

In-situ Measurement of Ni Valence in Nickel Hydroxide during Discharge

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Introduction – A nickel hydroxide has been widely used as an active material for a positive electrode of Ni-MH and Ni-Cd batteries. The mechanism of the charge-discharge reaction, however, has not been clarified yet. Alkaline elements in electrolytes¹⁾ or superoxide-ions such as $\text{KO}_2^{-2)}$ may contribute to the reaction of the nickel hydroxide as shown in previous reports. We have been studying on the mechanism of the charge-discharge reaction for a nickel hydroxide and previously reported about the insertion and exertion of a potassium ion in a nickel hydroxide during charge and discharge reactions³⁾. In this report, the change in Ni valence of a nickel hydroxide during the discharge reaction will be described.

Experimental – XAFS (X-ray absorption fine structure) measurement can be conducted during the charge-discharge reaction without taking the electrode out of the cell which has been developed for this study. The electrode consisting of nickel hydroxides, cobalt oxides, methyl cellulose and Teflon, was spread on a graphite sheet which worked as a current collector. A 5M KOH aqueous solution, an Hg/HgO standard electrode and a foamed nickel plate were used as an electrolyte, a reference electrode and a counter electrode, respectively. The electrode was charged at a C/5 rate for 6 hrs and discharged at a C/5 rate to 0 V. XAFS measurements were conducted during the discharge process. Ni valence in the nickel hydroxide could be determined by the shift of the energy for Ni K-edge X-ray absorption. The beam line BL16B2 at synchrotron radiation facility SPring-8 was utilized for XAFS measurement.

Results – The discharge curve is shown in Fig.1, and arrows indicate the measurement points where the current is off. The horizontal axis shows the utilization, which is defined as the ratio of the stored capacity to the calculated capacity for the reaction of Ni accompanied by one electron. Fig. 2 shows the energy of X-ray absorption for Ni K-edge (XANES spectra). The energy shifts to be lower with the decrease of the utilization. Ni valences have been determined by using the energies of $\text{Ni}(\text{OH})_2$ and LiNiO_2 (Co, Al, Mg-doped) as standard. The measurements were also conducted at 91, 47 and 0 % using another cell. Fig. 3 shows the relation between Ni valence and the utilization. The change in Ni valence is almost one, i.e. from about 3.1 to 2.1 when the utilization is changed from 100 to 0%. The change in Co valence determined by the same measurement is also shown in Fig. 3 and is almost constant, nearly 3, independent of the utilization. Therefore, it is concluded that the redox species of the reaction in the electrode may be nickel. The reaction mechanism of a nickel hydroxide will be discussed by taking the results in this and previous³⁾ studies into consideration.

References

- 1) R. Barnard, et al., J. Applied Electrochemistry, 10 (1980) 109.
- 2) H. Ogura, et al., The 198th Meeting of ECS (2000), Abstract No. 232.
- 3) Y. Kondo, et al., The 71st Meeting of ECSJ (2004) 3I07.

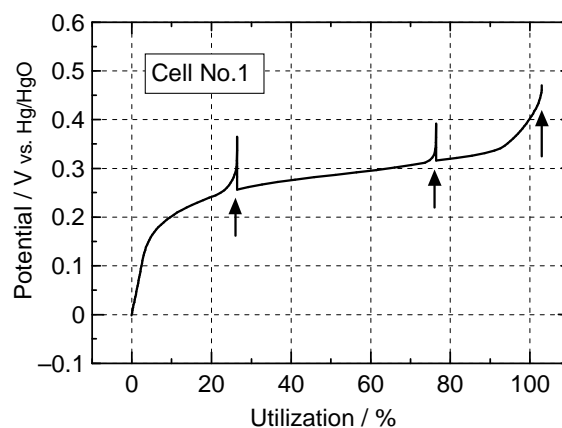


Fig. 1. Discharge curve of the electrode with nickel hydroxide and cobalt oxide. Arrows indicate the measurement points.

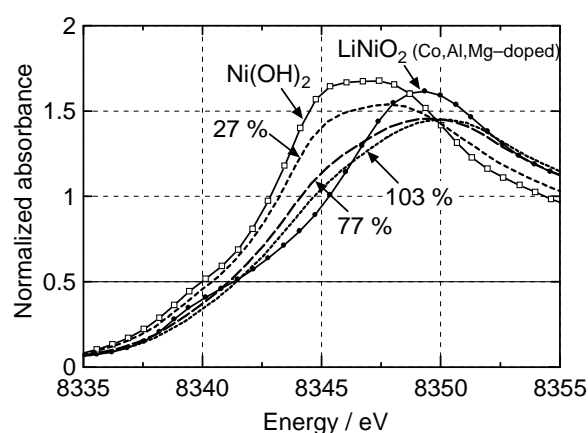


Fig. 2. Change in XANES spectra for Ni K-edge of the electrode with utilization.

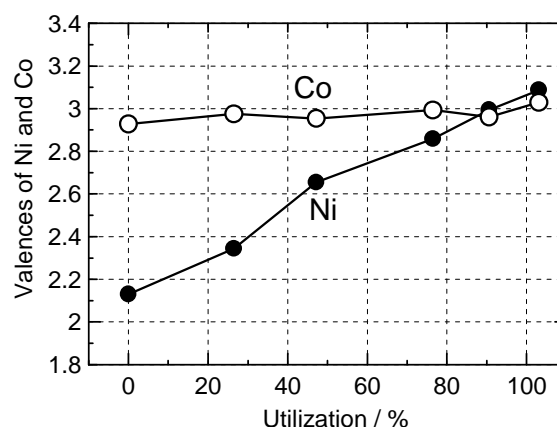


Fig. 3. Change in valences of Ni and Co for the electrode with utilization.