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XAFS characterization for alloy electrocatalysts

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1 Introduction

By electrolytic reduction, it is possible to convert carbon dioxide into useful organic compounds such as methane, formic acid and C_2H_4 using Cu-based electrodes as working electrode [1]. In order to enhance its practicality, it is necessary to enhance product selectivity, Faraday efficiency, and durability by developing alloy catalysts. Therefore, we aim to develop an electrode catalyst with high selectivity for methane and hydrocarbons by developing a carbon-supported metal catalyst, a binary alloy catalyst, and in situ measurement (EXAFS measurement) will be conducted for characterizing catalysts. We have prepared Cu-Ni, Cu-Zn, and Cu-Pd alloy catalysts with various relative ratios.

2 Experiment

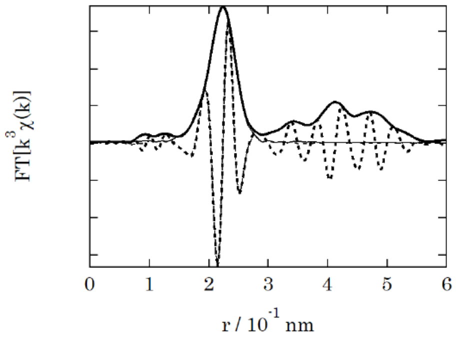
Alloy catalysts were prepared by a wet chemical method, where mixture of aqueous solutions of precursor nitrate salts are mixed and reduced with N_2H_4 in a Teflon autoclave at 120 ℃ for 6 hours. Extended X-ray absorption fine structure (EXAFS) measurements at the Cu-K edge were carried out in transmission 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. A Si(111) channel-cut crystal was used as a monochromator. Ionization chambers for incident X-rays (I_0) and transmitted X-rays (I) were filled with N_2(100%) and 25%Ar/N_2 gas, respectively. 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) Ni K-edge EXAFS for Cu-Ni alloy sample with 1:1 relative ratio. (Amplitude (solid curve) and imaginary part (dotted curve), thick curve (observed) and thin curve (fitted)). These spectra can be fitted with Cu-Ni path and Ni-Cu path, respectively, with good R factors, indicating that Cu and Ni atoms are mixed well.

We are preparing an in situ XAFS cell for measuring XAFS spectra for catalysts dispersed on a carbon paper as a working electrode in a H-type electrochemical cell in which CO_2RR is conducted.

(a)



(b)

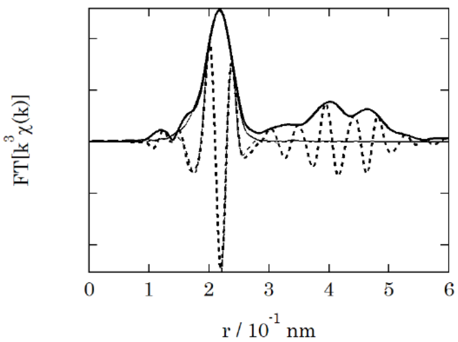


Fig. 1 Observed and fitted data for Fourier transforms of (a) Cu K-edge and (b) Ni K-edge EXAFS for Cu-Ni alloy sample. (Amplitude (solid curve) and imaginary part (dotted curve), thick curve (observed) and thin curve (fitted)).

Table 1: Summary of the EXAFS fitting results for the Cu-Ni alloy sample

Edge	Path	R (10^{-1} nm)	CN	DW (10^{-5} nm^2)	ΔE_0 (eV)	R_f (%)
Cu K	Cu-Ni	2.541±0.003	8.3±0.4	4.2±0.6	6.0±0.6	0.5
Ni K	Ni-Cu	2.479±0.005	6.9±0.3	9.8±0.6	-11.4±1.0	0.5

[a] Fitting was conducted in the range Δk: 3–12 (10^{-1} nm) and ΔR: 1.0–2.8 (10^{-1} nm). Amplitude reducing factor S_0^2 = 0.88 (Cu) and 0.80 (Ni)

References

[1] Y. Hori *et al*., *Journal of the Chemical Society-Faraday Transactions I,* **85**, 2309 (1989).

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