

***In situ and operando* soft X-ray emission spectroscopy of non-Pt fuel cell catalysts**

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Polymer electrolyte fuel cells (PEFCs) have attracted much attention in terms of applications in fuel cell vehicles and combined heat and power systems due to their high energy conversion efficiency. Carbon-based oxygen reduction catalysts show high oxygen reduction reaction (ORR) activities and are expected to be cathode catalyst alternative to conventional Pt catalysts for PEFCs. The origin of their ORR activity should be clarified to enhance the activity.

We have developed a vacuum compatible fuel cell cell for *in situ/operando* soft X-ray emission spectroscopy (XES) [1]. XES 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. Despite the above potential advantages, very few experimental results using XES under *in situ/operando* conditions have ever been reported, possibly due to the difficulty in the use of vacuum compatible soft X-rays.

Iron phthalocyanine (FePc) ink was used for *in situ* experiment under atmospheric gas condition and carbon-based cathode catalysts prepared by pyrolyzing a mixture of FePc and phenolic resin were used for *operando* experiment under PEFCs working condition. *In situ/operando* XES measurements were performed at BL07LSU in SPring-8 using ultrahigh resolution soft X-ray emission spectrometer [2].

In situ Fe 2*p* XES spectra of FePc under atmospheric O₂ and Ar gas conditions showed clearly different energy loss features. This spectral change directly indicates oxygen adsorption to iron and a charge transfer between Fe 3*d* of FePc and the π* state of adsorbed O₂. From *operando* Fe 2*p* XES spectra of FePc-based catalysts obtained at 1.0 V, it is found that an oxidized iron sites such as Fe-N_x sites exist and are active for oxygen adsorption, which is not expected from *ex situ* results in which metallic iron sites dominate. Detailed results and their ORR mechanism will be discussed.

References

- [1] H. Niwa et al., *Electrochem. Commun.* 35, 57 (2013).
- [2] Y. Harada *et al.*, *Rev. Sci. Instrum.* 83, 013116 (2012).

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