

## Time-Resolved DXAFS Study on Pt/C Fuel Cell Cathode under Operando Conditions

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### Introduction

Fuel cell is one of the key issues for environmental and energy problems in modern society, but the activity and life time of Pt/C cathode catalysts must be improved to make fuel-cell automobiles a reality. Towards this goal, we have observed the electrochemical reaction mechanism of a Pt/C cathode surface in a fuel cell by in-situ time-resolved energy-dispersive XAFS (DXAFS) and found a significant time lag between electron transfer processes and redox structural changes of a Pt-cathode catalyst for the first time<sup>[1]</sup>.

### Experimental

Pt/C (Pt 2 nm; 50 wt%) was used as a cathode catalyst and Pt-free Pd/C (Pd 20 wt%) was adopted as an anode catalyst. MEA was stacked between a prepared in-situ XAFS cell and H<sub>2</sub> and N<sub>2</sub>/air gases were bubbled through deionized water bathes at 323 K and heated at 333 K for introduction to the XAFS cell at 333 K. The heated gases with moisture entered into each electrode of the XAFS cell and reacted at the MEA as shown in Fig. 1.

Energy-dispersive XAFS at Pt L<sub>3</sub> edge was measured at PF-AR NW2A station, whose experimental set up was illustrated in Fig. 1. Photodiode array was used as a position sensitive detector for energy-dispersed X-ray and DXAFS was recorded every 4 ms. Electrochemical data was recorded every 100 μs on a potentiostat.

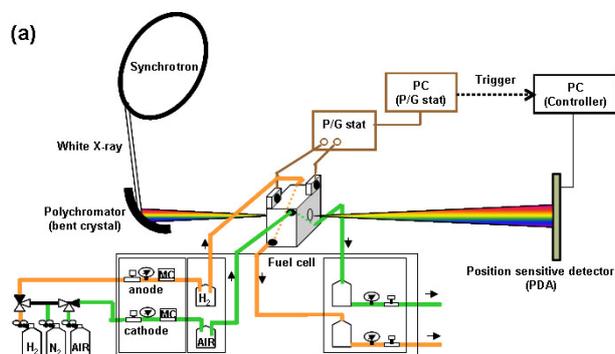


Fig. 1 DXAFS set up for the in-situ measurements of fuel-cell catalysts.

### Results and Discussion

When the cell voltage was stepped from 0.4 V to 1.4 V, electron transfers rapidly proceeded and the rate constants of the two electrochemical reactions on a fuel-cell cathode surface were estimated to be 0.40 s<sup>-1</sup> and 0.040 s<sup>-1</sup>. On the other hand, the Pt catalyst at the cathode surface slowly charged and the white line intensity of Pt L<sub>3</sub>-edge DXANES was almost constant within the initial 500 ms as shown in Fig. 2. The Rate constant of the slow Pt charging was 0.010 s<sup>-1</sup>. The similar time lag between electron transfer and Pt discharging was also observed at a reverse voltage-operating process from 1.4 V to 0.4 V. The first operando DXAFS measurements of a Pt/C cathode catalyst revealed the unique mechanism of the electrochemical reactions at the cathode surface of fuel cell for the first time.

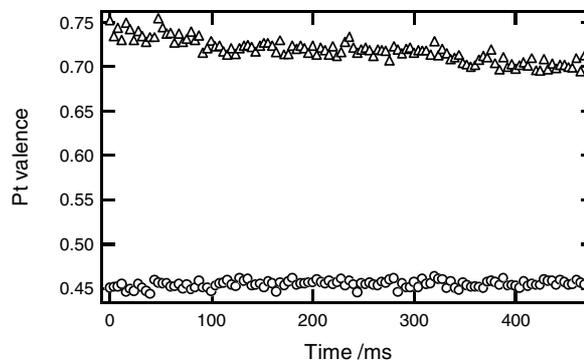


Fig. 2. Changes in Pt valences of the Pt/C cathode catalyst measured by Pt L<sub>3</sub>-edge DXANES at 4-ms time resolution. The bottom plots (○) represent the changes in Pt valence estimated by peak areas of DXANES for the voltage-operating process from 0.4 V to 1.4 V under N<sub>2</sub>. The above plots (Δ) represent the changes in Pt valence in the process from 1.4 V to 0.4 V.

### Reference

[1] M. Tada et al., *Angew. Chem. Int. Ed.* **46**, 4310 (2007).

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