalized through the π system of the ligand.