ORIGIN OF THE SECOND LOW VOLTAGE PLATEAU APPERAED DURING DISCHARGE OF NICKEL OXYHYDROXIDE

Masanori Morishita, Koichi Kobayakawa, and Yuichi Sato
Department of Applied Chemistry, Faculty of Engineering, Kanagawa University
Rokkakubashi, Kanagawa-ku, Yokohama 221-8686, Japan

Introduction: The “secondary low voltage plateau” often observed with Ni-Cd, Ni-H_2 and Ni-MH batteries is very likely related to the positive electrode behavior, (nevertheless, it remains the subject of theoretical controversies and experimental discrepancies. There are many papers on the origin of this phenomenon, i.e., due to an ohmic drop resulting from the formation of a barrier layer at the active material/electron collector interface [1)], the reduction of oxygen [2)], a direct transfer of γ-NiOOH to β-Ni$(OH)_2$ [3)], and the formation of a phase close to Ni$(OH)_2$ [4)]. We studied this peculiar phenomenon and found that the second plateau appears only in the graphite-added nickel oxide electrode and estimated that it may be due to the potassium ion intercalation into the graphite layer.

Experimental: The nickel electrode capacity-limited cell with about 100 mAh was fabricated, in which the nickel electrode consisted of Ni$(OH)_2$ and graphite as the conducting material. The cadmium electrode was taken from a sintered-type commercial AAA Ni/Cd battery.

Results and Discussion: Figure 1 shows the 5th cycle discharge curves of the Ni electrode capacity limited Ni-Cd cell with and without graphite as the conducting material. As seen in the figure, though the cell without graphite shows no second discharge plateau, the cell containing graphite shows the second discharge plateau, where the first and second discharge time increased with the increasing graphite content. The first increasing discharge time may be due to the increase in the utility of the Ni oxide. The γ-NiOOH electrode shows no second plateau. On the other hand, the discharge time of the second plateau of the electrode containing a constant amount of graphite with a different Ni$(OH)_2$ content increased showed a maximum value and then decreased with the increasing of Ni$(OH)_2$ content. Figure 2 shows the cyclic voltammograms of the various types of Ni-electrodes, where the anodic peak at 420 mV corresponds to the oxidation of β-Ni$(OH)_2$ to β-NiOOH and the cathodic peak at 150 mV corresponds the reduction of β-NiOOH to β-Ni$(OH)_2$. The cathodic peak at －300 mV appeared only in the graphite-containing electrode, of which the potential corresponds to the second plateau of the discharge curves B, C and D in Fig. 1. γ-NiOOH did not show such a cathodic peak. The ^{7}Li-NMR spectra of the graphite containg the Ni electrode discharged in the LiOH-containing KOH solution showed spinning side bands as seen in bottom of Fig. 3. All these results suggest that potassium ions intercalate into the graphite.

References

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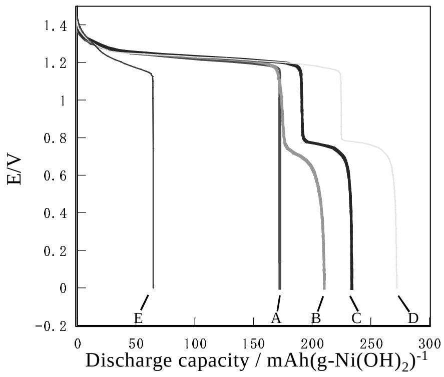

Fig. 1 5th cycle discharge curves of Ni capacity limited Ni-Cd cell obtained at 3.2 mA/cm^2.
A : Ni$(OH)_2$ electrode without graphite,
B : with 4.72% graphite, C : with 9.44% graphite,
D : with 14.16% graphite, E : γ -NiOOH electrode.

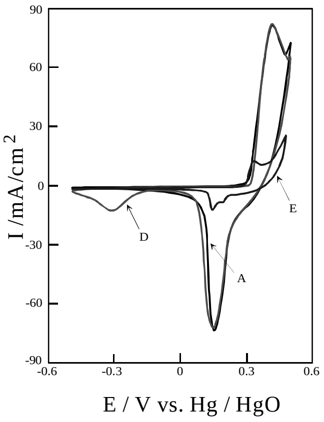

Fig. 2 Cyclic voltammograms of hand made Ni electrode at sweep rate of 6 mV/min.
A : Ni$(OH)_2$ electrode, D : 4.7 % graphite added Ni$(OH)_2$ electrode , E : γ-NiOOH electrode.

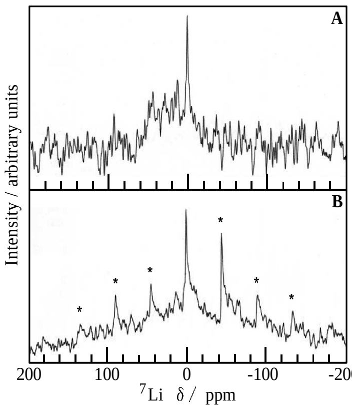

Fig. 3 ^{7}Li-NMR spectra of Ni$(OH)_2$ electrode with 9.44% graphite. Electrolytic solutior is 1M LiOH mixed with 7M KOH.
A : First charged state.
B : Discharged state after 5 cycles
Ref. is LiCl (δ = 0.0)
＊: ssb (spinning side bands)