In situ HERFD-XANES/RIXS measurements of adsorbed oxygen species on Pt/C electrocatalysts in polymer electrolyte fuel cells under operating conditions

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Polymer Electrolyte Fuel cell (PEFC) is one of the most promising power sources, which has great potential to realize low or even zero emissions. Performance and long-term durability of electrocatalysts especially on cathode, usually composed of Pt or Pt based nanoparticles as active components are critical problems to be solved for next-generation PEFC systems. Thus, obtaining atomistic insights of Pt nanoparticle catalysts under PEFC operation conditions are strongly required. Researches utilizing well-defined single crystal surfaces have been proceeded in the fundamental aspect to provide useful information about adsorbates and Pt surface structures. However, the adsorption and catalysis properties of the Pt nanoparticle electrocatalysts under PEFC operating conditions are still not clear, due to the lack of methodology.

We have applied an *in situ* High Energy Resolution Fluorescence Detected X-ray Absorption Near-Edge Structure (HERFD-XANES) spectroscopy for *operando* observations of Pt/C cathode catalysts in PEFCs under operating conditions at BL36XU beamline in SPring-8. Appling potential from 0.4 to 1.0 V (Figure 1), Pt L_{III}-edge HERFD-XANES difference spectra were well fitted with three characteristic absorption peaks. Moreover, another peak appeared by applying more than 1.1 V. FDMNES simulations of the spectra for DFT optimized structure models showed that three peaks observed at low potentials could be assigned to two adsorbed oxygen species (O, OH) and edge oxidation states, and the other peak observed at high potentials could be assigned to (111) facet oxidation states of Pt nanoparticles at the cathode.

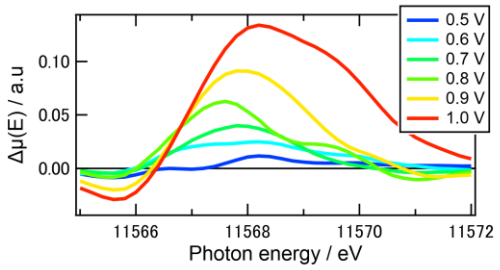

Figure 1. Pt L_{III}-edge HERFD-XANES difference spectra referred to the spectrum at 0.4 V.