CHARACTERISATION OF SINTERED NICKEL ELECTRODES FOR ALKALINE BATTERIES

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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-H₂ and Ni-MH [1]. The reaction at the nickel electrode during charge-discharge is:

\[
\text{NiOOH} + \text{H}_2\text{O} + \text{e}^- \leftrightarrow \text{Ni(OH)}_2 + \text{HO}^- ; \quad \varepsilon^0 = 0.490 \text{ V/NHE} \tag{1}
\]

The charge process of nickel electrode occurs usually in competition with O₂ evolution reaction (OER):

\[4\text{OH}^- \rightarrow \text{O}_2 \uparrow + 2\text{H}_2\text{O} + 4\text{e}^- \tag{2}\]

Two distinct couples, \(\beta\)-Ni(OH)₂/\(\beta\)-NiOOH and \(\alpha\)-Ni(OH)₂/\(\gamma\)-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 approx. 70% porosity, were prepared from nickel powder obtained by thermolysis of Ni(NO₃)₂·6H₂O. A mixture of Ni powder (80 wt%) and (NH₄)₂CO₃ (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 anodicaly 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 \(k_\alpha\) radiation (\(\lambda =1.57051\text{Å}\)).

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 mA: 1) charge curve; 2) discharge curve.

By charge (Fig.1, curve 1) the plateau A corresponds to oxidation of Ni(OH)$_2$ to 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 NiOOH to Ni(OH)$_2$. The abrupt decrease of the potential, determined by the low conductivity of 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>
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<th>Nr. electrode</th>
<th>Active mass (g)</th>
<th>$Q_t$ (mAh)</th>
<th>$t_d$ (h)</th>
<th>$Q_d$ (mAh)</th>
<th>$u$</th>
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<td>4</td>
<td>800</td>
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<td>901.68</td>
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</table>

The X-ray diffraction pattern in 2$\theta = 4-63^0$ 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 Ni(OH)$_2$ (curve b). In the charged nickel electrode, XRD reveals appreciable amounts of $\gamma$-NiOOH and $\beta$-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 represents the discharged active mass (curve d).
The electron micrographs of nickel electrodes revealed a microcrystalline-amorphous structure for unycled electrode, very small isometric crystals of $\gamma$-NiOOH (0.5–1 µm) and hexagonal crystals of $\beta$-NiOOH (0.5–3 µm) for charged electrode and two generations of Ni(OH)$_2$ crystals, attributed to $\alpha$-Ni(OH)$_2$ and $\beta$-Ni(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 unycled active material of the sintered nickel electrodes consists in principal of Ni(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 Ni(OH)$_2$ crystals, which can be attributed to $\alpha$-Ni(OH)$_2$ and $\beta$-Ni(OH)$_2$, were identified.

References