

## ***In operando* Soft X-ray Emission Spectroscopy of Iron Phthalocyanine-based Oxygen Reduction Catalysts for Polymer Electrolyte Fuel Cells**

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Carbon-based oxygen reduction catalysts show high oxygen reduction reaction (ORR) activity and are expected to be cathode catalysts alternative to Pt for Polymer Electrolyte Fuel Cells (PEFC) [1-3]. The origin of their ORR activity should be elucidated to enhance the activity. We have studied metal phthalocyanine-based catalysts by X-ray photoemission spectroscopy and soft X-ray absorption spectroscopy [4] under vacuum (*ex situ*) condition. However, to further explore the ORR mechanism of carbon-based cathode catalysts, *in operando* observation of the electronic structure in carbon-based cathode catalysts under PEFC working condition is strongly required. In this study, we have developed a vacuum compatible MEA cell for *in operando* soft X-ray emission spectroscopy (XES) to observe the element-specific electronic structure and to elucidate the role of each element in ORR.

A highly ORR active carbon-based cathode catalyst prepared by pyrolyzing a mixture of Fe phthalocyanine and phenolic resin (FePc/PhRs) in a multi-step pyrolysis method [5] was used for the experiment. The loading amount of Fe in the mixture was 3 wt%. First the FePc/PhRs mixture was pyrolyzed at 600 °C under nitrogen gas flow for 5 hours, heat-treated at 800 °C for an extra 1 hour in NH<sub>3</sub> gas, and finally heat-treated at 1000 °C for an extra 1 hour in NH<sub>3</sub>. Thus the multi-step pyrolyzed sample (multi-FePc/PhRs) was synthesized.

The MEA sample was prepared using PtRu/C as an anode catalyst and multi-FePc/PhRs as a cathode catalyst. These catalysts were coated onto Nafion 211 membranes. The coated areas of both anode and cathode catalyst layers are about 1 cm<sup>2</sup>.

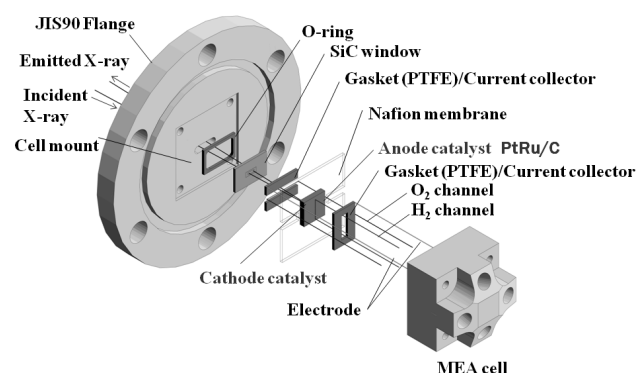
*In operando* XES measurements were performed at BL07LSU in SPring-8 using ultrahigh resolution soft X-ray emission spectrometer [6]. The XES spectra were recorded at room temperature. The total energy resolution is better than 260 meV ( $E/\Delta E > 2700$ ) at detection energy  $E = 710$  eV.

Figure 1 shows a schematic view of the MEA cell system for *in operando* XES. The vacuum condition for soft X-rays is separated by a 150 nm-thick SiC membrane from MEA and other components in the atmosphere. The electric potential between the anode and cathode electrodes can be manipulated by Potentio/Galvanostat without significant electrical noise.

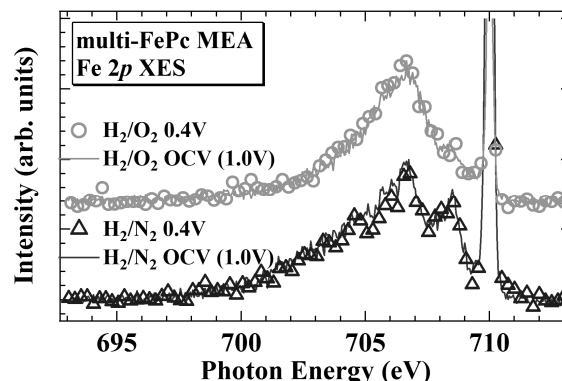
Figure 2 shows *in operando* Fe 2*p* XES spectra of the multi-FePc/PhRs catalyst. The peak intensity at around 709 eV was significantly reduced when N<sub>2</sub> gas in the cathode was replaced by O<sub>2</sub> gas. This change directly

indicates oxygen adsorption to iron and a charge transfer from Fe 3*d* to the  $\pi^*$  state of the adsorbed oxygen. This is a quite unexpected result since the FePc/PhRs catalyst powder pyrolyzed above 800 °C is usually metallic and does not adsorb oxygen [7]. When pyrolyzed in a multi-step way and/or mixed with Nafion, however, oxidized Fe species such as Fe-N<sub>x</sub> in the  $sp^2$  carbon network may exist and adsorb oxygen species. It should be also noted that the shape of Fe 2*p* XES spectra does not change with the cathode voltage, i.e. at OCV (1.0V) and at 0.4V under both gas conditions. This can be explained in either way; 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 ORR active sites where the rate-determining step of ORR is desorption of intermediates (such as H<sub>2</sub>O<sub>2</sub>) and/or product (H<sub>2</sub>O).

In summary, we have performed *in operando* XES of carbon-based cathode catalysts for PEFC under the control of electric potential and gas condition. To further discuss the ORR active site, *in operando* XES of light elements such as nitrogen is required.



**Figure 1.** Schematic view of the MEA cell for *in operando* XES measurements.



**Figure 2.** *In operando* Fe 2*p* XES spectra of the multi-FePc/PhRs catalyst.

### References

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