

# CHARACTERISATION OF SINTERED NICKEL ELECTRODES FOR ALKALINE BATTERIES

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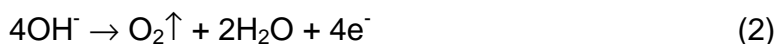
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## Introduction

The electrochemical and structural characteristics of nickel electrodes have been studied because their utilization as cathodes in alkaline batteries: Ni-Cd, Ni-Fe, Ni-Zn, Ni-H<sub>2</sub> and Ni-MH [1]. The reaction at the nickel electrode during charge-discharge is:



The charge process of nickel electrode occurs usually in competition with O<sub>2</sub> evolution reaction (OER):



Two distinct couples,  $\beta$ -Ni(OH)<sub>2</sub>/ $\beta$ -NiOOH and  $\alpha$ -Ni(OH)<sub>2</sub>/ $\gamma$ -NiOOH, can participate in the potential-determining reactions of the nickel electrodes [2]. The best conditions of charge-discharge processes require easy diffusion of electrolyte inside the electrode. From this point of view, the sintered type electrodes are extremely efficient[3-5]. In this paper, the results of the structural and electrochemical investigations of the sintered nickel electrodes prepared by us are presented.

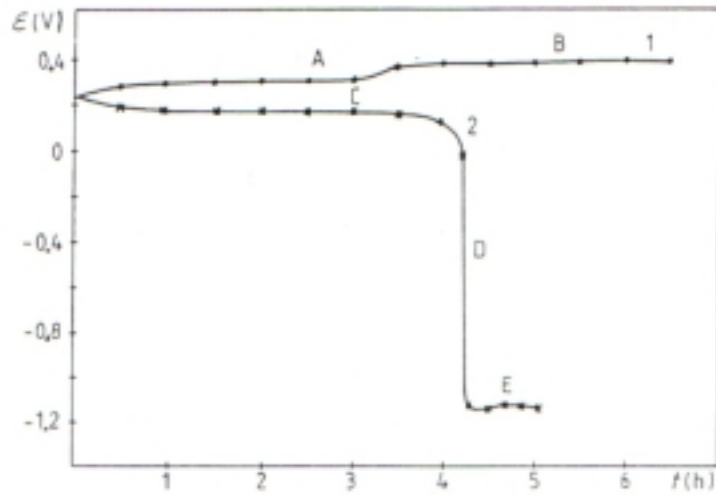
## Experimental

The sintered nickel supports (70 x 35 x 1 mm), having aprox. 70% porosity, were prepared from nickel powder obtained by thermolysis of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O. A mixture of Ni powder (80 wt%) and (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> (20 wt%) was pressed on a nickel plated iron screen and sintered at 800°C. For activation, the sintered supports, impregnated with nickel nitrate, were anodically polarized in 42 wt% KOH.

The electrochemical behaviour of these electrodes has been investigated by charge-discharge curves, in galvanostatic regime, in 6N KON. The curves were performed in 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 uncycled, charged and discharged electrodes were analyzed by XRD, with a DRON-3 type diffractometer with a Cu-cathode, using k<sub>α</sub> radiation ( $\lambda = 1.57051 \text{ \AA}$ ).

## Results and Discussion

The charge-discharge curves performed in galvanostatic conditions, for I = 200 mA, at room temperature, in 6N KOH electrolyte, are shown in Fig. 1



**Fig. 1.** Charge-discharge curves for nickel electrode, in 6N KOH, at  $I = 200 \text{ mA}$ : 1) charge curve; 2) discharge curve.

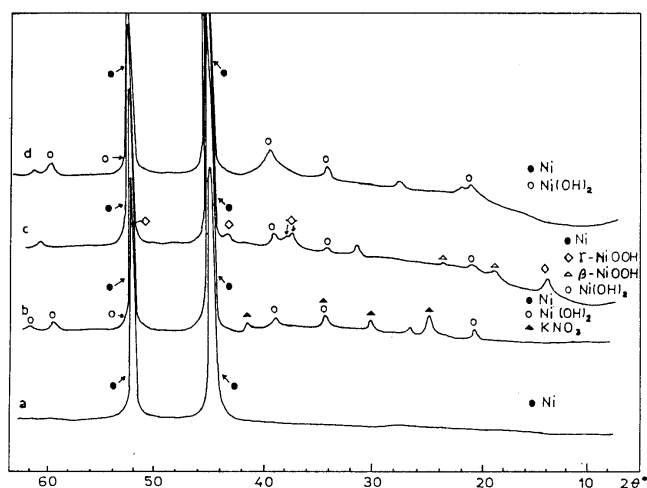
By charge (Fig.1, curve1) the plateau A corresponds to oxidation of  $\text{Ni(OH)}_2$  to  $\text{NiOOH}$ . The region B indicates the oxidation of active material in parallels with OER (overcharge). The plateau C of the discharge curve (Fig. 1, curve 2) corresponds to reduction of  $\text{NiOOH}$  to  $\text{Ni(OH)}_2$ . The abrupt decrease of the potential, determined by the low conductivity of  $\text{Ni(OH)}_2$ , indicates the end of discharge. The region E is related to HER (overdischarge).

Theoretical and practical discharge capacity values of four electrodes with different amounts of active mass were determined. The obtained overunity values of the active material utilization coefficient  $u$ , (representing the ratio between practical discharge capacity  $Q_d$  and theoretical capacity  $Q_t$ ) can be explained by the participation to the charge-discharge processes of nickel from the sintered support (Table 1).

**Table 1.** Utilization coefficients of active material of sintered nickel electrodes, for  $I_{\text{disch.}} = 200 \text{ mA}$

| Nr. electrode | Active mass (g) | $Q_t$ (mAh) | $t_d$ (h) | $Q_d$ (mAh) | $u$  |
|---------------|-----------------|-------------|-----------|-------------|------|
| 1             | 2.060           | 595.34      | 4         | 800         | 1.34 |
| 2             | 2.542           | 734.63      | 4.33      | 866         | 1.18 |
| 3             | 2.820           | 814.98      | 4.66      | 933         | 1.14 |
| 4             | 3.120           | 901.68      | 4.60      | 920         | 1.02 |

The X-ray diffraction pattern in  $2\theta = 4-63^\circ$  range, obtained on the powder scraped from uncycled nickel electrode, shows the well expressed (111) and (200) lines, corresponding to Ni from sintered support (Fig.2, curve a) and some lines corresponding to  $\text{Ni(OH)}_2$  (curve b). In the charged nickel electrode, XRD reveals appreciable amounts of  $\gamma\text{-NiOOH}$  and  $\beta\text{-NiOOH}$  (curve c). There is also a smaller amount of  $\text{Ni(OH)}_2$  remained uncharged due to parasitic  $\text{O}_2$  evolution reaction. In the discharged electrode, there are appreciable amounts of  $\text{Ni(OH)}_2$ , which represents the discharged active mass (curve d).



**Fig. 2.** X-ray diffractograms of: a) sintered support, b) uncycled electrode, c) charged electrode, d) discharged electrode.

The electron micrographs of nickel electrodes revealed a microcrystalline-amorphous structure for uncycled electrode, very small isometric crystals of  $\gamma$ -NiOOH (0.5-1  $\mu\text{m}$ ) and hexagonal crystals of  $\beta$ -NiOOH (0.5-3  $\mu\text{m}$ ) for charged electrode and two generations of  $\text{Ni}(\text{OH})_2$  crystals, attributed to  $\alpha$ - $\text{Ni}(\text{OH})_2$  and  $\beta$ - $\text{Ni}(\text{OH})_2$ , for discharged electrode[6].

## Conclusions

- Nickel electrodes were prepared by electrochemical activation of sintered nickel supports.
- From the investigation of structural and electrochemical characteristics of the prepared sintered nickel electrodes, the following conclusions can be drawn:
  - a) In the charge-discharge cycles, the transformation of some nickel particles of the sintered support in active material takes place. This fact was evidenced by the overunity values of active material utilization coefficient.
  - b) The uncycled active material of the sintered nickel electrodes consists in principal of  $\text{Ni}(\text{OH})_2$  in amorphous state.
  - c) In the charged nickel electrodes, two structural crystalline forms of active material,  $\gamma$ -NiOOH and  $\beta$ -NiOOH, were evidenced.
  - d) In the discharged nickel electrodes, two forms of  $\text{Ni}(\text{OH})_2$  crystals, which can be attributed to  $\alpha$ - $\text{Ni}(\text{OH})_2$  and  $\beta$ - $\text{Ni}(\text{OH})_2$ , were identified.

## References

1. L. Oniciu, E.M. Rus, *Surse electrochimice de putere*, Ed. Dacia, Cluj-Napoca, 1987.
2. J. Desilvestro, O. Haas, *J. Electrochem Soc.*, 1990, **137**, 5c.
3. L. Oniciu, E.M. Rus, P. Ilea, Violeta Voina, Delia Constantin, *Rev. Chim.*, 1985, **36**, 340.
4. L. Oniciu, D. Constantin, E. M. Rus, *Studia Univ. "Babes-Bolyai", Ser. Chem.*, 1994, **39**, 218.
5. Eleonora Maria Rus, Delia Constantin, L. Oniciu, L. Ghergari, *Croatica Chem. Acta*, 1999, **72**, 25.
6. Delia Maria Constantin, Ph.D. Thesis, "Babes-Bolyai" Univ., Cluj-Napoca, Romania, 1996.