

In Situ XAFS investigation of iron hydrous oxide in alkaline solution

Sunghyun KIM*¹, Hyukjae CHOI¹, Jae-Woo KIM², Su-Moon PARK², Toshiaki OHTA³

¹Department of Chemistry, Konkuk University, Seoul 143-701, Korea

²Department of Chemistry, Pohang University of Science and Technology, Pohang 790-784, Korea

³Department of Chemistry, School of Science, The University of Tokyo, Tokyo 113-0033, Japan

Introduction

Transition metal oxides play an important role in the field such as batteries, electrochromic displays, and electrocatalysis. Thus the structural elucidation is of importance to understand the system better. The XAFS study has mostly been centred on the nickel (hydr)oxide and additives. For example, it is well known that cobalt improves the charge acceptance of the nickel electrode in alkaline media, thus offering higher battery performance [1]. The role and structural aspects of cobalt both in nickel hydroxide lattice and in pure cobalt hydroxide systems have been thoroughly studied as a function of the oxidation states of Ni and Co [2].

The study of iron (hydr)oxide system is technologically important in that it is closely related to corrosion process or Fe/Ni, Fe/air battery systems. Electrochemically iron undergoes quite complex redox state changes and phase transformations. It is rather surprising that while synthesis and chemical conversion between iron oxides have been well established, the structural behavior of iron oxides is poorly understood.

Experimental

All the experiments was carried out *in situ* in a fluorescence mode using a cell developed by Kim et al., where the carbon sheet can serve as a working electrode as well as a window. Iron hydrous oxide was deposited onto the carbon surface by passing -5 mA for 10 min through the ferric nitrate containing solution, which causes OH⁻ near the surface, leading to iron hydroxide precipitate on the electrode surface. Before the XAFS measurements, cyclic voltammetry was performed to confirm the electrochemical behaviour. Iron hydrous oxide exhibits two main redox peaks corresponding to Fe²⁺ and Fe³⁺ whose potential was separated by ca. 350 mV. Potential was fixed where iron existed as +2, +3. To get the intermediate oxidation states, potential was scanned from the +2 state to the rising position of a voltammogram and came back to the +2 state. For the identification of electrochemically prepared iron species, iron(II) and iron (III) (hydr)oxides were prepared by adding ammonia to the solution containing FeSO₄ and Fe(NO₃)₃, respectively.

Results and Discussion

FeOOH samples from our lab (curve a) and Aldrich (curve b) show almost identical XANES spectra (Figure 1). A distinct pre-edge peak at 7114.1 eV is the indication of 1s → 3d transition, showing the symmetry around Fe is not hexagonal but little distorted. The similar behavior

has been observed for NiOOH. Iron(II) species shows very different XANES (curve c) in which a rather broad pre-edge peak appeared at 7112.8 eV and the edge position at $\mu = 0.5$ shifts considerably from 7123.2 eV to 7119.0 eV. The pre-edge shift approximately follows the rule that +1 oxidation change gives rise to ca. 1 eV. The absorption edge shift is usually much larger than that of a pre-edge. Notable is the highly increased white line intensity for iron(II) species, which is tentatively assigned as Fe(OH)₂. FT analysis shows d(Fe-O) at 1.474, and 1.572 Å for FeOOH (Aldrich) and Fe(OH)₂, respectively, showing the lattice contraction by oxidation.

Curves d to g are *in situ* XANES as a function of potential. The absorption edge gradually moves to the higher energy as the oxidation number increases. $E_{\mu=0.5} = 4.6$ eV indicates that the whole iron (II) state was converted to iron (III) state. This is in contrast to the case of cobalt, where only part of cobalt species undergoes oxidation state change. There are at least two isosbestic points (7131.1 and 7178.5 eV), indicating that only two principal species exist.

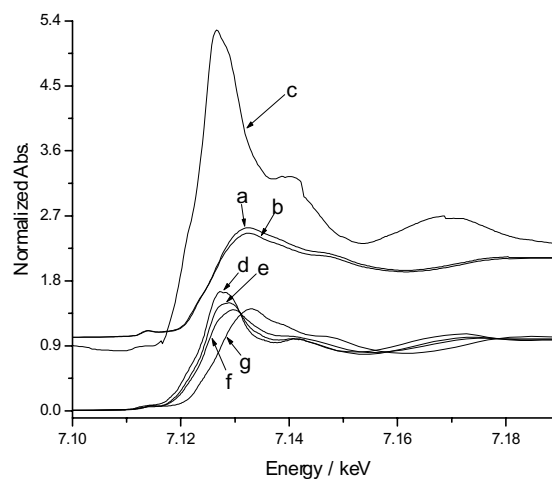


Figure 1. XANES spectra of FeOOH prepared in the lab (a) and from Aldrich (b), and Fe(OH)₂ (c). Curves d to g are *in situ* spectra obtained by sequentially polarizing the electrode from +2 (d) to +3 (g) state of iron.

References

- [1] S. Kim et al., J. Phys. Chem. **98**, 10269 (1994).
- [2] D. Totir et al. J. Electrochem. Soc. **147**, 4594 (2000).

* skim100@konkuk.ac.kr