

Operando XAS Study of the Structure Evolution on Co-N-C catalyst for Electrocatalytic CO₂ Reduction Reaction

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1 Introduction

Electrochemical CO₂ reduction reaction (CO₂RR) represents a promising pathway for generating carbon-based resources and fuels such as CO, CH₄, C₂₊ hydrocarbons, and so on.^[1] However, CO₂RR electrocatalysts show low activities in acidic electrolytes due to the high kinetics of H₂ evolution reaction (HER).^[2] Carbon-based metal single-atom catalysts (M-N-C) have been widely reported to produce CO with high selectivity and efficiency in alkaline and neutral electrolytes.^[3] However, they usually have a limited performance in acidic electrolyte. A Co-N-C catalyst,^[4] prepared from the pyrolysis of Co(NO₃)₂, P4VPy (poly 4-vinyl-pyridine) and carbon, showed high CO Faradic efficiency in 0.5 M H₂SO₄ electrolyte. In this work, we aimed to clarify the structure-change-to-activity relationship of the Co-N-C during acidic CO₂RR, mainly using *operando* XAS study under the three-phase catalysis (solid, polymer electrolyte and gas).

2 Experiment

The preparation of Co-N-C catalyst was described elsewhere.^[4] *Operando* XAS measurement was conducted in at BL12C of Photon Factory in the Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK-IMSS-PF) (2.5 GeV, 450 mA). Figure 1 shows the *operando* XAFS cell and its cell. A self-designed XAS cell was used, allowing the spontaneous XAS spectra collection and CO₂ reduction reaction on the catalyst. Membrane Electrode Assembly (MEA) was pressed from Co-P4-A and set in the cell which allows us to carry out the *operando* XAS under CO₂RR under the different potentials (open circuit potential (OCP) to -0.3 V to -0.7 V to OCP). The XAS data were measured in a fluorescence mode using Silicon Drift Detector (SDD) with Fe filter and home-made Soller slit.

3 Results and Discussion

Figure 2 shows the XAS spectra of Co-N-C catalyst under CO₂RR reaction with different applied potential

together with that of the Co-N-C catalyst measured in air. Figure 2(a) bottom show the XANES spectra at the potential from -0.3 V to -0.7 V, and we found the isosbestic point near the second peak (S). Interestingly, when the sample potential was released and returned to OCP, the XANES spectra gradually changed to the original spectra, as shown in Figure 2a middle. Figure 2b presents $k^3\chi(k)$ of the Co-N-C catalyst at different potentials. The spectra at OCP were similar to that of Co-N-C catalyst measured in air. Principle component analysis (PCA), which indicates that the first two main components explained whole the data with different applied potentials.

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References

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Fig. 1 *in situ* XAFS cell.

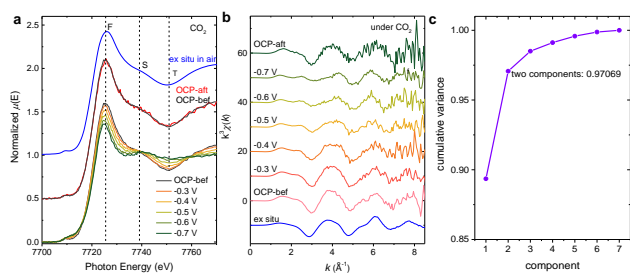


Fig. 2 a) Operando XANES spectra, b) EXAFS spectra and c) PCA result for Co-N-C catalyst during CO₂RR

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