

In Situ Soft X-ray Emission Spectroscopy of Carbon-based Oxygen Reduction Catalysts under Ambient Pressure

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Recently, fuel cells have attracted much attention as a clean energy storage system with the potential to solve the world's energy problems. In particular, polymer electrolyte fuel cells (PEFCs) are expected to be promising power sources of high efficiency, low operating temperature, and low pollution for transportation and residential applications. Conventionally, Pt, which is expensive and its resource is limited, has been used as a catalyst for slow oxygen reduction reaction (ORR) on cathode of PEFCs. Alternative to Pt for PEFCs, carbon-based catalysts show high ORR activities and are expected to be cathode catalysts [1-3]. The origin of their ORR activities should be elucidated to further enhance the activities.

We have studied metal phthalocyanine-based catalysts by X-ray photoemission spectroscopy [4] and soft X-ray absorption spectroscopy [5] under vacuum (*ex situ*) condition. However, *in situ* observation of electronic structure of the catalysts under ambient gas or under electrochemical potential environment is strongly desired to explore the ORR active mechanism of the catalysts. A lot of *in situ* measurements of Pt catalysts using hard X-ray source have been reported [6] due to relatively simple experimental setup and long attenuation length of hard X-rays, while it is difficult to analyze carbon-based catalysts by hard X-rays because core levels of the light elements such as C, N and O are in the soft X-ray region. However, using thin membrane which separates high vacuum environment and the sample, it is now feasible to perform *in situ* soft X-ray experiments for the electronic structure study of light elements [7]. In addition, soft X-ray region covers the *L*-edges of 3*d* metals such as Fe or Co. Therefore, soft X-ray emission spectroscopy (XES) is one of the most powerful methods to investigate the valence electronic states of carbon-based catalysts derived from 3*d* metal containing precursors under ambient environment.

In this study, we have fabricated an *in situ* sample cell for XES of carbon-based catalysts. Electronic structure of the catalysts before and after O₂ adsorption to the catalysts, which is the first step of ORR, was investigated using ultrahigh resolution soft x-ray emission spectrometer installed at BL07LSU in SPring-8 [8]. The XES spectra were recorded at room temperature. Total energy resolving power is more than $E/\Delta E > 2700$ ($E < 260$ meV) at 710 eV.

Carbon-based catalysts were derived from the mixture of Iron phthalocyanine (FePc) and phenolic resin by pyrolyzing at 600 °C or 800 °C in inert gas (Fe600 and Fe800, respectively). Electrochemical measurements under oxygen saturated H₂SO₄ solution

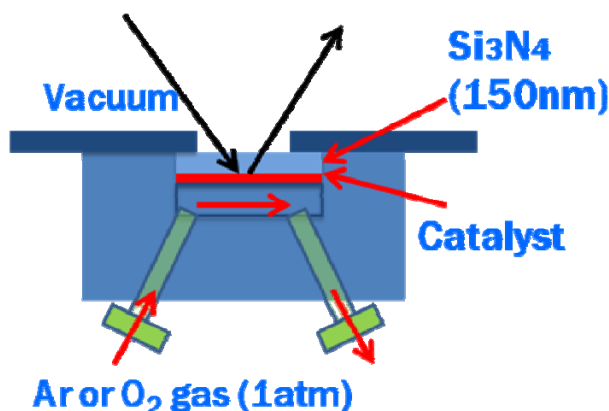


Figure 1. Schematic of *in situ* cell for XES.

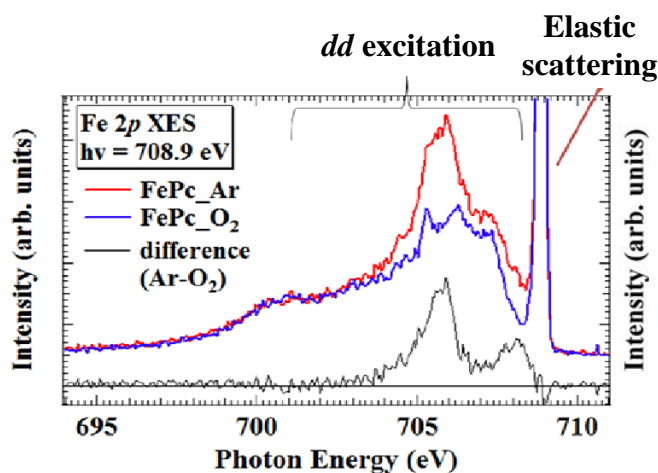


Figure 2. *In situ* XES spectra of FePc.

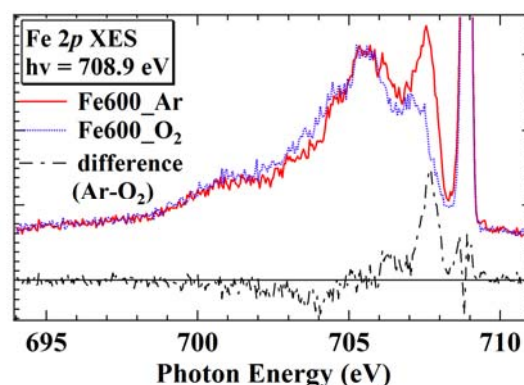


Figure 3. *In situ* XES spectra of Fe600.

demonstrated both Fe600 and Fe800 have better ORR activity than the precursor FePc.

Figure 1 shows a schematic of the *in situ* cell for XES measurements. A thin Si_3N_4 membrane (150 nm) separates vacuum condition from the atmospheric environment. Ink catalysts as mixture of the catalysts and Nafion ionomer were coated on the surface of Si_3N_4 membrane by drop casting technique. 1 atm Ar or O_2 gas was introduced via channel during XES measurements.

Figure 2 shows Fe 2*p* XES spectra of the precursor FePc. Incident photon energy is 708.9 eV, which corresponds to Fe 2*p*-3*d* resonances of FePc. The XES spectrum obtained under Ar atmosphere has two features. One is the narrow elastic scattering and the other is *dd* excitation. Comparing the XES spectra obtained under Ar and O_2 atmosphere, it is found that the intensity of the *dd* excitation is decreased after exposure to oxygen. This directly indicates the presence of charge transfer from *d*-electron of Fe to π^* orbital of adsorbed oxygen, namely, back donation process. The oxygen adsorption occurs at Fe- N_4 site in the center of the FePc molecule.

Figure 3 shows Fe 2*p* XES spectra of Fe600. The spectrum of Fe600 is different from the precursor FePc, indicating Fe in the Fe600 is modified after pyrolysis. As in the case of FePc, *dd* excitation is decreased after exposure to oxygen. The difference spectrum in Fig. 3 shows a different profile compared to FePc, indicating that O_2 adsorption site of Fe600 is different from FePc. Therefore, other types of Fe sites such as FeN_x site in carbon network [3] should be responsible for O_2 adsorption in Fe600. On the other hand, the profile of Fe 2*p* XES spectra of Fe800 does not change after oxygen exposure. Therefore, oxygen molecule does not adsorb on any Fe sites of Fe800. It follows that light elements composed of carbon, nitrogen and so on should be responsible for oxygen adsorption in Fe800.

In conclusion, several O_2 adsorption sites as the first step of ORR have been investigated by *in situ* XES. In the future, *in situ* N 1*s* XES should be measured to confirm the active site which is composed of light elements.

References

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