

In-Situ XAFS Analysis for Reduction Process of CuCl₂ on Carbon

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There is an urgent need to develop a battery system with a capacity that greatly exceeds that of conventional lithium-ion batteries to solve the energy demands of modern society. One of the leading candidates is a halogen shuttle-type battery system, which utilizes the chemical state conversion between metal chlorides and metals for the electrode reaction. The CuCl₂/Cu redox couple has a theoretical capacity of 399 mA h g⁻¹ and is expected to become an alternative of current secondary battery materials [1]. Therefore, microscopic analysis of the chemical conversion between CuCl₂ and Cu is necessary for understanding the electrode reaction mechanism and establishing a high-capacity electrode system. In the battery electrode, the active material particles are mixed with carbon as a conductive additive and a binder material is also included. As a reference for analyzing the state change of the Cu species under such conditions, the analysis of the thermochemical conversion process, in which CuCl₂ particles supported on carbon are reduced to metallic Cu particles, is quite useful. In this study, *in-situ* XAFS analysis of the temperature-programmed reduction process of CuCl₂ supported on active carbon (AC) was performed under the H₂ gas atmosphere.

CuCl₂ species was loaded at 40 wt% on AC by the incipient wetness impregnation method with drying at 60 °C. *In-situ* XAFS measurements at the Cu K edge were carried out at BL-3 of the SR Center during the heating process under a He-diluted H₂ flow (10 vol%, 100 cm³ min⁻¹).

The XANES spectral change is given in Fig. 1 during the reduction process of CuCl₂/AC. The initial spectrum was consistent with that of dihydrate of CuCl₂, and it was changed to that of anhydrous CuCl₂ at around 75 °C. At above 350 °C, the spectrum almost matched that of metallic copper, indicating that the CuCl₂ particles were reduced by H₂ gas. Fig. 2 shows the change in X-ray absorbance as a function of temperature at 8982 eV, which is the characteristic peak of CuCl, and at 8992 eV, which is the white line peak of CuCl₂. It was clarified that CuCl₂ is reduced to Cu(0) via an intermediate oxidation state, CuCl, which is formed at the temperature around 270 °C. The two-step reduction is consistent with the reactions on silica, whereas the temperature at which CuCl exists is slightly lower on AC than on silica. The results of this study are important as a reference when analyzing electrochemical conversion of CuCl₂.

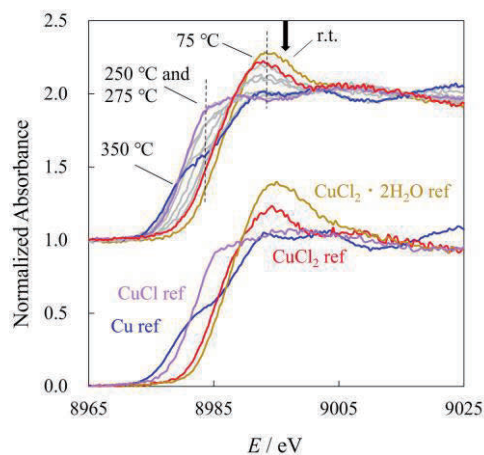


Fig. 1 Observed XANES spectral change during the reduction process under a He-diluted H₂ gas flow for CuCl₂/AC.

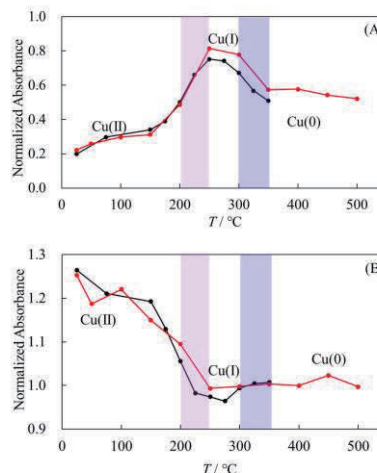


Fig. 2 X-ray absorbance change as a function of temperature at 8982 eV (A) and 8992 eV (B).

References

- [1] S. Dobayashi, K. Hashizaki, H. Yakuma, T. Hirai, J. Yamaki and Z. Ogumi, *J. Electrochem. Soc.*, **2015**, 162, A2747.