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In memoriam prof. dr. Liviu Oniciu

PASTED NICKEL ELECTRODES FOR ALKALINE BATTERIES

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ABSTRACT. Pasted nickel electrodes for alkaline batteries were prepared by deposition of the electrodic mixture slurry (active material, conductive additives and binder) on nickel foam substrate and on nickelated iron grid, respectively.The electrochemical behaviour of these electrodes in 6N KOH electrolyte has been investigated by cyclic voltammetry and performance curves. From cyclic voltammograms were determined the electrochemical processes that occur on the electrodes in normal conditions, at overcharge and overdischarge.The coulombic efficiencies, calculated from charge-discharge curves in galvanostatic regime, demonstrated the better performance of pasted electrodes on nickel foam substrate.

Key words: *Pasted nickel electrodes, coulombic efficiencies, charge-discharge curves, Cyclic Voltammetry.*

INTRODUCTION

The structural and electrochemical characteristics of a given cathode material have a great influence on the performance of electrochemical power sources. Nickel hydroxide is a successful cathode material used in Ni-Cd, Ni-Zn, Ni-Fe, Ni-H_2 and in the more environmentally friendly Ni-MH systems [1-3].

Nickel based alkaline batteries are attractive since the nickel electrode can be fabricated with very large surface areas which lead to high capacities and high current densities. The electrolyte does not enter into the electrode reaction so that conductivity stays at a high level throughout the usable capacity of the battery. In addition, the nickel active material is insoluble in KOH electrolyte which leads to longer life and better abuse tolerance. Only a proton is involved in the charge/discharge reaction leading to very small density changes and improved mechanical stability of the electrode during cycling. Also, the gravimetric and volumetric energy densities are very good for the nickel electrode [4, 5].

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The processes that take place during charge-discharge of the nickel electrode are represented by the equation:

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

The active material of the nickel electrode consists of Ni(II) hydroxide in discharged state and Ni(III) oxihydroxide in charged state.

There are two primary commercial technologies for manufacturing nickel electrodes (which have been in existence for some 100 years): sintering and pasting.

A sintered electrode consists of a substrate, a porous Ni plaque sintered on the substrate, and an active mass of nickel hydroxide filled in the pores of the plaque. Sintered electrodes are characterized by high rate capability, good longevity, long-term storage, and low self-discharge. The electrode is widely used in portable NiCd and NiMH batteries and is highly preferred for high drain-rate applications.

Pasted electrodes, however, are gaining in popularity due to a reduced complexity in mass production, higher specific capacity, and lower environmental concerns. The performance of NiMH batteries using pasted nickel electrodes has advanced quickly and even the power density is approaching and outperforming those with sintered electrodes. A pasted electrode is made by pasting a slurry of active mass that contains nickel hydroxide, additives and binder materials into a porous substrate followed by drying and calendaring to finish the electrode [6, 7].

In our paper, the electrochemical behaviour of pasted nickel electrodes prepared by us on nickel foam substrate and on nickelated iron grid, respectively, is presented.

RESULTS AND DISCUSSION

Cyclic Voltammetry

The voltammograms recorded on a nickel plate in 6N KOH at different potential sweep rates are shown in Fig. 1.

The potential was scanned between the values at which oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) occurred. Previously, the surface of the electrode was electrochemically treated by cathodic polarization at -1.1V for 5 minutes. The stabilized form of voltammograms was obtained, at v = 20 mV/s, only after 8 oxidation-reduction cycles.

This stabilized profile of voltammograms corresponds to obtaining of some reproductible discharge capacities of electrodes in batteries.

In the anodic sweep at $\varepsilon = -0.550$ V, the formation of $Ni(OH)_2$ (peak A) takes place which at potentials between 0.530 - 0.630 V is oxidized to NiOOH (peak B). OER begins at 0.700 - 0.750 V, depending of sweep rates.

In the cathodic sweep, the reduction of NiOOH to $Ni(OH)_2$ (peak C) occurs at potentials between 0.300 - 0.400 V, while the reduction of $Ni(OH)_2$ to Ni is not observable because of HER.

The average potential, $\varepsilon' = \dfrac{\varepsilon_{a,p} + \varepsilon_{c,p}}{2}$, and the difference of peak positions, $\Delta\varepsilon_p = \varepsilon_{a,p} - \varepsilon_{c,p}$ of NiOOH / $Ni(OH)_2$ couple, was calculated from anodic and cathodic peak potential values , for all the sweep rates.

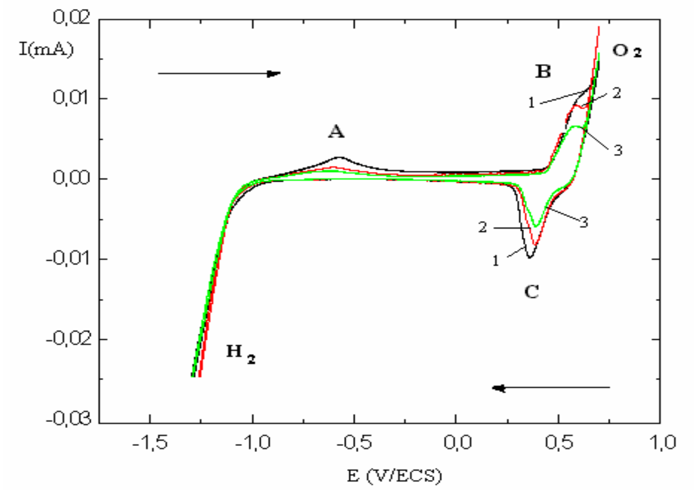

Figure 1. Cyclic voltammograms of nickel plate electrode in 6N KOH at v = 50 mV/s (1), v = 30 mV/s (2) and v = 20 mV/s (3)

The efficiency of processes was estimated from the anodic and cathodic peak currents ratio values ($I_{c,p} / I_{a,p}$) (table 1).

It was observed that the reversibility of oxidation-reduction processes estimated from $\Delta\varepsilon_p$ values is better as the sweep rates are smaller. The anodic and cathodic peak currents ($I_{a,p}$ and $I_{c,p}$) are higher as sweep rates increase. The $I_{c,p} / I_{a,p}$ ratio increases when sweep rate decreases.

The stabilized form of voltammograms for pasted nickel electrodes on nickelated iron grid and on nickel foam substrate, obtained after 5 oxidation-reduction cycles, for three sweep rates, are presented in figure 2 and figure 3.

Figure 2 shows that in the anodic sweep the peak B, corresponding to the charge process, is not observable because of OER (overcharge process) which take place at more negative potentials. But, the peak C recorded in the cathodic sweep is associated with the reduction of NiOOH formed in anodic sweep concomitantly with O_2 evolution.

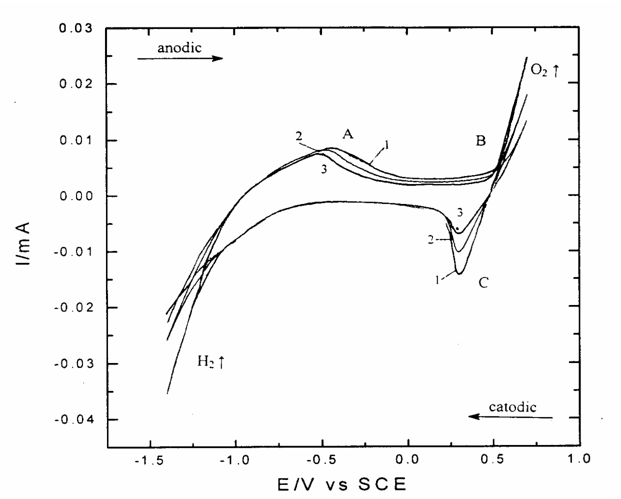

Figure 2. Cyclic voltammograms of pasted nickel electrode on nickelated iron grid in 6N KOH at v = 50 mV/s (1), v = 30 mV/s (2) and v = 20 mV/s (3)

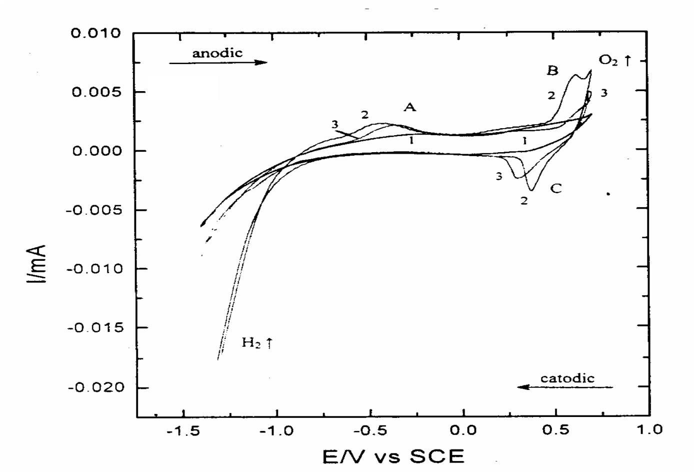

Figure 3. Cyclic voltammograms of pasted nickel electrode on nickel foam substrate in 6N KOH at v = 50 mV/s (1), v = 30 mV/s (2) and v = 20 mV/s (3)

For an efficient charge of the pasted nickel electrode on grid support, the oxygen evolution must be minimized.

The voltammograms presented in figure 3 show that OER occurs at more positive potential so that the charge process of electrode is better.

Thus, using nickel foam as support, the performance of pasted nickel electrodes in alkaline batteries is enhanced by minimizing of the parasitic O_2 evolution reaction and by improving the charge process, compared to electrodes on grid support.

The results of cyclic voltammetry measurements of tested electrodes related to the peak B and C are tabulated in Table 1.

Table 1.

Cyclic voltammetry measurements of tested electrodes in 6N KOH at 20 mV/s

Electrode	$\varepsilon_{a,p}$(B) (V)	$\varepsilon_{c,p}$(C) (V)	$\Delta\varepsilon_p$ (V)	ε' (V)	$I_{a,p}$(B) (μA)	$I_{c,p}$(C) (μA)	$I_{c,p} / I_{a,p}$
Ni plate	0.529	0.408	0.121	0.468	6.6	5.8	0.97
Grid support	-	0. 308	-	-	-	6	-
Foam support	0.700	0.307	0.393	0.503	2.7	2.2	0.81

For pasted nickel electrode on foam support, the $I_{c,p} / I_{a,p}$ ratio value demonstrates that the charge recovered on the cathodic sweep was very close with that of the previous anodic sweep, suggesting the high efficiency of processes.

Galvanostatic Charge-Discharge Curves

The discharge curves of tested electrodes are shown in Fig. 4 and Fig. 5.

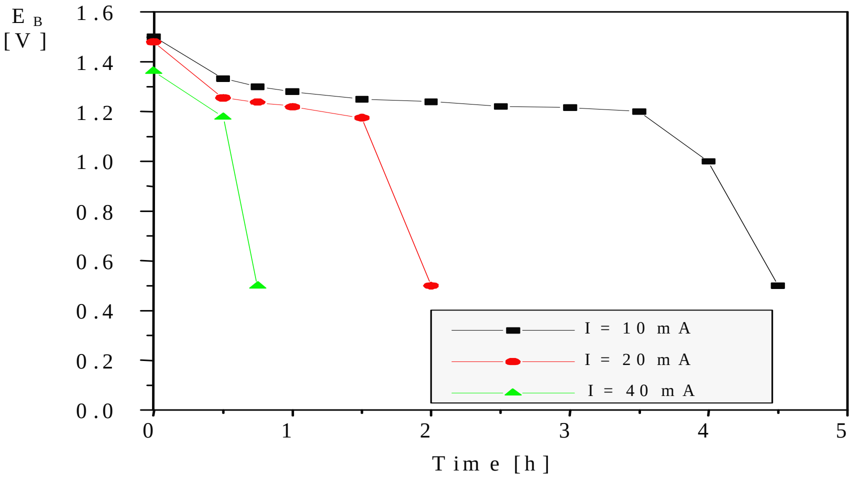

Figure 4. Discharge curves for pasted nickel electrode on nickelated iron grid at three discharge rates.

The charge capacities, C_{charge}, correspond to charging for 4h at I = 15 mA and the discharge capacities were determined from the plateaus of the discharge curves. The coulombic efficiencies r_F, calculated from the charge-discharge characteristics, are presented in table 2.

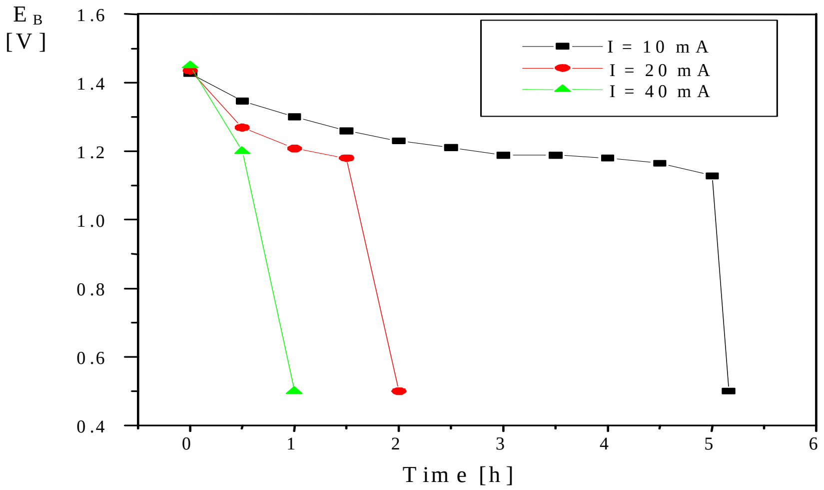

Figure 5. Discharge curves for pasted nickel electrode on nickel foam support at three discharge rates.

Table 2.

Coulombic efficiencies of tested electrodes

Electrode	C_{charge} (mAh)	$I_{discharge}$ (mA)	$t_{discharge}$ (h)	$C_{discharge}$ (mAh)	r_F (%)
Grid support	60	10	4.08	40.8	68.00
	60	20	1.66	33.2	55.33
	60	40	0.70	28.0	46.66
Foam support	60	10	5.16	51.6	86.00
	60	20	2.15	43.0	71.66
	60	40	0.92	36.8	61.33

It is obvious that the discharge capacities and coulombic efficiencies of the pasted nickel electrodes on nickel foam support are substantially increased compared to the electrodes on nickelated iron grid.

The pasted nickel electrodes on nickel foam support can be recomended for successful utilization as cathodes in alkaline batteries due to their electrochemical characteristics.

CONCLUSIONS

Two types of pasted nickel electrodes were realized by deposition of the electrodic mixture slurry consisting of NiOOH as active material, nickel powder and graphite as conductive additives and polyvinyl alcohol as binder on nickel foam substrate and on nickelated iron grid, respectively.

The electrochemical behaviour of these electrodes in 6N KOH electrolyte has been investigated by cyclic voltammetry and charge-discharge curves in galvanostatic regime, at room temperature.

It was established that both electrodes require five charge-discharge cycles to achieve a stabilized capacity, corresponding to formation process.

The charge process of nickel electrodes occurs in competition with OER and for an efficient charge of pasted nickel electrodes the oxygen evolution must be minimized.

Using nickel foam as support, the performance of pasted nickel electrodes in alkaline batteries is enhanced by minimizing of the parasitic O_2 evolution reaction and by improving the charge process, compared to electrodes on grid support.

The pasted nickel electrodes on nickel foam support can be recommended for successful utilization as cathodes in alkaline batteries due to their electrochemical characteristics.

EXPERIMENTAL SECTION

Pasted nickel electrodes for alkaline batteries were prepared by the following important steps:

- preparation of active material;
- preparation of electrodic mixture;
- realization of electrodes.

Active material was prepared in the charged form by chemical precipitation of $Ni(OH)_2$ from a $NiSO_4.7H_2O$ solution with a KOH solution followed by a chemical oxidation of $Ni(OH)_2$ to NiOOH [8].

The prepared electrodic mixture consists of NiOOH as active material, nickel powder and graphite as conductive additives and polyvinyl alcohol as binder. Two types of electrodes were realized by depositon of the electrodic mixture slurry on nickel foam substrate and on nickelated iron grid, respectively.

The electrochemical behaviour of these electrodes in 6N KOH electrolyte has been investigated by cyclic voltammetry and charge-discharge curves in galvanostatic regime, at room temperature.

The cyclic voltammetry experiments were performed by means of an Wenking HP 72 potentiostat, a PV2 programmer Meinsberg type, a MV 87 Pracitronic digital milivoltmeter and a NE 230 X-Y recorder. A platinum wire as counter electrode and a saturated calomel electrode (SCE) as reference were used.

The charge-discharge curves were performed in a half-cell consisting of pasted nickel electrode as working electrode, a nickel plate as counter electrode and a SCE as reference electrode. All the potentials given in this paper are referred to SCE.

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