Mem. SR Center Ritsumeikan Univ. No. 25, 27 (2023)

XAFS Analysis for Electrochemical Reduction Process of $NiCl_2$ Supported on Active Carbon

Yuki Sugimura, Takuto Nishikawa, Takaya Ishida and Yasuhiro Inada
Department of Applied Chemistry, Faculty of Life Sciences, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu 525-8577, Japan

Halide ion shuttle battery systems are expected as next-generation secondary batteries because they have the potential to surpass the capacity of lithium ion batteries. The electrochemical conversion between metal halides and metals in the electrode composite is the essence of the battery system. Evaluating the relationship between the change in chemical state of metal halides and the charge/discharge characteristics is important for the development of high-performance battery systems. X-ray absorption fine structure (XAFS) is the most powerful technique to analyze the chemical state of metal species in the solid phase. In the case of elements that have absorption edges in the hard X-ray region, *in situ* chemical state analysis is possible under battery driving conditions. The purpose of this study is to analyze the chemical state of the electrochemical reduction process by using the XAFS method for an electrode with the active material in which nickel chloride species are supported on activated carbon (AC).

$NiCl_2$ species was loaded at 20 wt% on AC by the incipient wetness impregnation method with drying at 80 °C. After vacuum drying at 150 °C and mixing with the binder material, the composite was applied on the Al foil to prepare the $NiCl_2$/AC electrode. The Al-laminated cells consisting of the $NiCl_2$/AC electrode, separator, Li foil counter electrode, and $LiPF_6$ electrolyte solution was fabricated. *In-situ* XAFS measurements at the Ni K edge were carried out at BL-3 of the SR Center for the electrochemical reduction process.

The observed XANES change is given in Fig. 1 during the reduction process of the $NiCl_2$/AC electrode. The initial spectrum, matched to anhydrous $NiCl_2$, changed distinctly as the reduction progressed and finally matched that of metallic Ni supported on AC. The details of the chemical state change of Ni species were analyzed based on the Fourier transform function of EXAFS oscillation given in Fig. 2. The initial Fourier transform function consistent with $NiCl_2$ was unchanged at the beginning of reduction. In the capacity range from 200 to 500 mA h g^{-1}, the function of $NiCl_2$ changed to metallic Ni, and no change was observed in the capacity range thereafter. The expected capacity for the reduction of $NiCl_2$ to metallic Ni is 414 mA h g^{-1}, which corresponds to the capacity range when the change in XAFS was observed. This result provides useful information for establishing a battery system using the $NiCl_2$/Ni pair.

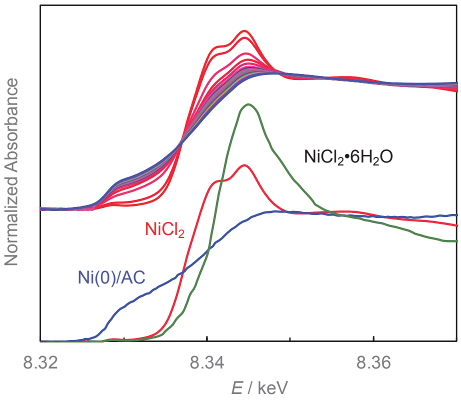

Fig. 1 Observed XANES spectral change during the reduction process of $NiCl_2$/AC electrode.

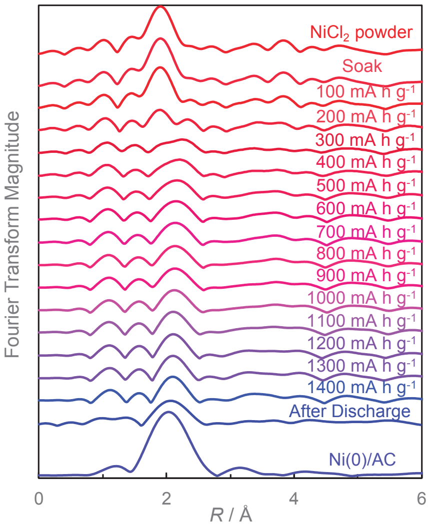

Fig. 2 Change of the Fourier transform magnitudes of the EXAFS oscillation during the reduction process of $NiCl_2$/AC electrode.