

Simultaneous operando time-resolved XAFS-XRD measurements of a Pt/C cathode catalyst in a polymer electrolyte fuel cell under transient potential cyclic operations

Crucial issues in developing next-generation polymer electrolyte fuel cells (PEFCs) are improving the oxygen reduction reaction (ORR) activity and long-term durability, and reducing the cost of cathode catalysts. To resolve these issues, it is necessary to determine and understand the dynamic aspects of the structures and electronic states of cathode catalysts and also the reaction mechanisms at the cathode catalyst surface under PEFC operating conditions by operando time-resolved analysis methods. Time-resolved quick X-ray absorption fine structure (QXAFS) enables the element-selective investigation of the dynamic transformations of the local structures and oxidation states of Pt nanoparticles in Pt/C cathode catalysts. Time-resolved X-ray diffraction (XRD) enables measurements of the dynamic transformation of the crystalline structures of Pt nanoparticles in Pt/C cathode catalysts. Thus, we have designed a combined system for simultaneous time-resolved QXAFS-XRD measurements of Pt/C cathode catalysts in PEFCs [1,2]. Here, we summarize the simultaneous operando time-resolved QXAFS-XRD measurements and the application of the technique to determine the dynamic structural and electronic behavior of a Pt/C cathode catalyst in PEFC under transient voltage cyclic operations.

Simultaneous time-resolved QXAFS-XRD measurements at 60 ms time resolution (20 ms QXAFS $\times$ 2 + 20 ms XRD $\times$ 1 = 60 ms) were performed

at SPring-8 BL36XU [3] by using a servomotor-driven Si channel-cut crystal monochromator. The experimental setup for the simultaneous operando time-resolved QXAFS-XRD measurements of a PEFC is shown in Figs. 1(A-C), where a high-speed regulation pattern of monochromator angles for the simultaneous QXAFS-XRD measurements is also shown. The cell voltage was changed from the open-circuit voltage (OCV) to 0.4 V_{RHE} , which was maintained for 300 s, followed by a rapid voltage jump from 0.4 to 1.4 V_{RHE} . This voltage was maintained for 300 s, and then reversely the cell voltage was changed rapidly from 1.4 to 0.4 V_{RHE} (anode: H_2 , cathode: N_2).

The series of time-resolved QXANES spectra, QEXAFS Fourier transforms and XRD patterns of the Pt/C in the transient potential operations are respectively shown in Figs. 1(D-F). The transient response time profiles of the QXANES white line peak height (proportional to Pt valence), CN(Pt-Pt), and CN(Pt-O) are plotted against the reaction time after the voltage jump in Figs. 1(G-I), respectively, and the Pt metallic phase size estimated using Scherrer's formula with the XRD (220) peak is also shown in Fig. 1(J). All transient responses to the voltage cyclic operations 0.4 $V_{RHE} \rightarrow 1.4 V_{RHE} \rightarrow 0.4 V_{RHE}$ were analyzed by the following one- or two-exponential functions: $f(t) = y_0 + a_1 \exp(-k_1 t)$ or $f(t) = y_0 + a_1 \exp(-k_1 t) + a_2 \exp(-k_2 t)$, as shown by red curves in Figs. 1(G-J). The parameters k_1 , k_2 , a_1 , a_2 , and t are the rate constants

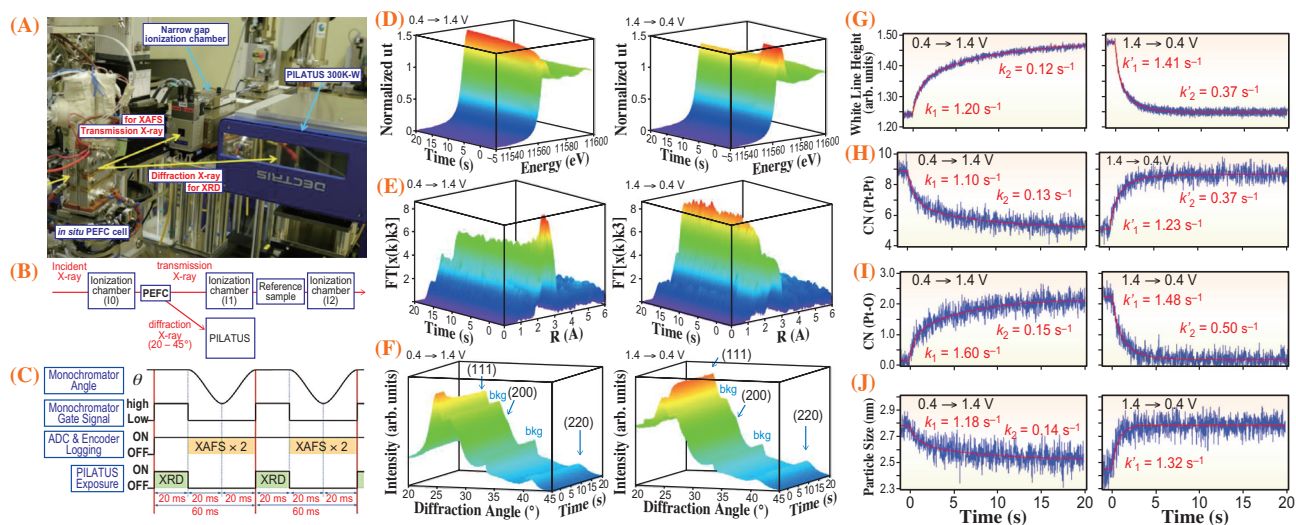


Fig. 1. (Left) Experimental setup for operando simultaneous time-resolved XAFS-XRD measurements of PEFC. (A) XAFS-XRD measurement setup, (B) schematic diagram of the setup, and (C) high-speed regulation pattern of monochromator angles with gate signals and recording time charts of detectors. (Center) Series of time-resolved (D) QXANES spectra, (E) QEXAFS Fourier transforms, and (F) XRD patterns. (Right) Transient response curves of (G) white line peak height, (H) CN(Pt-Pt), (I) CN(Pt-O), and (J) Pt metallic phase size. Potential cyclic operations, 0.4 $V_{RHE} \rightarrow 1.4 V_{RHE} \rightarrow 0.4 V_{RHE}$; gas, H_2 (anode)- N_2 (cathode); cell temp., 353 K; relative humidity, ~93%.

k_1 and k_2 , the amounts of variations, a_1 and a_2 , and the reaction time t for the two-stage (fast and slow) structural kinetics of the Pt nanoparticles. The Pt nanoparticles in the Pt/C cathode catalyst under the transient voltage operation $0.4 V_{\text{RHE}} \rightarrow 1.4 V_{\text{RHE}}$ transform at the fast and slow successive steps with the rate constants k_1 and k_2 , respectively. The surface Pt-O bond formation event was followed by decreases in Pt metallic phase size and CN(Pt-Pt), and an increase in Pt valence. The results suggest that the surface Pt-O bond formation induces the partial disordering (rearrangement) of the outermost Pt layer, resulting in an apparent half-layer decrease in metallic phase size at the saturated O layer from 2.78 to 2.64 nm as shown in Fig. 2. The first fast surface event was followed by the second slow transformations of Pt-O bond formation, Pt charging, Pt-Pt bond dissociation, and the decrease in Pt metallic phase size. These rate constants are similar to each other within the error ranges, suggesting that these slow events occur concertedly to finally produce the tetragonal Pt²⁺-O layer (Pt-O = 0.201 nm) at the Pt surface (Fig. 2). At the transient voltage operation $1.4 V_{\text{RHE}} \rightarrow 0.4 V_{\text{RHE}}$, the first fast steps of Pt-O bond dissociation, the decrease in Pt valence, Pt-Pt bond reformation, and the increase in Pt metallic phase size proceed concertedly at similar rates within the experimental error range as shown in Fig. 2. The second slow steps of Pt-O bond dissociation, the decrease in Pt valence, and Pt-Pt bond reformation under $1.4 V_{\text{RHE}} \rightarrow 0.4 V_{\text{RHE}}$ also occur concertedly.

However, the XRD data indicated a one-step event as shown by the one-wave fitting (Fig. 1(J)). These results suggest that the size of the Pt metallic phase increases in one step under $1.4 V_{\text{RHE}} \rightarrow 0.4 V_{\text{RHE}}$, unlike the two-stage decrease under $0.4 V_{\text{RHE}} \rightarrow 1.4 V_{\text{RHE}}$. The change in metallic phase size is completed in the fast step, and the changes in Pt valence, Pt-O bond dissociation, and Pt-Pt bond reformation at the surface proceed further at lower rates as shown in Fig. 2. Although the Pt/C cathode catalysis in a PEFC for the ORR performance is reversible under the voltage operations $0.4 V_{\text{RHE}} \rightarrow 1.4 V_{\text{RHE}}$ and $1.4 V_{\text{RHE}} \rightarrow 0.4 V_{\text{RHE}}$, note that the structural and electronic transformations and reaction kinetics for the 15 elementary steps did not trace similar transformations and kinetics in the forward and backward voltage operation processes, and revealed different structural transformations and kinetics and a definite hysteresis as illustrated in Fig. 2.

The simultaneous operando time-resolved QXAFS-XRD approach to the Pt/C cathode catalysis in PEFCs provide a new insight into the molecular-level reaction mechanism and dynamic transformations in the Pt surface layer and bulk under the transient potential operations. The simultaneous operando time-resolved QXAFS-XRD technique is promising and powerful, and can promote further understanding and improvement of next-generation PEFC performance and durability by providing the key material properties and the relationship of the macroscopic electrochemical data with the structural kinetics.

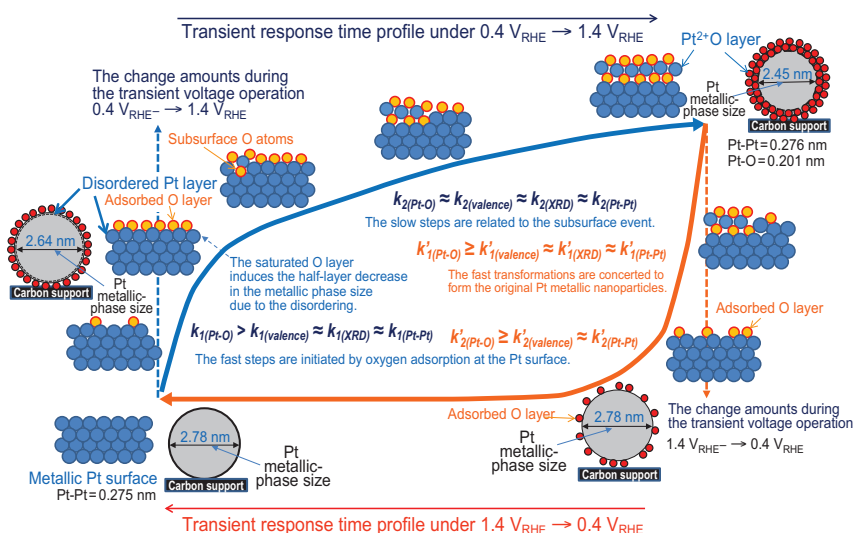


Fig. 2. Reaction mechanism and structural kinetics for Pt surface events of Pt/C cathode catalyst under transient voltage cyclic operations $0.4 V_{\text{RHE}} \rightarrow 1.4 V_{\text{RHE}} \rightarrow 0.4 V_{\text{RHE}}$ under H_2 (anode)- N_2 (cathode). $k_1(\text{Pt-O})$ and $k_2(\text{Pt-O})$, Pt-O bond formation; $k_1(\text{valence})$ and $k_2(\text{valence})$, Pt charging; $k_1(\text{Pt-Pt})$ and $k_2(\text{Pt-Pt})$, Pt-Pt bond dissociation; $k_1(\text{XRD})$ and $k_2(\text{XRD})$, decrease in Pt metallic phase size; $k'_1(\text{Pt-O})$ and $k'_2(\text{Pt-O})$, Pt-O bond dissociation; $k'_1(\text{valence})$ and $k'_2(\text{valence})$, Pt discharging; $k'_1(\text{Pt-Pt})$ and $k'_2(\text{Pt-Pt})$, Pt-Pt bond reformation; $k'_1(\text{XRD})$, increase in Pt metallic phase size.

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