

Observation of Electronic State Related to Fe Bonding in Fe-N-C Catalyst by X-ray Emission Spectroscopy

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Oxygen reduction reaction (ORR) on cathode catalyst is an important electrochemical reaction related to fuel cell performance. Fe-N-C catalysts are well known as non-noble cathode catalysts, and their active sites have been discussed by X-ray methods such as X-ray absorption fine structure (XAFS) analysis [1]. However, it is difficult for XAFS to distinguish coordination elements of carbon, nitrogen, and oxygen atoms around Fe. To solve this problem, we have employed a method of the valence-to-core X-ray emission spectroscopy (XES) that is known as a method of the observation of electronic state related to ligands around an absorption atom. $K\beta''$ and $K\beta_{2,5}$ emission specially reflect ligand information because of transition from ligand ns and np to metal $1s$ [2]. In this work, we have observed $K\beta$ emission to investigate the electronic state of several real catalysts having Fe-N-C structures. Then, we will show better indexes to develop Fe-N-C catalysts based on the information on the electronic state related to Fe-bonding obtained by XES.

XES was carried out at BL11XU in SPring-8. Incident X-ray from undulator was monochromatized by double crystal monochromators made of Si (111), and its energy was fixed at 8100 eV, which is about 1000 eV above the Fe K-edge. The energy of $K\beta$ emission X-rays from the pelletized sample was analyzed by three focusing crystals with Ge (620), and was detected using PILATUS located on the Rowland circle. As-prepared catalysts were Fe-PpmA, Fe-Ncb, Fe-AAPy and Fe-Phen made from pipemidic acid, nicarbazin, aminoantipyrine, and phenanthroline precursors, respectively. In measurement of the reference samples, the incident and emission angles were set at 80° and 10° measured from the sample surface, respectively. In the case of *in situ* measurement, Fe-PpmA sprayed on the carbon paper was placed at the carbon electrode as a working electrode in 1 M KOH. Both the incident and emission angles were 45° .

Carbon steel, iron nitride and iron oxides have $K\beta''$ peak assigned as Fe-C (at 7099 eV), Fe-N (at 7094 eV) and Fe-O (at 7092 eV). In particular, the energy position of $K\beta''$ peak in iron oxides was found to be almost the same each other. This indicates the $K\beta''$ is insensitive to oxidation states of Fe and structures, and is sensitive to a kind of ligands. Moreover, potassium ferrocyanide (II) and potassium ferricyanide (III) have broad $K\beta''$ peak at 7092 eV, which is close to the energy of $K\beta''$ of Fe-O although they have no oxygen atom. This peak is considered as transition from hybridized orbital of CN $2s2s \sigma$ to Fe- $1s$ state [3]. $K\beta''$ peak position of Fe-CN is lower than that of Fe-N, which is affected by hybridization. Phthalocyanine iron (II) have also broad $K\beta''$ peak between Fe-N and Fe-O position at 7093 eV. This peak could be caused by a transition from hybridized orbital of NC $2s2s \sigma$, the same as Fe-CN. Fe-PpmA have stronger

K β '' peak at Fe-N-C than Fe-AAPyr. This result indicates Fe-PpmA have more Fe-N-C structures than Fe-AAPyr. Details of catalysts, K $\beta_{2,5}$ and *in situ* experiment will be discussed in the presentation.

In summary, we demonstrate XES is a powerful method for observation of electronic states related to ligand bonding with metals. Coordination elements of carbon, nitrogen, and oxygen atoms around Fe can be distinguished, and we have found that Fe-N-C structures in real catalyst can be observed from K β '' peak.

[1] U. Tylus, et al., *Journal of Physical Chemistry C*, 118, 8999 (2014)

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[3] E. R. Hall, et al., *Journal of the American Chemistry*, 136, 10076 (2014)

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