

## Operando soft X-ray emission spectroscopy of iron phthalocyanine-based oxygen reduction catalysts

Polymer electrolyte fuel cells (PEFCs) have attracted much attention as clean and high efficient electrochemical devices for energy conversion. Conventionally, Pt-based materials are used as cathode catalysts for slow oxygen reduction reaction (ORR). Alternative ORR catalysts of low cost and high activity are desired because Pt is expensive and their resources are limited. Carbon-based materials are expected to be cathode catalysts alternative to conventional Pt catalysts for PEFCs. Carbon-based catalysts are usually synthesized by pyrolyzing precursors such as metal-phthalocyanine or metal-porphyrine with/without other carbon resources such as resins [1,2]. Accordingly, carbon-based catalysts are generally composed of C, N, O, H, and 3d transition metals. Thus, elucidation of ORR active sites is strongly required for further improving the ORR activity. There are two major candidates for the ORR active site, i.e.  $TM-N_x$  sites ( $TM$ : Fe or Co,  $x$ : 2 or 4), and nitrogen functional groups. In order to discuss the active site of carbon-based catalysts, their electronic structure has been investigated under *ex situ* conditions [2]. However, to further explore the ORR mechanism, study in *operando* condition is strongly required.

We have developed a novel electrochemical cell system for *operando* soft X-ray emission (SXE) spectroscopy of cathode catalysts for polymer electrolyte fuel cells at BL07LSU [3]. Incorporating a membrane electrode assembly (MEA) on a vacuum compatible flange, the system enables direct observation of element-specific electronic structure that changes with gaseous and potential conditions. SXE essentially provides element specific information involving transition within a particular element and

is sensitive to valence electronic states of transition metals and light elements due to dipole-allowed transition at  $L$ -edge of transition metals and at  $K$ -edge of light elements.

A carbon-based catalyst was prepared by pyrolyzing a mixture of iron phthalocyanine and phenolic resin using a multi-step pyrolysis method (multi-FePc/PhRs).  $0.4 \text{ mg}\cdot\text{cm}^{-2}$  of PtRu/C (TKK) and  $4 \text{ mg}\cdot\text{cm}^{-2}$  of multi-FePc/PhRs were used as the anode and cathode catalysts of the MEA, respectively.

*Operando* SXE measurements were performed at BL07LSU using an ultrahigh resolution SXE spectrometer [4]. The gas flow rates were the same as those for CV measurements except for the introduction of  $N_2$  and  $O_2$  to the cathode with the rates of  $45$  and  $5 \text{ mL}\cdot\text{min}^{-1}$ , respectively.

Figure 1 shows a schematic view of the MEA cell system. The vacuum environment is separated by a  $150 \text{ nm}$ -thick SiC membrane from the MEA in the atmosphere. An O-ring, SiC membrane, PTFE gasket sheets with Au foils as current collectors, and the MEA are sandwiched between a vacuum flange and the MEA cell. The electric potential between both electrodes can be manipulated by a Potentio/Galvanostat.

Figure 2 shows the  $H_2$ - $O_2$  fuel cell polarization plots obtained by measuring stable current densities at each potential. The gas flow rates were regulated to  $10 \text{ mL}\cdot\text{min}^{-1}$   $H_2$  flow to the anode and  $50 \text{ mL}\cdot\text{min}^{-1}$   $N_2$  or a mixture of  $40 \text{ mL}\cdot\text{min}^{-1}$   $N_2$  and  $10 \text{ mL}\cdot\text{min}^{-1}$   $O_2$  flow to the cathode. Only  $H_2$  was humidified. The shape of the polarization plots of the MEA cell was similar to that of a standard fuel cell, demonstrating that the system can stably produce electricity by  $H_2$  and  $O_2$  gases. From Fig. 2, working voltage of the

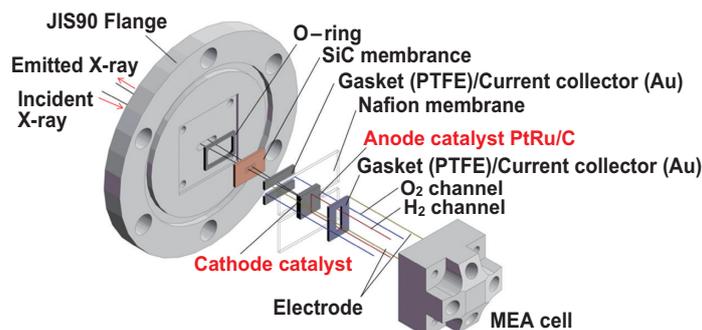


Fig. 1. Schematic view of the MEA cell for *operando* SXE measurements.

fuel cell was selected to 0.4 V. Also, 1.0 V, which is slightly above the open circuit voltage was chosen for SXE measurements.

The excitation energy for Fe 2p SXE was tuned to the Fe  $L_3$  resonance at 710.0 eV. Figure 3 shows a comparison of *operando* Fe 2p SXE spectra of the MEA sample under various gaseous and operating conditions. Broad SXE features appear below an intense elastic line at 710.0 eV, reflecting energy loss due to Fe 3d-related states. The appearance of the energy-loss feature around 1.5 eV below the elastic peak is characteristic for iron species with planar ligand coordination, rather than typical iron oxides having larger *dd* excitation energies. The intensity of the 1.5 eV peak is significantly reduced when N<sub>2</sub> gas in the cathode is replaced by the mixture of N<sub>2</sub> and O<sub>2</sub> gases (lower panel of Fig. 3(b)). This change implies that oxygen may adsorb on an iron site with planar ligand coordination, such as Fe-N<sub>x</sub> embedded into the *sp*<sup>2</sup> carbon network [1] considering the structure of the precursor.

As shown in upper panel of Fig. 3(b), it is noted that the shape of the Fe 2p SXE spectra does not change with the cell voltage under both gas conditions. This result can be explained by either of the following; that the Fe sites in the multi-FePc/PhRs catalyst are not ORR active because they adsorb oxygen too strongly to release oxygen, or the Fe sites are still ORR active where the rate-determining step of ORR is desorption of intermediates (such as H<sub>2</sub>O<sub>2</sub>) and/or reaction product (H<sub>2</sub>O). However, it is difficult to exclude either of the above interpretations only using the present SXE results.

The experimental system developed in this study can also be applied to observe the electronic structure

of solid-gas and solid-liquid interfaces under potential control, such as PEFC anode catalysts, metal-air battery electrodes and lithium-ion battery electrodes.

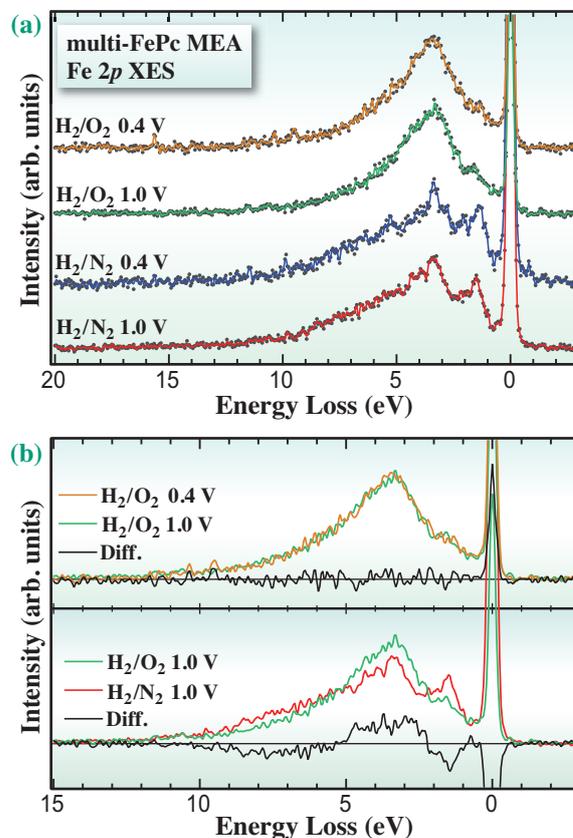


Fig. 3. (a) *Operando* Fe 2p SXE spectra of the multi-FePc/PhRs catalyst. Dotted lines are raw data. Solid lines are smoothed data as an eye guide. (b) Smoothed Fe 2p SXE spectra compared with 1.0 V (lower panel) and the same gas conditions (upper panel). Black solid lines are difference spectra.

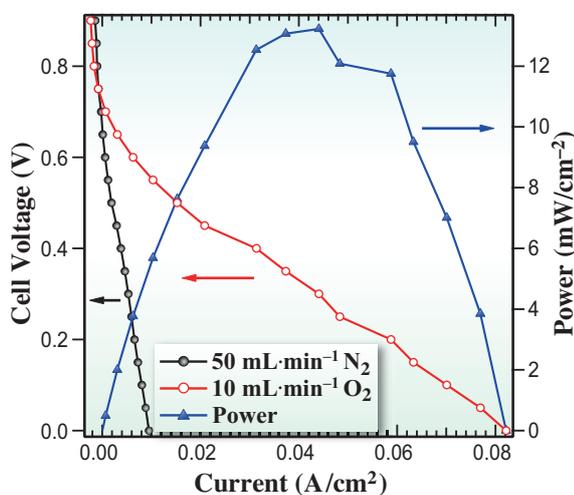


Fig. 2. H<sub>2</sub>-O<sub>2</sub> fuel cell polarization plots.

Hideharu Niwa<sup>a,b,\*</sup>, Yoshihisa Harada<sup>a,b</sup> and Masaharu Oshima<sup>b</sup>

<sup>a</sup>Institute for Solid State Physics, The University of Tokyo  
<sup>b</sup>Synchrotron Radiation Research Organization, The University of Tokyo

\*E-mail: hniwa@issp.u-tokyo.ac.jp

References

- [1] M. Lefèvre *et al.*: Science **324** (2009) 71.
- [2] H. Niwa *et al.*: J. Power Sources **223** (2013) 30.
- [3] H. Niwa, H. Kiuchi, J. Miyawaki, Y. Harada, M. Oshima, Y. Nabaie, T. Aoki: *Electrochem. Commun.* **35** (2013) 57.
- [4] Y. Harada *et al.*: Rev. Sci. Instrum. **83** (2012) 013116.