THE ELECTROCHEMICAL BEHAVIOUR OF SINTERED NICKEL ELECTRODES IN ALKALINE ELECTROLYTE

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Introduction

The electrochemical characteristics of nickel electrodes have been the object of many studies, because their utilization as cathodes in various alkaline batteries: Ni-Cd, Ni-Fe, Ni-Zn, $Ni\text{-}H_2$ and recently, in Ni-MH systems [1]. The reaction at the nickel electrode during charge-discharge is:

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

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 [2-4]. In this paper the influence of LiOH addition into electrolyte on the electrochemical characteristics of sintered nickel electrodes was investigated by cyclic voltammetry.

Experimental

Sintered nickel electrodes were prepared by impregnation of sintered nickel supports with $Ni(NO_3)_2{\cdot}6H_2O$ and anodical polarization in 42 wt% KOH solution [5]. The electrochemical behaviour of these electrodes has been investigated by cyclic voltammetry, in 6N KOH and 6N KOH containing 35 g/l LiOH as additive. All the potentials given in this paper are referred to SCE.

Results and Discussion

The voltammograms recorded on sintered nickel electrode with an apparent surface area of 1cm^2 in 6N KOH at different potential sweep rates are shown in Fig. 1. The potential was scanned between the values at which O_2 evolution reaction (OER) and H_2 evolution reaction (HER) occured.

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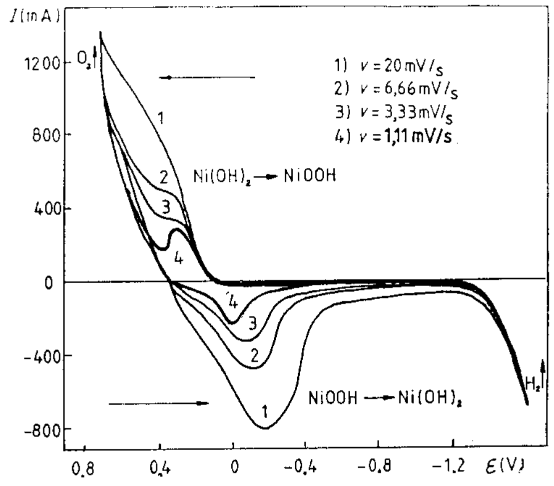

***Fig. 1** Cyclic voltammograms of sintered nickel electrode in 6N KOH*

The stabilized form of voltammograms for activated sintered nickel electrode was attained after 5 oxidation-reduction cycles, in 0.7-1.4 V range, at v = 20 mV/s.

The average potential of NiOOH / $Ni(OH)_2$ couple was calculated for all the sweep rates, using the anodic and cathodic peak potentials:

$$\varepsilon' = \frac{\varepsilon_{a,p} + \varepsilon_{c,p}}{2} \qquad (2)$$

The reversibility of oxidation-reduction processes may be estimated by $\Delta\varepsilon_p$:

$$\Delta\varepsilon_p = \varepsilon_{a,p} - \varepsilon_{c,p} \qquad (3)$$

and it 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 (Table 1).

***Table 1** Cyclic voltammetry measurements of sintered nickel electrode, in 6N KOH.*

v (mV/s)	$\varepsilon_{a,p}$ (V)	$\varepsilon_{c,p}$ (V)	$\Delta\varepsilon_p$ (V)	ε' (V)	$\frac{I_{c,p}}{I_{a,p}}$	Q_c (C)
20	-	-0.180	-	-	-	17.20
6.66	0.390	-0.095	0.485	0.148	0.85	25.31
3.33	0.375	-0.050	0.162	0.425	0.86	29.35
1.11	0.350	0.050	0.200	0.300	0.88	33.55

The cathodic charges, Q_c, corresponding to discharge capacities, were determined from cathodic peak areas.

After addition of 35 g/l LiOH in 6N KOH electrolyte, the stabilized form of voltammograms was obtained in the second cycle after LiOH addition (Fig 2, curve 2), probably after incorporation of LiOH in the active material lattice in the oxidation process.

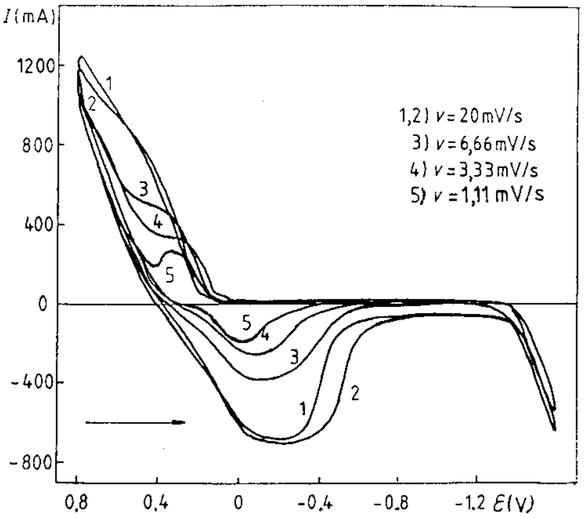

Fig. 2 *Cyclic voltammograms of sintered nickel electrode in 6N KOH + 35 g/l LiOH, at v = 20 (1, 2), 6.66 (3), 3.33 (4), and 1.11 (5) mV/s.*

The addition of 35 g/l LiOH in 6N KOH electrolyte determins the shift of average potential ε' to more anodic values and a slight increase of $I_{c,p}$ / $I_{a,p}$ ratio (Table 2).

Table 2 *Cyclic voltammetry measurements of sintered nickel electrode, in 6N KOH+35 g/l LiOH.*

v (mV/s)	$\varepsilon_{p,a}$ (V)	$\varepsilon_{p,c}$ (V)	$\Delta\varepsilon_p$ (V)	ε' (V)	$\frac{I_{c,p}}{I_{a,p}}$	Q_c (C)
20	-	-0.220	-	-	-	23.56
6.66	0.400	-0.080	0.480	0.160	0.86	34.80
3.33	0.380	-0.040	0.420	0.170	0.88	39.25
1.11	0.340	0.085	0.255	0.212	0.89	45.75

In the presence of 35 g/l LiOH in electrolyte the cathodic charges increased with 34 -37 %.

Conclusions

Nickel electrodes were prepared by electrochemical activation of sintered nickel supports. The cyclic voltammetry measurements demonstrated the beneficial effects of 35 g/l LiOH addition into 6N KOH electrolyte on the discharge capacity of sintered nickel electrodes.

References

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