BL-12C/2022G525

Operando XAS Study of the Structure Evolution on Co-N-C catalyst for Electrocatalytic CO_2 Reduction Reaction

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1 Introduction

Electrochemical CO_2 reduction reaction (CO_2RR) represents a promising pathway for generating carbon-based resources and fuels such as CO, CH_4, C_{2+} hydrocarbons, and so on.[1] However, CO_2RR electrocatalysts show low activities in acidic electrolytes due to the high kinetics of H_2 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 $Co(NO_3)_2$, P4VPy(poly 4-vinyl-pyridine) and carbon, showed high CO Faradic efficiency in 0.5 M H_2SO_4 electrolyte. In this work, we aimed to clarify the structure-change-to-activity relationship of the Co-N-C during acidic CO_2RR, 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 CO_2 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 CO_2RR 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 CO_2RR 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.

Acknowledgement

This work was financially supported by NEDO project.

References

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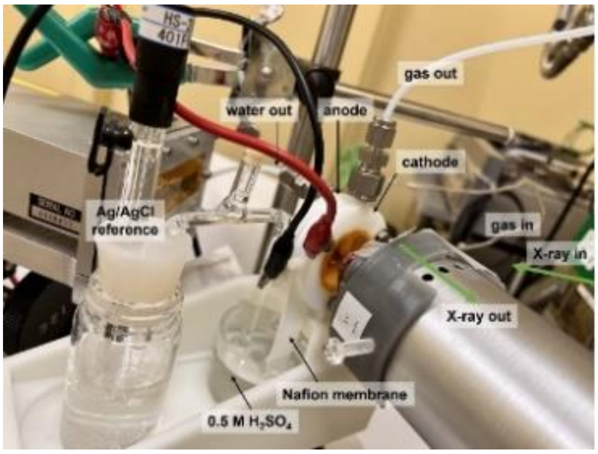

Fig. 1 *in situ* XAFS cell.

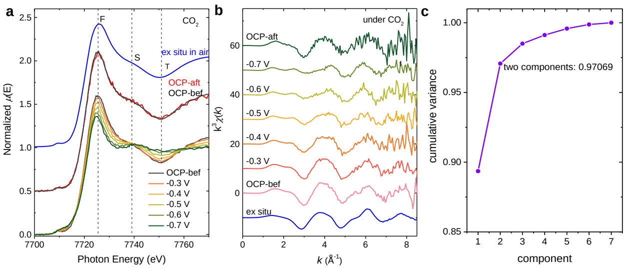

Fig. 2 a) *Operando* XANES spectra, b) EXAFS spectra and c) PCA result for Co-N-C catalyst during CO_2RR