

In situ analysis of electrochemical reaction inside a fuel cell: Growth limit in behavior of platinum oxides formed on Pt-skin layers on Pt-Co bimetallic electrocatalysts

Fuel cells that convert the chemical energy of hydrogen and oxygen directly into electricity will offer a clean and highly efficient energy conversion system in the near future. Owing to extensive research, the basic performance of such fuel cells is about to reach a level suitable for widespread use. Major car manufacturers will be ready to launch the first commercial fuel-cell vehicles by the end of 2015. The current research interest is shifting to practical issues such as ensuring long-term reliability and reducing the total cost of fuel cells.

The need for platinum electrocatalysts that catalyze the oxygen-reduction reaction at the cathode has been one major obstacle to commercialization because the high cost of platinum and its instability in high-potential regions limit the practical use of fuel cells. Bimetallic electrocatalysts such as Pt₃Co have been attracting a great deal of attention, since they have demonstrated both higher oxygen reduction activity and improved stability with much smaller amounts of platinum. Less-stable transition metals (such as Co) are removed from the surface regions by acid leaching in advance to prevent transition-metal components from dissolving further. This creates platinum-rich surface domains, viz., Pt-skin layers that are responsible for superior catalytic properties (Fig. 1).

Whereas the mechanism responsible for the enhanced catalytic oxygen-reduction activity of Pt-skin layers has been quite well explained by the d-band center shift in the outermost Pt-layers, the factors that increase stability remain elusive. We, therefore, investigated the dynamical oxidation and reduction processes in Pt-skin layers on Pt₃Co bimetallic particles via *in situ* time-resolved X-ray absorption spectroscopy (XAS) combined with electrochemical measurements [1].

The *in situ* and time-resolved X-ray absorption spectroscopy (XAS) measurements were carried out at the Pt L₃ edge on **BL40XU** beamline using a quick-scanning XAS measurement system with quasi-monochromatic undulator radiation (time resolution: 100 ms). The catalysts were mounted onto a thin carbon electrode and the potential step oxidation/reduction was measured using a three-electrode cell in 0.5M H₂SO₄ under N₂ atmosphere.

The oxidation behavior of Pt-skin layers on Pt₃Co differs from that of Pt. Figures 2(a–d) show the results of XAS analyses of Pt and Pt-skin layers on Pt₃Co bimetallic nanoparticles after oxidation/reduction cycles between 0.4 and 1.4 V. Figures 2(a) and 2(c)

show plots of the time variations in FT amplitude at around 2.6 Å corresponding to the coordination number (CN) of the first-nearest-neighbor Pt-Pt bond for platinum metal. They thus represent relative changes in the volume of Pt metal. Figures 2(b) and 2(d), on the other hand, show time variations in the white-line intensity in the XANES spectra. The increase in the white-line intensity when oxides are formed on the surface owing to electron transfer from the Pt 5d-band to oxygen reflects an increase in the volume of platinum oxide.

Whereas the surface of pure Pt was continuously oxidized and then reduced without any saturation behavior (Figs. 2(a) and 2(b)), the oxidation and reduction of Pt-skin layers of Pt₃Co nanoparticles occurred discontinuously with saturation behavior (Figs. 2(c) and 2(d)). Both the FT amplitude and white-line intensity for Pt₃Co exhibit saturation behaviors at around 40 s, indicating that oxidation was suppressed at a certain level of oxidation. The detailed EXAFS analysis revealed that the formation of higher-order platinum oxides such as β-PtO₂ is truly suppressed in the oxidation process of Pt-skin layers on Pt₃Co.

The durable nature of Pt-skin layers may be a result of the existence of a growth limit and particularly

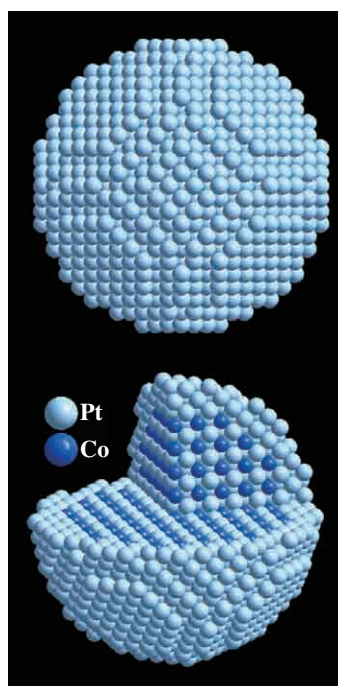


Fig. 1. Average structure of Pt₃Co nanoparticles with Pt-skin layers, determined by Pt-L₃ EXAFS analysis.

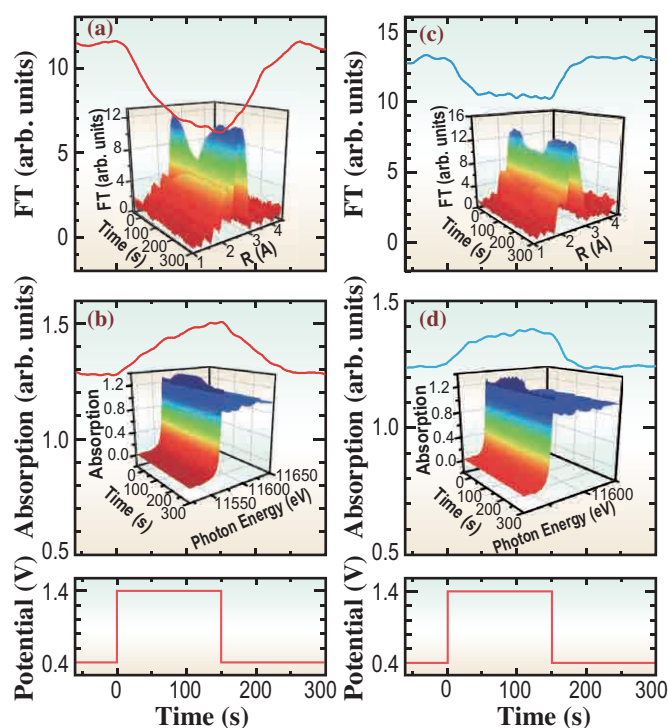


Fig. 2. Time variations in XANES spectra and radial structure functions (FT) during potential-step oxidation/reduction cycle between 0.4 and 1.4 V. Bottom graphs show potential step sequence. (a) and (c): Time variations in peak maximum of radial structure functions at 2.6 Å, which correspond to first-nearest-neighbor Pt-Pt bonds for platinum and Pt₃Co. (b) and (d): Time variations in XANES spectra (white line intensity at maximum) for pure platinum and Pt₃Co bimetallic particles.

the suppression of higher-order oxides. When higher-order oxides formed by atomic oxygen diffusion into platinum or platinum oxide lattices, there were large platinum atom displacements, particularly at the α - to β -PtO₂ transition. Up to α -PtO₂, oxide can grow almost epitaxially, but for β -PtO₂, half the surface Pt atoms are lift toward surface. In the reduction process to metallic platinum, in turn, platinum atoms move greatly, producing energetically unstable platinum

atoms at the solution-oxide interface. This enhances the dissolution of platinum to electrolytes. Thus, Pt-skin layers in which higher-order oxide formation is suppressed could have higher corrosion resistance than that of pure platinum, suppressing the formation of unstable platinum atoms in oxide-reduction processes. Currently, on the basis of the above results, the development of a catalyst with higher corrosion-protection performance is under way.

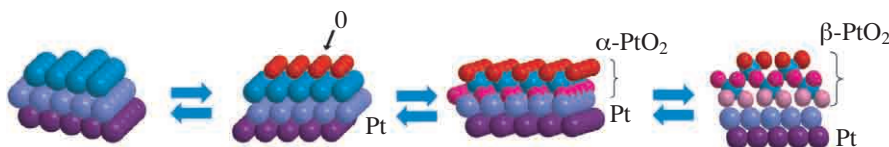


Fig. 3. Schematic drawing of surface oxidation/reduction processes of platinum nanoparticles at 1.4 V.

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References

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