

Electrochemical Redox Processes between Nickel Oxide and Metallic Nickel Supported on Carbon

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Redox reactions between NiO and metallic Ni species have a potential to be utilized for next-generation rechargeable batteries. The electrically conductive material such as acetylene black (AB) is necessary to operate the redox reactions, and the particle size of NiO is also an important parameter of the battery performance. We have synthesized the NiO nanoparticle supported on AB using the impregnation method. For a rechargeable battery composed of the NiO/AB cathode and a Li anode, the chemical state of the Ni species have been analyzed using the XAFS method during the discharge and charge processes.

An aqueous solution of $\text{Ni}(\text{NO}_3)_2$ was mixed with AB, and the mixture was dried at 70 °C for 3 days. The obtained powder was calcined at 300 °C for 2 h in air. The obtained NiO/AB powder with the NiO loading of 10 wt% was mixed with polyvinylidene difluoride as the binder, and the mixed slurry diluted with 1-methyl-2-pyrrolidone was applied on a Cu sheet. The electrochemical cell was assembled using the NiO/AB electrode, a Li anode, and 1 mol dm^{-3} LiPF_6 solution dissolved in a mixed solvent of ethylene carbonate and ethyl methyl carbonate. In this study, the discharge process corresponds to the cathode reaction for the NiO/AB electrode. The battery capacity was calculated on the basis of the total weight of NiO and AB. The XANES spectra for the disassembled electrodes were measured at the Ni K edge at BL-4 of SR Center in the fluorescence yield mode.

The discharge-charge profiles for the NiO/AB electrode are shown in Fig. 1. The first discharge process to 0.1 V vs. Li^+/Li showed the large capacity of ca. 900 mA h g^{-1} . The capacity of the following charge process to 3.0 V was 300 mA h g^{-1} , and thus a large irreversible capacity loss was observed at the first cycle. The theoretical capacity for NiO of the prepared electrode is only 72 mA h g^{-1} , and thus the larger capacity especially at the first discharge process may be attributed to the reduction of Li^+ . The XANES spectra (a–d in Fig. 2) of the NiO/AB electrodes at above 0.7 V during the first discharge process clearly demonstrated that the NiO species was maintained. The reduced Ni species was generated after the discharge reaction at 0.1 V (e). The next charge process to 3.0 V regenerated the initial NiO species (f). In the second cycle, the chemical state conversions between NiO and Ni

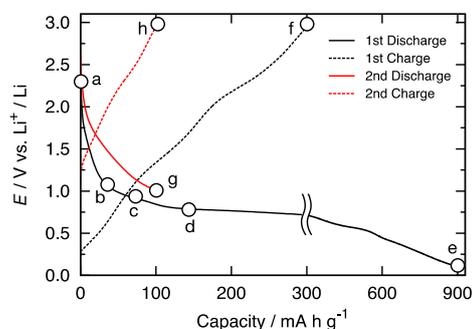


Fig. 1 Discharge-charge profiles of NiO/AB cathode. The electrodes at the circles (a–h) were used for the XANES measurements.

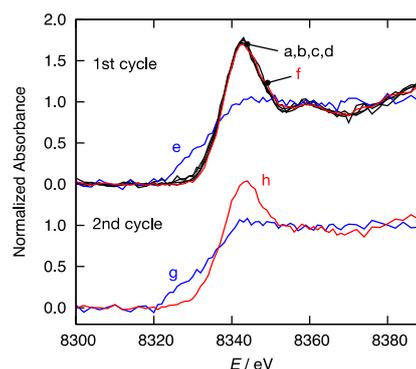


Fig. 2 XANES spectra of NiO/AB electrodes during the discharge and charge processes.

were reversibly observed at the potential range between 1.0 and 3.0 V (f–h). The discharge capacity of 100 mA h g^{-1} above 1.0 V at the second cycle was almost consistent with the theoretical one of NiO, and the stored charge by the cathode reaction was reversibly released at the second charge process until 3.0 V. At the second cycle, the XANES spectra supported the reversible redox reactions of the Ni species on AB. This study indicated that the first discharge process accompanied by the reduction of Li^+ was necessary to activate the conversion process of the NiO species.