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Operando Ni K-edge XAS of Surface-Alloyed Ni–Cu Nanowires for Electrochemical Nitrate Reduction to Ammonia

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1 Introduction

Electrochemical nitrate reduction reaction (NO_3RR) has attracted considerable attention as an alternative route for sustainable ammonia synthesis using renewable energy, compared to the Haber–Bosch process. Cu-based catalysts exhibit high activity for NO_3RR. In our previous operando Cu K-edge X-ray absorption spectroscopy (XAS) study, Cu_2O microcrystals were found to undergo gradual reduction to metallic Cu during NO_3RR, demonstrating that Cu dynamically changes its oxidation state under reaction conditions.[1]

Building on this finding, the present study investigates surface-alloyed Ni–Cu nanowires (Ni–Cu NWs), in which dilute Ni species are incorporated into the surface of Cu nanowires (Cu NWs) while preserving the nanostructured morphology. Unlike bulk alloys, both Cu and Ni are directly exposed at the catalyst–electrolyte interface. The chemical state of the surface Ni species has not been clarified in previous studies.[2–3]

The dilute surface Ni atoms are expected to undergo reversible oxidation and reduction under alkaline reaction conditions. Therefore, operando Ni K-edge XAS was employed to monitor the changes in the Ni oxidation state and provide insight into the dynamic behavior of surface Ni species associated with the enhanced ammonia production of surface-alloyed Ni–Cu nanowire catalysts.

2 Experiment

Ni K-edge XAS measurements were performed at beamline BL-9C of the Photon Factory (KEK, Japan). Monochromatic X-rays were obtained using a Si(111) double-crystal monochromator. Operando XAS spectra were collected in fluorescence mode, whereas Ni foil, NiO, and $Ni(OH)_2$ reference spectra were recorded in transmission mode. All measurements were performed in step-scan mode.

Surface-alloyed Ni–Cu NWs (approximately 2 mg cm^{-2}) were prepared by electrochemical anodization of Cu_2O on carbon paper[1] to form $Cu(OH)_2$ nanowires, followed by immersion in an aqueous $NiCl_2$ solution for 24 h. The precursor was heat-treated under Ar and subsequently reduced in H_2 at 200 °C for 2 h each to obtain polycrystalline Ni–Cu NWs containing 1.40 at% Ni as determined by XRF.

The catalyst electrode (geometrical area: 3.6 cm^2) was used in a custom-built operando cell containing 20 mL of 0.1 M $NaNO_3$ and 1 M NaOH. An Hg/HgO electrode (+0.12 V vs. SHE) and a Pt wire served as the reference and counter electrodes, respectively. The applied potentials were referenced to the reversible hydrogen electrode (RHE) scale using the Nernst equation.

Operando XAS measurements were conducted sequentially in the dry state, at open-circuit potential (OCP), at 0 V, and at −0.5 V vs. RHE. Each condition was maintained for 40 min, and XAS acquisition began after 10 min of stabilization.

3 Results and Discussion

Incorporation of dilute Ni species significantly improved NO_3RR performance compared with Cu NWs (Fig. 1a). The surface-alloyed Ni–Cu NWs exhibited a higher cathodic current density and a markedly improved Faradaic efficiency toward NH_3 formation, accompanied by a lower NO_2^- yield, indicating that Ni promotes the subsequent reduction of nitrogen-containing intermediates after nitrate activation.[2–3]

Structural characterization confirmed the successful preparation of Ni–Cu NWs (Fig. 1b). XRD showed only a slight shift of the Cu diffraction peaks after Ni incorporation without the appearance of additional diffraction peaks corresponding to metallic Ni or nickel oxides, indicating that the bulk structure remained predominantly composed of Cu. XPS analysis revealed that the catalyst surface consisted mainly of oxidized Ni species together with a small metallic Ni component. Following Ar sputtering in the XPS chamber, the metallic Ni contribution increased while the overall Ni atomic concentration decreased from 1.73 to 1.41 at%, suggesting that Ni is enriched near the catalyst surface. FE–SEM and STEM–EDS elemental mapping further confirmed the preservation of the nanowire morphology and the homogeneous distribution of dilute Ni throughout the Cu NWs. These characterization results support the formation of a dilute surface-alloyed Ni–Cu catalyst without segregated Ni phases.

Because the Ni species are highly dispersed and directly exposed at the catalyst surface, their chemical state is expected to respond sensitively to the environment. Therefore, operando Ni K-edge XAS measurements were performed to directly monitor changes in the Ni oxidation state during NO_3RR. Operando Ni K-edge XAS was carried out to investigate the changes in the Ni state under reaction conditions (Fig. 1c). Linear combination fitting (LCF) of the XANES spectra using Ni foil and $Ni(OH)_2$ reference spectra revealed that the dry catalyst contained approximately 49.0% metallic Ni. Upon immersion in the alkaline nitrate electrolyte at OCP, the metallic Ni fraction decreased to 28.3%, while the Ni^{2+} fraction increased to

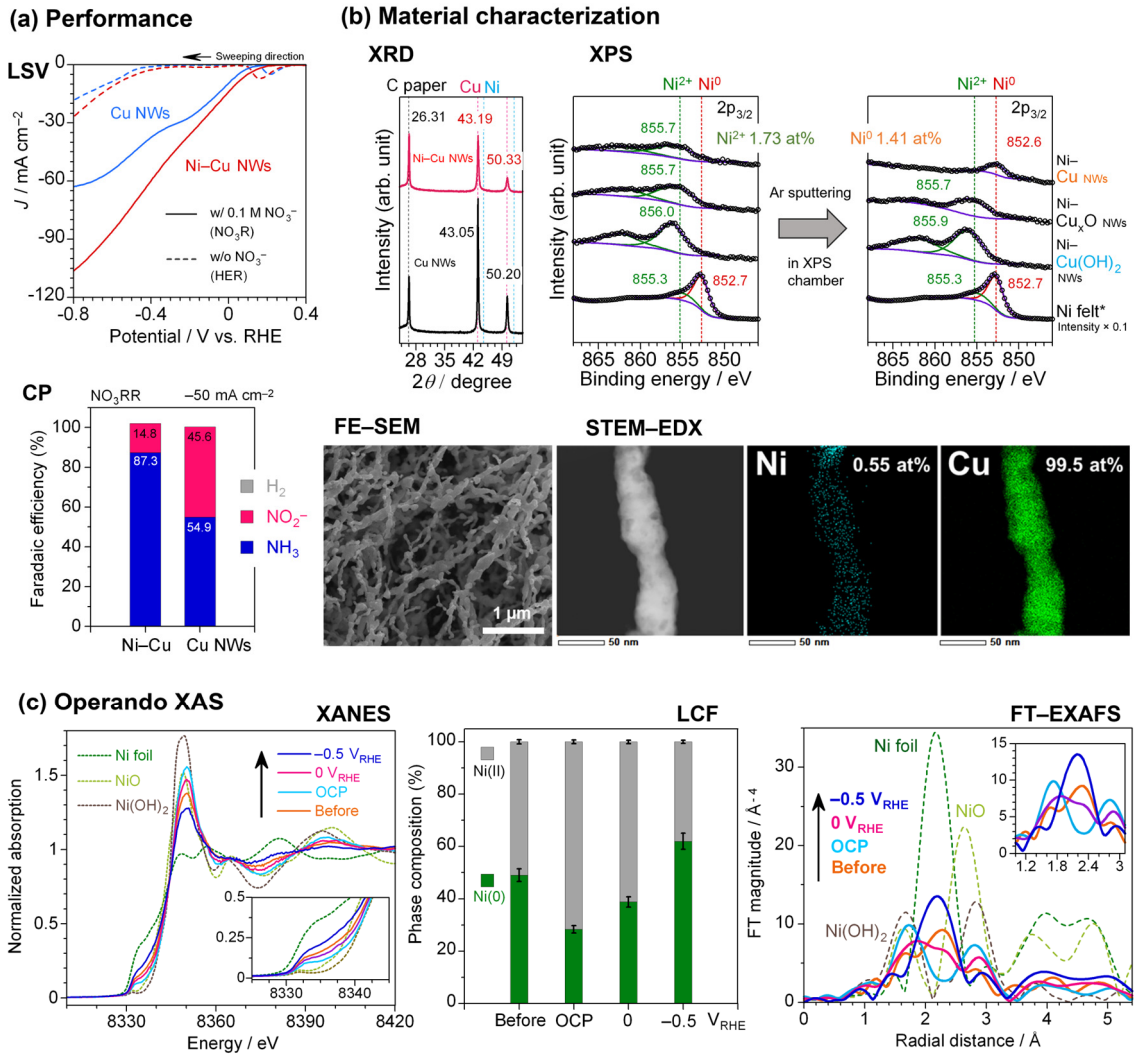

Fig. 1: (a) Linear sweep voltammograms (LSVs) of Cu NWs and Ni–Cu NWs in 0.1 M $NaNO_3$ and NaOH, and Faradaic efficiencies for NO_3RR obtained by chronopotentiometry (CP) at −50 mA cm^{-2}. (b) Structural characterization of the Ni–Cu NWs by XRD, XPS, FE–SEM, and STEM–EDS. (c) Operando Ni K-edge XAS analysis of Ni–Cu NWs during NO_3RR, including XANES, LCF, and FT-EXAFS under dry, OCP, 0 V, and −0.5 V vs. RHE conditions.

71.7%, indicating rapid oxidation of the surface Ni species. When applying cathodic potentials, the metallic Ni fraction gradually recovered to 38.8% at 0 V vs. RHE and further increased to 62.0% at −0.5 V vs. RHE, demonstrating the reversible redox changes of the surface Ni species during NO_3RR.

The Fourier-transformed EXAFS (FT-EXAFS) spectra exhibited both metallic and oxide coordination features throughout the operando measurements. The metallic coordination peak appeared at a radial distance similar to that of Ni foil, while its peak amplitude remained substantially lower than that of bulk metallic Ni. Because Ni and Cu possess similar atomic numbers and backscattering properties, FT-EXAFS alone cannot distinguish between Ni–Ni and Ni–Cu coordination environments. Nevertheless, the suppressed metallic peak amplitude, together with the STEM–EDS results, is consistent with highly dispersed Ni species incorporated into the Cu surface rather than the formation of Ni particles.

Operando Ni K-edge XAS provides direct evidence for the dynamic evolution of the Ni state under realistic reaction conditions. The dilute surface-alloyed Ni species remain in a mixed-valence state and undergo reversible redox changes throughout the reaction. These findings complement our previous Cu K-edge study, in which surface Cu_2O was gradually reduced to metallic Cu during NO_3RR,[1] and provide a more comprehensive understanding of the dynamic behavior in surface-alloyed Ni–Cu catalysts during electrochemical NO_3RR.

References

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