

Reaction Dynamics of Pt/C Cathode Surface in Fuel Cell by In-Situ Time-Resolved XAFS Under Operating Conditions

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Introduction

Environment-friendly PEMFC can be used in both fuel-cell automobiles and energy systems to address the serious environmental and energy problems faced in our modern society. For commercial applications of fuel-cell systems to automobiles, power-on/off processes with huge energy transfer are indispensable. However, surface atoms of the active metal particles tend to dissolve into the electrolyte that is in contact with the cathode catalyst layer. It is required to overcome this problem for fuel-cell automobiles that require the continual repetition of the on/off processes with rapid changes in cell voltages to alter the car's speed. We have investigated the mechanism of the electrochemical processes involved in rapid voltage-controlled processes on a Pt/C cathode catalyst by novel in-situ time-resolved time-gating QXAFS (TG-QXAFS (1 s time resolution) and DXAFS (4 ms time resolution)) for the first time under the operating conditions and found surface reaction dynamics at cathode including 8 elementary steps and significant time lags between the electrochemical reactions and structural changes of Pt catalysts.

Materials and Methods

Pt/C (Tanaka Kikinzo Kogyo, particle size: 2 nm) was used as a cathode catalyst, and Pt-free Pd/C (Pd 20 wt%) was adopted as anode. The MEA was stacked in a prepared XAFS cell. H₂ for anode and N₂ or air for cathode were dewed through deionized water baths and introduced to the XAFS cell at 333 K. Potentiostat was synchronized with the synchrotron XAFS system for in-situ real-time XAFS measurements.

Results and Discussion

The in-situ time-resolved XAFS measurements of Pt/C fuel-cell catalysts were performed by novel TG-QXAFS and DXAFS we developed. Figure 1(left) shows the series of time-resolved TG-QXAFS Fourier transforms for a voltage-stepping process from 0.4 V to 1.0 V under H₂-N₂ gas conditions. The analysis of XANES, EXAFS and electrochemical data recorded on potentiostat revealed the valence of Pt nanoparticles, the coordination numbers(CN) and distances of Pt-O and Pt-Pt, and electron transfer in the fuel cell, respectively. Such structural parameters about active metal nanoparticles cannot be obtained by other spectroscopic techniques, and operando measurements of the both structural and electronic kinetics at 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 hysteresis loop for the structural changes in the Pt particles in the both processes (Fig. 1(right)). It should be noted that there is 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 next process for the 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 by the d-electron density of states. On the other hand, the CN of Pt-Pt particles remained constant at about 9 between 0.4-1.0 V, which indicates that decomposition of the Pt catalyst or significant leaching to the electrolyte did not occur.

When the cell voltage was increased to 1.4 V, the Pt particles were gradually oxidized and Pt-Pt bonds decreased. The 20% decrease in the CN of Pt-Pt 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 numbers of Pt-O bonds returned to its original value when the cell voltage returned to 0.4 V. Thus the Pt ions do not dissolve into the electrolyte under N₂, although the voltage (1.4 V) exceeds the threshold voltage for H-O-H bond dissociation and promotes 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 electrode surfaces, dissolution of the Pt ions gradually occurs, resulting in serious deterioration of Pt-cathode catalysts.

Significance

We have succeeded in in-situ observing the reaction mechanisms occurring on the Pt/C catalyst surface in a fuel-cell cathode in real time 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 decided. 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 Pt/C catalyst in a fuel cell.

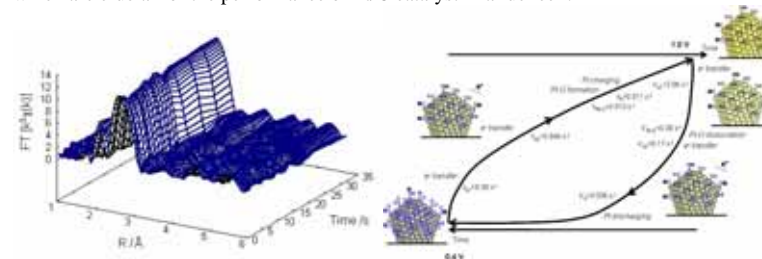


Figure 1. (left) A series of TG-QXAFS Fourier transforms (0.4 → 1.0 V). (right) Reaction mechanism for structural and electronic changes of the Pt/C fuel-cell catalysts in cell voltages of 0.4/1.0 V under H₂ (anode) and N₂ (cathode) at 333 K.