Quick *operando* ambient-pressure hard X-ray photoelectron spectroscopy for reaction kinetic measurements of polymer electrolyte fuel cells

Operando ambient-pressure hard X-ray photoelectron spectroscopy (AP-HAXPES) has become a powerful tool for the investigation of surface catalytic reactions. It is, however, very important to perform time-resolved measurements to gain an understanding of the reaction mechanisms. In the present work, we have exploited a subsecond *operando* AP-HAXPES system for the investigation of reaction kinetics in electrochemical cells under working conditions and have conducted demonstrative experiments concerning the redox cycles of the Pt cathode in the polymer electrolyte fuel cell (PEFC) upon applying stepwise bias voltage and the poisonous S^{2-} adsorption/desorption kinetics at the Pt cathode of PEFC.

The present HAXPES apparatus, Scienta-Omicron R4000 Hipp-2, installed at SPring-8 **BL36XU** allows us to measure a photoelectron spectrum with one shot. The available energy range is ~19 eV at the electron pass energy of 200 eV, which is sufficiently wide to detect many species with different oxidation numbers. The one-shot exposure time of the present CCD camera is 14 ms (70 fps), which corresponds to the maximum ideal time resolution. Figure 1(a) shows the one-shot XPS signals from a Au(111)/mica single crystal obtained using the laboratory X-ray source of monochromatized Al Kα. Although there can be seen only some pulse signals within one shot, the repeated accumulation with the time resolution of 14 ms for 0.42, 4.2, and 42 s successfully yields the Au 4*f* XPS with a good signal-to-noise ratio, as is seen in Fig. 1(b).

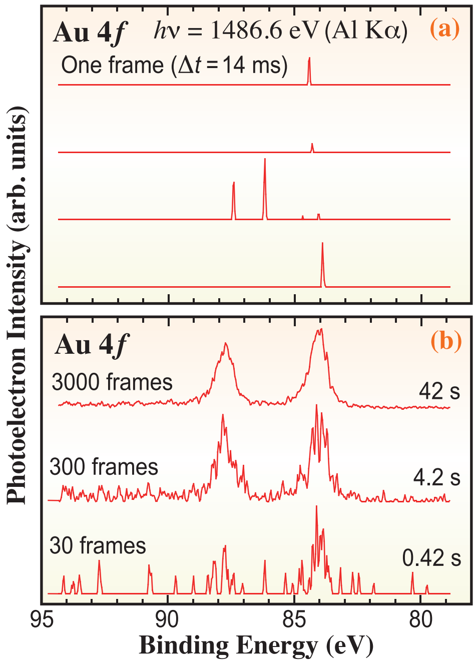

Fig. 1. Time-resolved XPS from the Au(111)/mica single crystal measured using the laboratory Al Kα monochromatized X-ray source. **(a)** One-shot spectra with the time resolution of 14 ms. **(b)** Accumulated one-shot XPS signals for 0.42, 4.2, and 42 s, with constant time resolution.

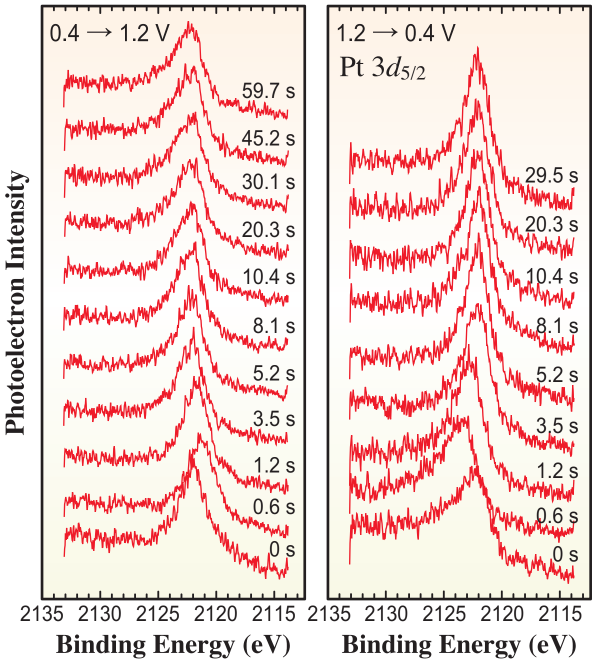

Fig. 2. Time dependence of Pt $3d_{5/2}$ HAXPES from the Pt cathode of working PEFC upon applying abrupt cathode-anode bias voltage steps of 0.4 → 1.2 V (left panel, oxidation process) and 1.2 → 0.4 V (right panel, reduction process). The time resolution was set at 500 ms and the measurements were repeated for 300 cycles (60 s for the oxidation process and 30 s for the reduction process) in both experiments.

The redox cycles of the Pt cathode electrode in a working PEFC have been investigated at BL36XU by measuring the Pt $3d_{5/2}$ HAXPES upon applying abrupt cathode-anode bias voltage steps (0.4 ↔ 1.2 V). It takes around 90 s to complete one cycle at room temperature and we set the time resolution at 500 ms. 300 cycles (30 s at 0.4 V and 60 s at 1.2 V) were repeated, and the total measurement period amounted to ~27,000 s. The time evolution of the resultant Pt $3d_{5/2}$ spectra is shown in Fig. 2. Through the curve-fitting analysis for the spectra in Fig. 2, the time dependence of the Pt amounts of Pt^0, Pt^{1+} (oxygen-adsorbed Pt), and Pt^{2+} (oxidized Pt) are obtained as shown in Fig. 3. In the oxidation of the bias voltage step from 0.4 to 1.2 V, the Pt^0 species (metallic Pt) gradually decreases with an increase in the amount of oxidative Pt^{1+} and Pt^{2+} species. On the other hand, in the reduction of the bias voltage step from 1.2 to 0.4 V, the metallic Pt species is reproduced very quickly. By assuming the two-step reaction mechanism shown in Fig. 4, we can evaluate the reaction rate constants; the obtained results are k_1=0.11 s^{-1}, k_2=0.017 s^{-1}, k_{-1} = 0.37 s^{-1}, and k_{-2} = 1.09 s^{-1}. These results are consistent with those obtained by time-resolved XAFS measurements, although the measurement temperatures are different (HAXPES at 30°C and XAFS at 80°C). The reduction process is found to be much faster than the oxidation process, because the oxidation process consists of several steps to overcome the rather high activation energies, such as dissociative oxygen adsorption, Pt–Pt metallic bond cleavage, and oxygen embedding into the subsurface area.

The adsorption/desorption kinetics of poisonous S^{2-} have also been investigated at the Pt cathode upon applying abrupt bias voltage steps of 1.0 ↔ 0.0 V. At the 1.0 → 0.0 V step, the S^{2-} species is adsorbed rather slowly, while it is desorbed rather quickly at the 0.0 → 1.0 V step. The reason for a much slower adsorption step is that the adsorption step requires dissociation of SO_3^{2-} or SO_4^{2-} to yield S^{2-}, the activation energy barrier of which may be larger than any reaction step in the desorption process. For details, see the original literature [1].

The present quick *operando* HAXPES measurement technique has never been reported, to the best of our knowledge, and is widely applicable for the investigation of surface chemical kinetics not only for fuel cells but also for various catalytic reactions.

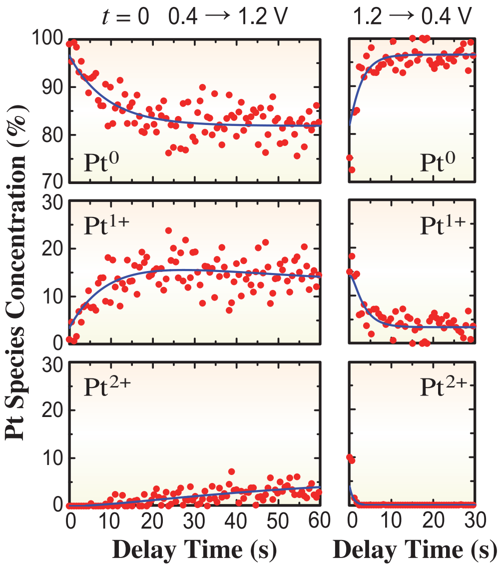

Fig. 3. Time dependence of the amounts of Pt species, Pt^0 (metallic), Pt^{1+} (O adsorbed), and P^{2+} (oxidized). The blue lines are the data fitted assuming the reaction mechanism shown in Fig. 4.

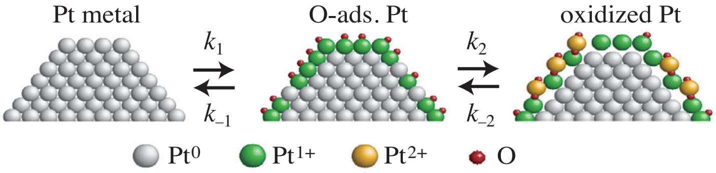

Fig. 4. Assumed reaction mechanism of the redox cycle in the Pt cathode upon changing bias voltage. At the first step, oxygen is dissociatively adsorbed on the Pt surface to yield Pt^{1+}, and at the second step, oxygen is embedded into the subsurface to provide oxidized Pt^{2+} at the surface. The rate constants are evaluated using the experimental data shown in Fig. 3.

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References

[1] *T. Nakamura, Y. Takagi, S. Chaveanghong, T. Uruga, M. Tada, Y. Iwasawa and T. Yokoyama: J. Phys. Chem. C* ***124*** *(2020) 17520.*