

In situ Time-resolved XAFS Study for ADT Processes of Pt/C and Pt₃Co/C PEFC Cathode Electrocatalysts

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Practical application of polymer electrolyte fuel cells (PEFCs) remains challenging because of the insufficient durability of cathode electrocatalysts under operating conditions. Pt-M bimetallic catalysts such as Pt-Co have been reported to exhibit better durability compared to Pt catalysts, but the structural response and reaction mechanism of the bimetallic catalysts for accelerated durability test (ADT) of PEFC are not clear. In this study, we investigated the structural kinetics of Pt/C and Pt₃Co/C cathode electrocatalysts in MEAs at the different stages of ADT cycles by in situ time-resolved XAFS [1].

MEAs (3×3 cm²) with commercial Pt/C or Pt₃Co/C cathode electrocatalyst (0.5 mg cm⁻²-Pt₃Co) and Pd/C anode electrocatalyst (0.5 mg cm⁻²-Pd) were used for in situ XAFS measurements. PEFC was operated at 353 K, supplying N₂ or air at cathode and H₂ at anode bubbled by humidifier at 351 K. In situ Pt L_{III}-edge time-resolved quick-XAFS was measured every 100 ms for cell voltage-cycling processes between 0.4 and 1.0 V at the SPring-8 BL36XU station. Changes in electronic and local structures of the Pt catalysts were estimated by the analysis of time-resolved XANES and EXAFS spectra. ADT was performed by the repetition of voltage cycling between 0.6 V (3 s) and 1.0 V (3 s).

Time-resolved XAFS were measured for as-prepared MEA and MEA after several cycles of ADTs (2k and 17.5k: Pt/C, 5k and 35k: Pt₃Co/C). Changes in Pt valence were estimated by the white-line heights of Pt L_{III}-edge XANES spectra (Fig. 1) and the coordination numbers of Pt-Pt, Pt-Co, and Pt-O were estimated by the curve-fitting of Pt L_{III}-edge EXAFS FT. From the fitting analysis of the time profiles of these structural parameters, their rate constants were estimated.

In the case of Pt/C, as the number of ADT cycles increased, structural changes for Pt redox reactions became less sensitive because of Pt agglomeration, while their rates were almost constant (Fig. 1 B1). Although similar aggregation of the Pt₃Co catalyst was caused similar decreases in the sensitivity of the structural parameter changes, their rate constants also decreased as the number of ADT cycles increased. The time-resolved XAFS suggested the dissolution of Co from Pt-Co alloy particles led to gradual decreases of the rates of the redox reactions at the surface of the bimetallic catalyst. These results indicated the limitation of activity/stability enhancements of the Pt-Co alloy catalysts in PEFC [1].

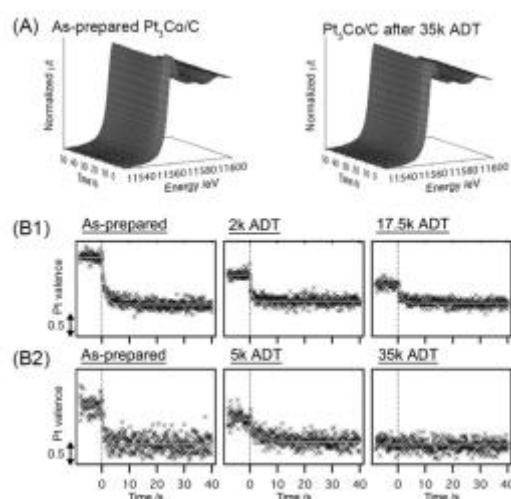


Fig. 1. (A) Series of in situ time-resolved Pt L_{III}-edge XANES spectra of as-prepared Pt₃Co/C and Pt₃Co/C after 35k ADT, and (B) the time profiles of Pt valence of (1) Pt/C and (2) Pt₃Co/C for voltage cycling 1.0 → 0.4 V.

REFERENCES

- [1] N. Ishiguro, S. Kityakarn, O. Sekizawa, T. Uruga, H. Matsui, M. Taguchi, K. Nagasawa, T. Yokoyama, and M. Tada, *J. Phys. Chem. C*, **120** (2016) 19642.