

## In Situ Time-resolved Time-gating Quick XAFS Study for Dynamic Surface Events on Pt/C Cathode in a Fuel Cell

Environmentally friendly proton-exchange-membrane fuel cells (PEMFC) can be used in both fuel-cell automobiles and energy systems to address the serious environmental and energy problems faced by society. For the commercial applications of fuel-cell systems to automobiles, power-on/off processes with a large energy transfer are indispensable. However, the surface atoms of the active metal particles tend to dissolve into the electrolyte in contact with the cathode catalyst layer when we repeatedly rapidly change cell voltages to alter a car's speed. We have developed a novel time-gating quick XAFS method (TG-QXAFS) for *in situ* time-resolved XAFS measurements of Pt/C cathode catalysts in fuel cells and succeeded in determining all the kinetic parameters of the 8 elementary steps involved in rapid voltage-operating processes. Significant time lags between the electrochemical reactions and the structural changes of the Pt catalysts were observed for the first time.

The acquisition of QXAFS spectra at a Pt  $L_{III}$  edge requires at least 15 s due to the slow mechanical rotation of a monochromator; however, the time resolution of 15 s is too slow to observe the reaction mechanism of a Pt/C cathode in a fuel cell for rapid voltage-operating processes completed within a few seconds. We developed TG-QXAFS, whose schematic is illustrated in Fig. 1(a), at beamline BL01B1. The QXAFS system was synchronized with a potentiostat connected to a homemade electrode XAFS cell (Fig. 1(c)), and the cell voltage was rapidly changed between 0.4 V and 1.0/1.4 V ( $t = 0$ ) while the current in the fuel cell was recorded in real time. A trigger signal was initially sent from the potentiostat to the QXAFS system, and a series of QXAFS measurements with delay time  $t$  shifted by 1 s for each measurement (Fig. 1(a)) were repeated. The obtained QXAFS spectra with the different delay times were divided into 15 fragments in  $k$  space, and the 15 fragments of the EXAFS oscillations obtained from the 15 different QXAFS measurements were combined into one interval. Thus, we can obtain a TG-QXAFS spectrum with a time resolution of 1 s, which is much faster than the conventional QXAFS method (15 s).  $H_2$  for the anode and  $N_2$  or air for the cathode were dewed through deionized water baths and introduced into the XAFS cell at 333 K (Fig. 1(b)).

Figure 2(a) shows the series of time-resolved

TG-QXAFS Fourier transforms for a voltage-stepping process from 0.4 V to 1.0 V under  $H_2$ - $N_2$  gas conditions. Analysis of XANES, EXAFS and electrochemical data recorded on the potentiostat revealed the valence of Pt nanoparticles, the coordination numbers (CN) and distances of Pt-O and Pt-Pt bonds, and the electron transfer in the fuel cell, respectively. Such structural parameters for active metal nanoparticles cannot be obtained by other spectroscopic techniques, and the operando measurements of both structural and electronic kinetics of a Pt/C fuel-cell catalyst were successfully performed for the first time.

We have succeeded in determining the eight rate constants for the oxidation and reduction processes, which are related to the electron transfer, structural change, and d-electron density change at the Pt/C cathode catalyst, which are significantly different from each other. The TG-QXAFS analysis revealed a

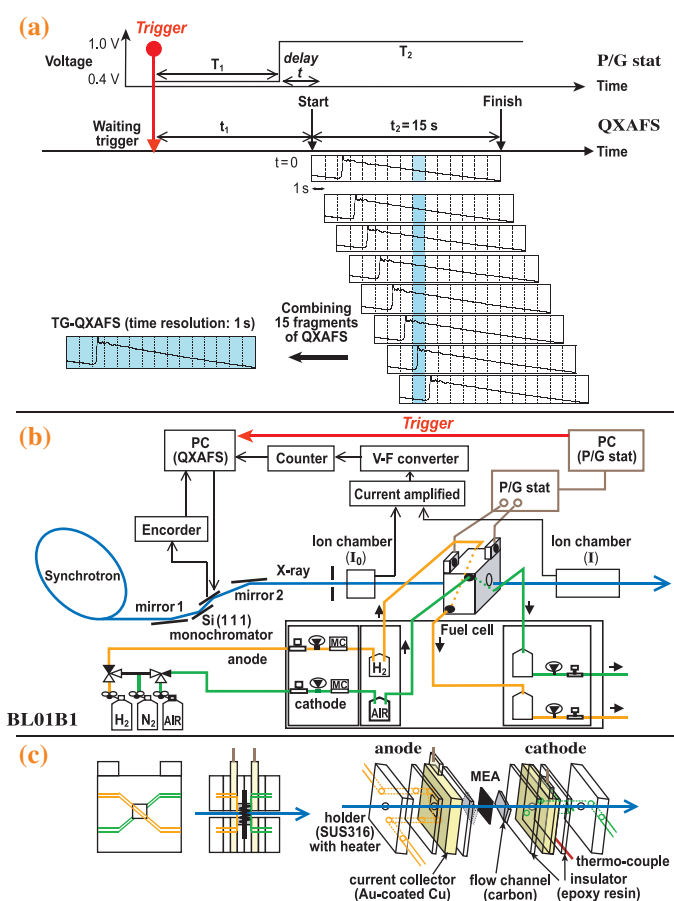


Fig. 1. (a) Procedure for TG-QXAFS with a time resolution of 1 s. (b) Schematic of the fuel cell and in situ time-resolved TG-QXAFS system at BL01B1 beamline. (c) Homemade in situ XAFS cell.

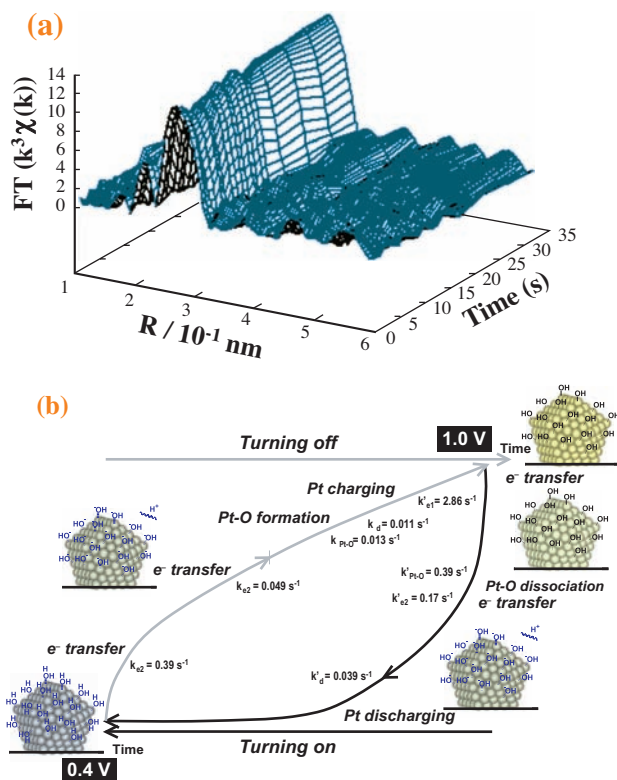


Fig. 2. (a) Series of TG-QXAFS Fourier transforms at Pt  $L_{III}$  edge for a voltage-operating process from 0.4 V to 1.0 V. (b) Reaction mechanism for structural and electronic changes in the Pt/C fuel-cell catalysts at cell voltages of 0.4/1.0 V under  $H_2$  (anode) and  $N_2$  (cathode) at 333 K.

hysteresis loop for the structural changes in the Pt particles in both processes (Fig. 2(b)). It should be noted that there is a significant time lag between the four processes on the cathode surface. In the oxidation process from 0.4 V to 1.0 V, the first dramatic electron transfer ( $k_{e1} = 0.39 \text{ s}^{-1}$ ) was 8 times faster than the subsequent second electron transfer ( $k_{e2} = 0.049 \text{ s}^{-1}$ ). After the first electron transfer, the Pt particles were only slightly charged, and there were no chemical bonds with oxygen on the Pt surface. Then Pt-O bonds slowly formed ( $k_{Pt-O} = 0.013 \text{ s}^{-1}$ ) in conjunction with Pt charging with  $k_d = 0.011 \text{ s}^{-1}$ , which was monitored through the  $d$ -electron density of

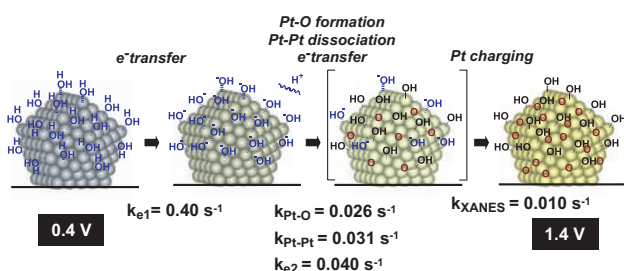


Fig. 3. Structural model of the Pt nanoparticles for the voltage-operating process from 0.4 V to 1.4 V suggested by *in situ* time-resolved QXAFS.

states. On the other hand, the CN of Pt-Pt particles remained constant at about 9 between 0.4 V and 1.0 V, which indicates that no decomposition of the Pt catalyst or significant leaching to the electrolyte occurred.

When the cell voltage was increased to 1.4 V, the Pt particles were gradually oxidized and the CN of Pt-Pt bonds decreased, the reaction mechanism for which is presented in Fig. 3. The 20% decrease in the CN of Pt-Pt bonds and the CN of 0.8 for Pt-O bonds demonstrate that oxygen atoms enter the subsurface of the Pt particles at 1.4 V. Repeated voltage manipulations did not cause any decrease in electric charges, and the number of Pt-Pt bonds returned to its original value when the cell voltage returned to 0.4 V. Thus, the Pt ions do not dissolve in the electrolyte under  $N_2$ , although the voltage (1.4 V) exceeds the threshold voltage for H-O-H bond dissociation and promotes the penetration of oxygen into the Pt subsurface. However, when the cell voltage was increased to 1.4 V in air, the Pt-Pt bonds immediately broke, and the Pt nanoparticles disintegrated. The CN of the Pt-Pt bonds did not recover when the cell voltage was returned to 0.4 V. If a local inclination of electric potential forms on the electrode surfaces, the dissolution of Pt ions gradually occurs, resulting in the serious deterioration of Pt-cathode catalysts.

In conclusion, we have succeeded in the *in situ* observation of the reaction mechanisms occurring on a Pt/C catalyst surface in a fuel-cell cathode for the first time. The reaction kinetics of the electron transfer processes and redox structural changes, which involve eight elementary steps, on the Pt-cathode catalysts were determined. The significant time lag between the electron transfer, the redox structural changes and the Pt charging of the Pt/C catalysts characterizes the property of Pt nanoparticles on a carbon support as well as the population of the bound OH species, which are crucial for the performance of a Pt/C catalyst in a fuel cell [1].

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### References

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