

XAFS characterization for Cu-Fe alloy NRR electrocatalysts

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1 Introduction

The electrochemical N_2 reduction reaction (NRR) is one of the promising alternatives to generate ammonia under ambient condition. The electricity for the reaction can be provided by renewable source like solar or wind energy and it uses H_2O as the hydrogen source instead of gaseous hydrogen, indicating it is a cleaner and safer method. However, the relatively low yield of ammonia and Faradaic efficiency (FE) of NRR restricts the further application [1,2]. There are two reasons for such disadvantages. One reason is that the bond energy of nitrogen molecular (N_2) is so high that it is difficult to break under ambient condition. Another reason is the competition of hydrogen evolution reaction (HER). In order to overcome these disadvantages, we aim to develop binary alloy catalyst. XAFS analysis was adopted as a characterization method. We have prepared Cu-Fe alloy catalyst and achieved EXAFS measurements with various relative ratios.

2 Experiment

Alloy catalyst Cu_1Fe_2 sample was prepared by a wet chemical method, where mixture of aqueous solutions of precursor nitrate salts are mixed and reduced with N_2H_4 in a Teflon autoclave at 120 °C for 6 hours. Extended X-ray absorption fine structure (EXAFS) measurements at the Cu-K edge and Fe-K edge were carried out in transmission mode at room temperature at the BL9C station of the Photon Factory at the Institute of Materials Structure Science, High Energy Accelerator Research Organization in Japan (KEK-IMSS-PF). The electron storage ring was operated at 2.5 GeV. EXAFS data were analyzed and fitted using Athena and Artemis package based on IFFEFFIT program Backscattering amplitude, and phase shift were obtained by FEFF calculation.

3 Results and Discussion

Fig. 1 show the observed and fitted data for Fourier transforms of (a) Cu K-edge and (b) Fe K-edge EXAFS for Cu_1Fe_2 alloy sample. The NRR activity for this sample was best among prepared alloy samples; NH_3 yield rate $50 \mu g \cdot h^{-1} \cdot mg_{cat}^{-1}$ and Faradaic Efficiency 20 %.

Cu K-edge EXAFS and Fe K-edge EXAFS spectra were analyzed and it was found that the sample consisted of Cu-Fe alloy component (Cu-Fe distance of 0.26 nm) covered with oxide phase. Cu K-edge insitu XANES spectra were measured during electro-catalytic reaction and found that surface oxide phase was reduced during the reaction.

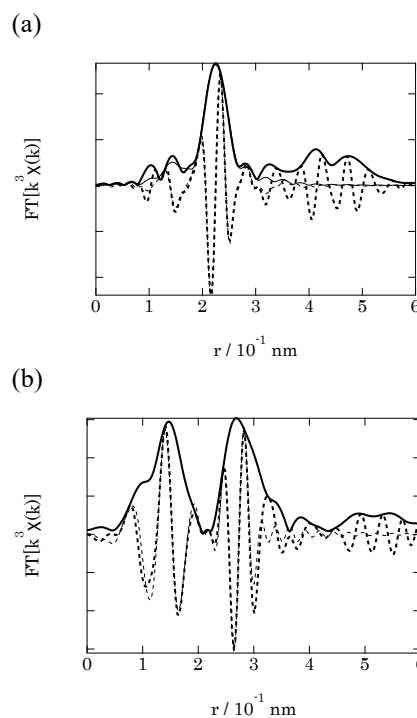


Fig. 1 Observed and fitted data for Fourier transforms of (a) Cu K-edge and (b) Fe K-edge EXAFS for Cu-2Fe alloy sample. (Amplitude (solid curve) and imaginary part (dotted curve), thick curve (observed) and thin curve (fitted)).

Table 1: Summary of the EXAFS fitting results

Edge	Path	R (10^{-1} nm)	CN	DW (10^{-5} nm ²)	ΔE_0 (eV)	R _i (%)
Cu K	Cu-O	1.915±0.029	6.6±0.9	13.1±4.1	5.1±3.7	0.4
Cu K	Cu-Fe	2.559±0.013	4.4±0.7	6.7±1.0		
Cu K	Cu-Cu	2.982±0.098	8.1±2.7	7.3±0.7		

^a Fitting was conducted in the range Δk : 3–13.5 (10^{-1} nm) and ΔR : 1.2–3.0 (10^{-1} nm). Amplitude reducing factor $So^2 = 0.95$

References

- [1] H. D. Yang et al., *ACS Energy Lett.* 2018, 3, 1219–1224.
 [2] L. Zhang, et al., *Adv. Mater.* 2018, 30, 1800191.

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