Bulletin of Electrochemistry 6 (6) June 1990, pp 592–593

Cyclic voltammetric studies on the nickel oxide electrodes in alkaline solutions

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Cyclic voltammetric studies on nickel oxide electrodes were made to determine the reversibility of the electrodes. Influence of additives in 6.0M KOH on this reversibility is discussed.

Key words: Ni oxide electrode, cyclic voltammetry, Ni-Fe battery

INTRODUCTION

The voltammetric studies on pure nickel, electrodeposited $Ni(OH)_2$ and nickel oxyhydroxide [1] revealed the charge storage reaction as $Ni_3O_2(OH)_4 + OH^- \rightleftharpoons 3NiOOH + H_2O + e$. The present work deals with the voltammetric studies on impregnated nickel oxide electrodes.

EXPERIMENTAL

Detailed preparation of sintered nickel electrodes from INCO nickel 255 powder and impregnation of $Ni(OH)_2$, the cyclic voltammetric set up and other details were presented earlier [2].

RESULTS AND DISCUSSION

The electrochemical spectrum for the impregnated $Ni(OH)_2$ electrode in 6.0N KOH, when polarised from 800 mV to −100 mV at different sweep rates revealed a cathodic peak at +70 mV during forward scan [2]. The reverse scan revealed a peak at 650 mV followed by severe O_2 evolution at 700 mV. The charges flowed under these peaks increased with the scan number suggesting that they are couples. The $E_{p,c}$ shifted to more negative values and $E_{p,a}$ to noble values with v.

Various amounts of As_2O_3(10^{-6} to 10^{-3}M) and Sb_2O_3 (10^{-7} to 10^{-4}M) were added to 6M KOH solutions. Excursions from +900 mV to −200 mV in 10^{-4}M arsenite (Fig. 1) revealed a cathodic peak at 140 mV, while the reverse scan exhibited a plateau around 600 mV followed by oxygen evolution at 750 mV. Arsenate ion formed at 900 mV undergoes reduction along with higher valent nickel oxide to lower valent arsenite. Addition of antimonate shifts the O_2 evolution potential preventing O^-_{ads} ion to undergo oxidation. During the forward scan in 10^{-7}M antimonate the ZCP occured at 515 mV followed by a peak at 125 mV. The reverse scan exhibited a plateau around 550 mV followed by O_2 evolution potential.

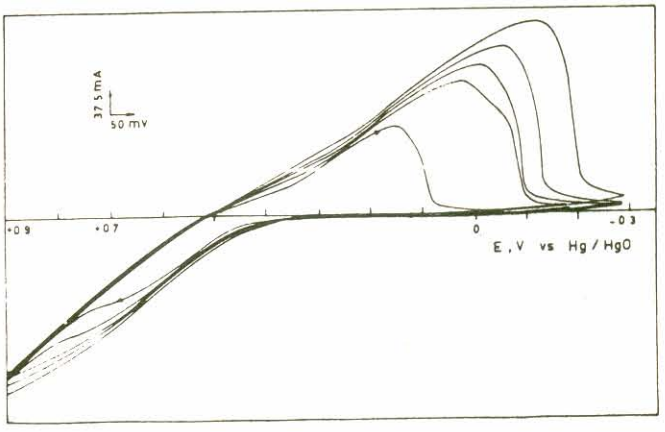

Fig. 1: (A) 0.1 mV.s^{-1} (B) 0.2 (C) 0.3 (D) 0.4 (E) 0.5

Various amounts of Na_2S (10^{-2} to 10^{-5}M) and FeS (10^{-2} to 10^{-5}M) were added to 6M KOH. In 10^{-3}M Na_2S, the ZCP occurred at 515 mV (Fig. 2) followed by a peak at 300 mV during forward scan. On the reverse scan, O_2 starts evolving from 400 mV. Addition of sulphides lower the O_2 evolution potential and favour the reduction of higher oxides of nickel. In FeS solution ZCP occurred at 480 mV followed by a peak at 180 mV during forward scan. On the reverse scan, O_2 evolution takes place at 400 mV.

The overall reaction may be complex on the impregnated $Ni(OH)_2$ electrode as the oxidation state of nickel varies from 3.67 to 2.25 over a wide range of potentials. For γ-phase to (0.125 NiO_2.0.875 $Ni(OH)_2$] 0.67 H_2O, the electrochemical step may involve

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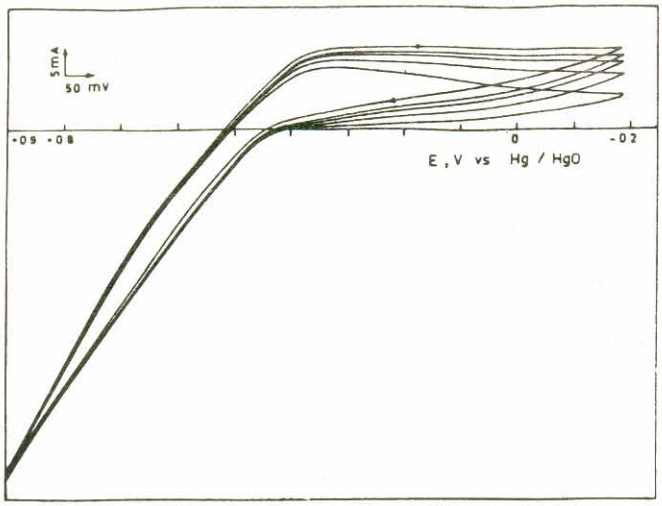

Fig. 2: (A) 0.1 mV.s^{-1} (B) 0.2 (C) 0.3 (D) 0.4 (E) 0.5

$$[NiOOH.M^{+}OH. \times H_2O] + H^{+} + e \longrightarrow Ni_3O_2(OH)_4 + M^{+}y.H_2O$$

as indicated earlier [1]. At higher v, and in presence of additives the appearance of single anodic and cathodic peaks is due to this redox couple. ΔE_p (peak potential separation) is a measure of reversibility. The more the value of $\Delta E_p = E_{p,a} - E_{p,c}$, the more is irreversibility of the electrode process. (ΔE_p) varies with v and (ΔE_p) and $(\delta E_p)_{v \to o}$ is used to evaluate the reversibility. As (Q_c/Q_a) varies with v, $(Q_c/Q_a)_{v \to o}$ is also taken as a measure of reversibility. Addition of LiOH gradually increases the reversibility and 0.63M LiOH is the best additive (Table I). Additions of Sb_2O_3 and As_2O_3 improve the reversibility and at higher concentrations of these additives, reversibility is less.

TABLE–I: Effect of various additives in the electrolyte on the reversibility of charge storage reaction in 6 M KOH

Electrolyte composition		$(\Delta E_p)_{v=o}$ mV	$(\theta_a/\theta_c)_{v=o}$
6M KOH		600	0.69
6M KOH	+ 0.84 M LiOH	430	0.63
	+ 0.63 M LiOH	517	0.72
	+ 0.42 M LiOH	520	0.53
	+ 0.21 M LiOH	645	0.53
6M KOH	+ 10^{-4}M Sb_2O_3	560	0.22
	+ 10^{-5}M Sb_2O_3	500	0.32
	+ 10^{-6}M Sb_2O_3	455	0.44
	+ 10^{-7}M Sb_2O_3	390	0.62
6M KOH	+ 10^{-3}M As_2O_3	435	0.58
	+ 10^{-4}M As_2O_3	410	0.64
	+ 10^{-5}M As_2O_3	400	0.48
	+ 10^{-6}M As_2O_3	370	0.21

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