

Industrial Applications

REAL-TIME MONITORING OF AN ELECTROCHEMICAL REACTION INSIDE A FUEL CELL: A TIME-RESOLVED HARD X-RAY DIFFRACTION STUDY

Fuel cells that convert the chemical energy of fuel, such as hydrogen or methanol, directly into electricity can offer clean and highly efficient energy conversion systems in the near future. Owing to recent extensive studies, the basic performance of such fuel cells are now about to reach practical levels. For example, car manufacturers are showing prototypes of hydrogen fuel cell cars, and electronic companies are looking at a new battery market for portable electronics by replacing Li-ion batteries with longer-lasting direct methanol fuel cells.

There are, however, still several hurdles to be overcome before such fuel cells can be truly commercialized. One such technological hurdle is the improvement of the durability and reliability of fuel cells, particularly electrocatalysts that promote electrochemical reactions in the fuel cells. During long-term operation, the power of fuel cells gradually decreases due to the oxidative degradation of platinum catalysts. Since the platinum catalysts' surface is exposed to extremely severe chemical conditions, i.e., in a strong acid or under high electrochemical potential, platinum catalysts dissolve into the electrolyte causing considerable reduction in the fuel cell performance. Consequently, the development of innovative electrocatalysts with high

corrosion protection performance is one of the main research interests in this research field.

To obtain information for designing better electrocatalysts, there is a great interest in the direct monitoring of the oxidative degradation behaviors of platinum catalysts in a real operating condition. A hard X-ray diffraction method using with the high penetration ability of high-energy X-rays through components of fuel cells such as electrolyte and electrode materials is one of the suitable experimental techniques for such purpose. Here, we present the results of time-resolved hard X-ray diffraction studies on the electrochemical oxidation process of platinum electrocatalysts, which shows how platinum oxides are formed on the catalyst surface and how such oxides affect the properties of nanoparticles [1].

Time-resolved *in situ* X-ray diffraction (XRD) measurements were performed in the transmission geometry at beamline **BL16XU**. The photon energy used was 30 keV. Diffraction profiles were collected using a CCD camera in every 0.5 s. Carbon supported platinum nanoparticles (*ca.* 3 nm, 50 wt%-Pt loading) were spread onto a carbon electrode. This electrode was placed in an electrochemical cell with 0.5 mol dm⁻³ H₂SO₄ electrolytes, and the potential of the electrode was controlled by an electrochemical analyzer.

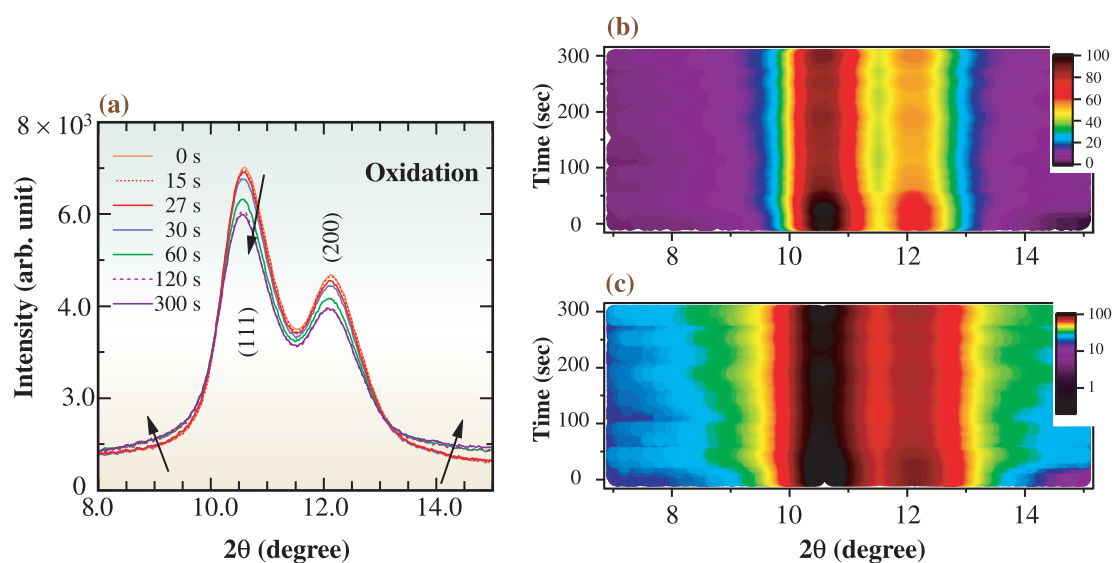


Fig. 1. (a) Time variation of *in situ* X-ray diffraction profiles of platinum nanoparticles upon oxidation at 1.4 V (vs RHE). XRD intensity maps with respect to 2-theta and time, in normal scale (b) and in log scale (c). Diffractions from platinum and platinum oxides are highlighted respectively.

Figure 1(a) shows the evolution of the X-ray diffraction profiles in the first oxidation process at 1.4V vs. RHE (Reversible Hydrogen Electrode). Upon oxidation, the intensities of platinum (111) and (200) diffraction peaks gradually decreased; simultaneously, the background intensity, which is attributed to the diffuse scattering from the amorphous-like PtO_x , increased. This indicates that the surface of platinum nanoparticles was gradually oxidized into amorphous-like platinum oxides. The fraction of oxides is 40%, as estimated by the diffraction peak area loss, corresponding to the monolayer of the particles' surface. (The detailed structure of surface oxides is similar to that of β - PtO_2 as determined by our DXAFS (dispersive X-ray absorption fine structure) measurements performed at beamline **BL28B2** [2]). Interestingly, during the first 15 s, (111) and (220) diffraction intensities did not significantly change. OH adsorption and/or atomic O adsorption, which do not cause significant surface reconstruction, would occur at this stage.

We show the XRD intensity map with respect to both 2θ and time in Figs. 1(b) and 1(c). The time variation of surface oxide formation is more clear in these figures. In addition to the diffraction intensity change, we also observed clear peak shifts to the lower diffraction angle. This suggests that the core parts of the platinum nanoparticles are expanded when the nanoparticles' surfaces are covered with their oxides (Fig. 2). This result is somewhat surprising, since such lattice expansion is not observed at the bulk surface. This lattice expansion observed only at the nanoparticles' surface could be one reason why nanoscaled catalysts show the accelerated oxidative degradation phenomenon.

Observed surface oxides and structural change in the core part of nanoparticles should be closely related with corrosion phenomena of platinum catalysts. Currently, on the basis of the above results, the development of the catalyst with higher corrosion protection performance is under the way.

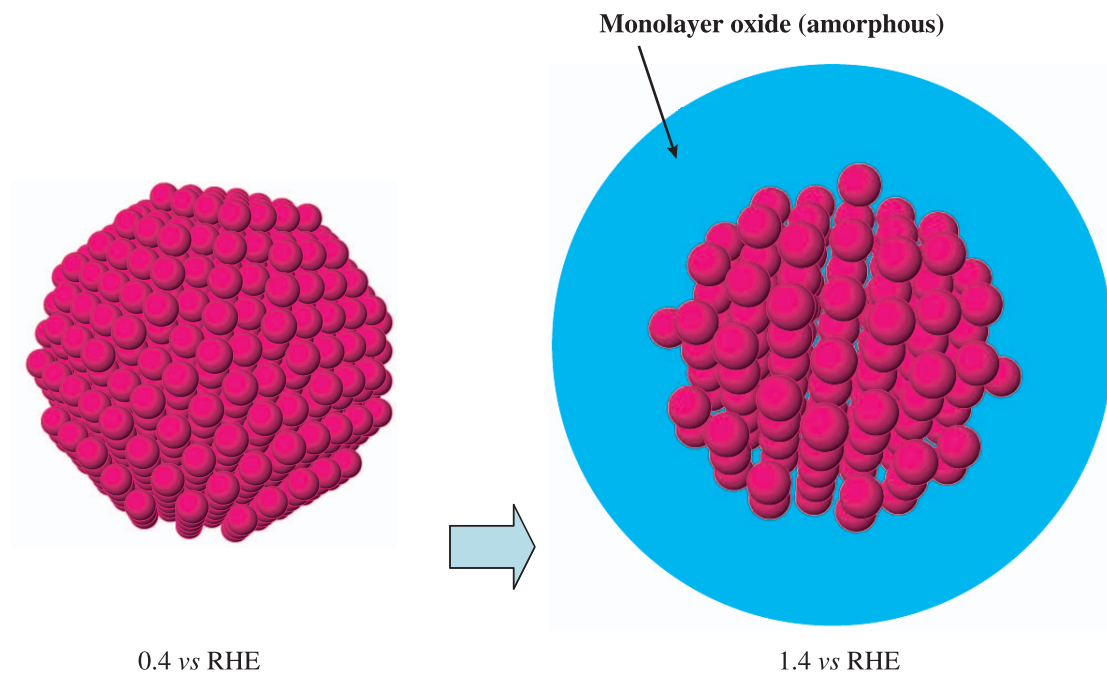


Fig. 2. Schematic drawing of surface oxidation process of platinum nanoparticles at 1.4 V.

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References

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