# ELECTROCHEMICAL AND STRUCTURAL CHARACTERISTICS OF SINTERED NICKEL ELECTRODES CONTAINING CADMIUM HYDROXIDE ADDITIVE

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## Introduction

The general physico-chemical and electrochemical characteristics of a given cathode material have a great influence on the performance of electrochemical sources. Nickel hydroxide is a successful cathode material used in Ni-Cd, Ni-Zn, Ni-Fe, Ni-$H_2$ and Ni- MH alkaline batteries [1]. The processes that take place during charge-discharge of the nickel electrode are represented by equation:

$$NiOOH + H_2O + e^- \Leftrightarrow Ni(OH)_2 + HO^- \; ; \quad \varepsilon^0 = 0.490 \text{ V/NHE} \qquad (1)$$

Two distinct couples, $\beta$-$Ni(OH)_2$/$\beta$-NiOOH and $\alpha$-$Ni(OH)_2$/$\gamma$-NiOOH, can participate in the charge-discharge reactions of the nickel electrode [2]. The charge process occurs usually in competition with oxygen evolution reaction (OER).

For an efficient charge of nickel cathode, the oxygen evolution must be minimized. The addition of some metal hydroxides to the active material has a great influence on the electrochemical behaviour of the nickel electrode [3].

In our paper, electrochemical and structural investigations of nickel electrodes containing Cd hydroxide as additive in active material are presented.

## Experimental

Sintered nickel supports (70 x 35 x 1 mm) were impregnated with nickel nitrate and anodicaly polarized in 42 wt% KOH. A binary electrode, Ni+Cd, containing 10 wt% $Cd(OH)_2$ as additive, was prepared by immersing the nickel support in a solution of $Ni(NO_3)_2 \cdot 6H_2O$ and $Cd(NO_3)_2 \cdot 6H_2O$ before anodic polarization.

The electrochemical behaviour of these electrodes in 6N KOH and 6N KOH containing 35 g/l LiOH as additive, respectively, has been investigated by charge-discharge curves in galvanostatic regime, using a half-cell consisting of the sintered nickel electrode as working electrode, a nickel plate as counter electrode and a SCE as reference electrode.

Phase compositions of electrodes in different states (uncycled, charged and discharged) were analyzed by X-ray diffraction (XRD) with a DRON-3 type diffractometer with a Cu-cathode.

## Results and Discussion

The charge-discharge curves of nickel electrodes in 6N KOH and in 6N KOH + 35 g/l LiOH electrolyte are shown in Fig. 1 and Fig. 2.

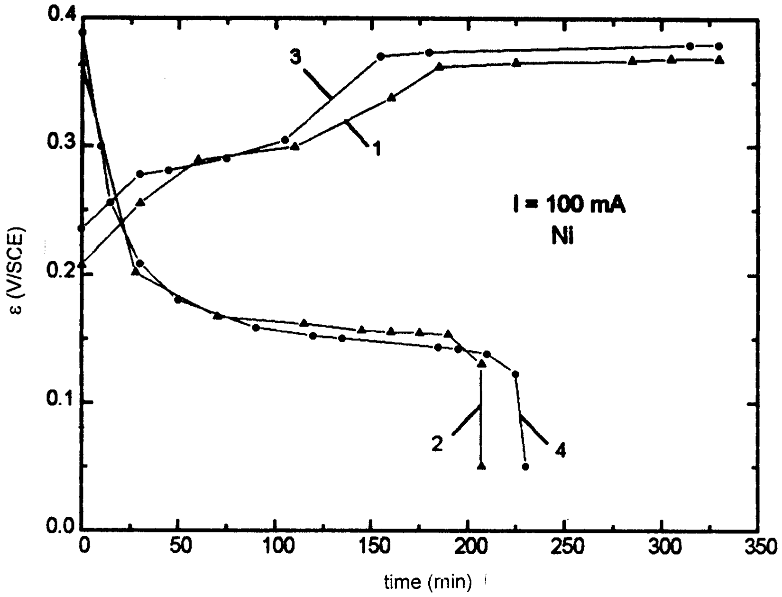

***Fig. 1*** *Charge-discharge curves of Ni electrode in 6N KOH (1-2), and in 6N KOH+35 g/l LiOH (3-4)*

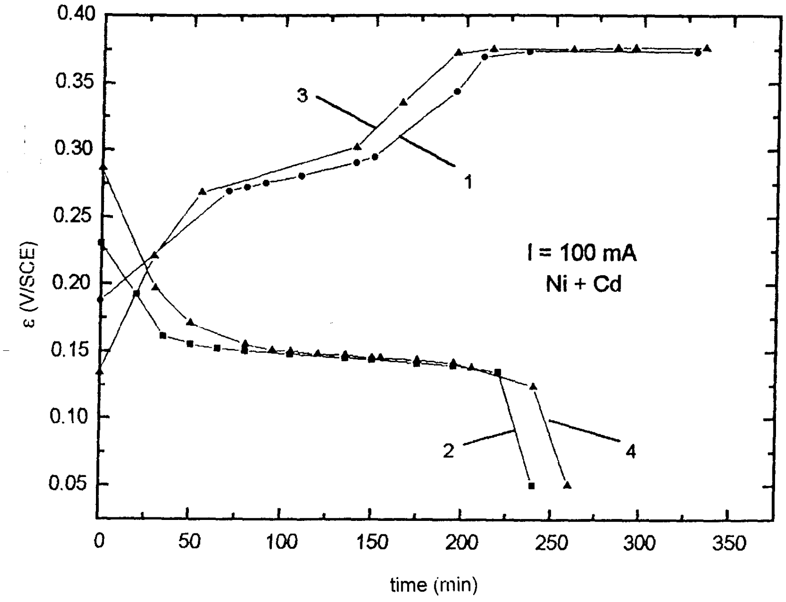

***Fig. 2*** *Charge-discharge curves of Ni+Cd electrode in 6N KOH (1-2), and in 6N KOH+35 g/l LiOH (3-4)*

The coulombic efficiencies, demonstrate the beneficial effects of LiOH addition into electrolyte and of cadmium hydroxide addition in active material (Table 1).

***Table 1*** *Electrochemical characteristics of nickel electrodes.*

| Electrode | Electrolyte | $Q_{charge}$ (mAh) | $Q_{discharge}$ (mAh) | $r_F$ (%) |
|---|---|---|---|---|
| Ni | 6N KOH | 550 | 350 | 63.63 |
| Ni + Cd | | 550 | 400 | 72.73 |
| Ni | 6N KOH + 35 g/l LiOH | 550 | 383 | 69.64 |
| Ni + Cd | | 550 | 475 | 78.73 |

Charge capacities correspond to charging for 5.5 h at I = 100 mA. The decrease of plateaus corresponding to OER from charge curves of Fig.2, demonstrates the increase of the charge efficiency by minimizing of the parasitic OER and hence, the improvement of the discharge characteristics of Ni+Cd electrode. On the other hand, it is considered that the presence of Cd $(OH)_2$ in active material improves the reversibility of the electrode processes [4].

The X-ray diffraction pattern in $2\theta = 4\text{-}63^0$ range, for uncycled nickel electrode without additives, shows the well expresed (111) and (200) lines, corresponding to Ni from sintered support (Fig.3, curve a) and some lines corresponding to $Ni(OH)_2$ (curve b). In the charged nickel electrode, XRD reveals appreciable amounts of γ-NiOOH and β-NiOOH (curve c). There is also a smaller amount of $Ni(OH)_2$ remained uncharged due to parasitic $O_2$ evolution reaction. In the discharged electrode, there are appreciable amounts of $Ni(OH)_2$, which is the discharged active mass (curve d).

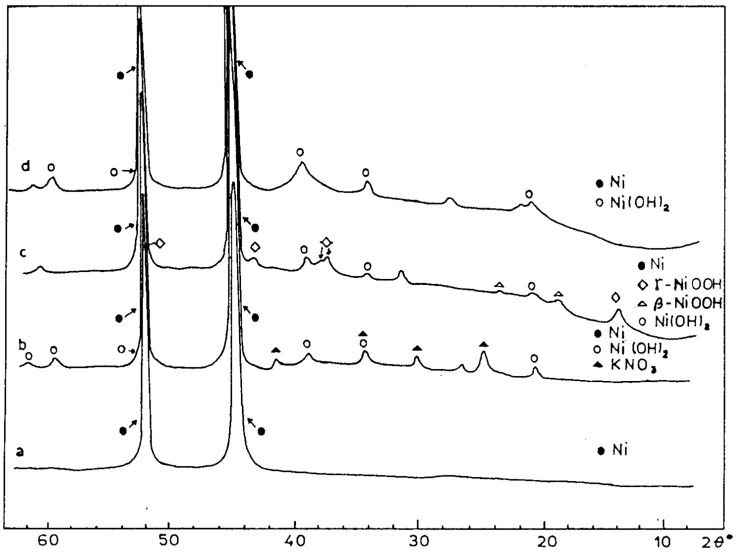

***Fig. 3*** *X-ray diffractograms of sintered nickel electrode: a) sintered support, b) uncycled, c) charged, d) discharged.*

The XRD structural investigations for Ni+Cd electrode confirmed the presence of CdO in the charged electrode and $Cd(OH)_2$ in the discharged electrode (Fig. 4). The presence of $CdCO_3$ in the uncycled active material of Ni+Cd electrode is a result of the action of $CO_2$ from air on KOH electrolyte solution and of the pronounced tendency of substitution of $NO_3^-$ ions, remained from the preparation step, by $CO_3^{2-}$ ions.

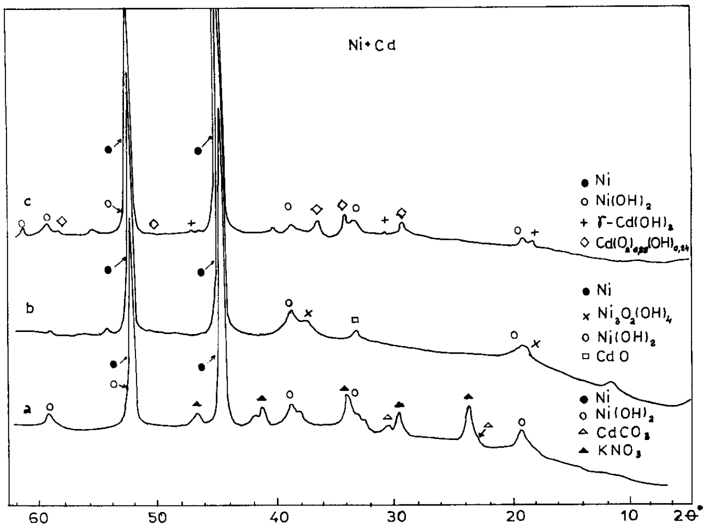

***Fig. 4*** *X-ray diffractograms of Ni+Cd electrode: a) uncycled, b) charged, c) discharged.*

The Ni+Cd electrodes can be recomended for succesful utilization as cathodes in alkaline batteries due to their electrochemical characteristics. In addition, the presence of $Cd(OH)_2$ as antipolar mass ensures the protection of sealed batteries against accidental overdischarges.

## Conclusions

A binary electrode, Ni+Cd, containing nickel hydroxide active material and Cd $(OH)_2$ as additive was prepared by electrochemical activation of sintered nickel support. The coulombic efficiencies determined from charge-discharge curves, demonstrated the beneficial effects of LiOH addition into electrolyte and of Cd hydroxide addition in active material.

The cadmium hydroxide addition enhanced the electrode performance by minimizing of the parasitic $O_2$ evolution reaction and by improving the reversibility of the electrode processes. The electrochemical characteristics of Ni+Cd electrodes point to the possibility of their successful utilization as cathodes in alkaline batteries.

## References

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