

ELECTROCHEMICAL BEHAVIOUR OF NICKEL AND NICKEL OXYHYDROXIDE IN ALKALINE CARBONATE SOLUTIONS

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[Received: 1990 July; Accepted: 1991 July]

Carbonation is a serious problem in alkaline batteries affecting the performance and cycle life. Cyclic voltammetric studies on pure nickel and electrodeposited NiOOH have been made in 0.1 to 10M KOH solutions containing carbonates. In presence of carbonate, nickel carbonate formed prevents the oxidation of divalent hydroxides. The diffusion of protons away from the oxide and of hydroxyl ion towards the electrode is hindered thereby influencing the charge storage reaction. The oxygen evolution reaction and self-discharge are enhanced by the presence of carbonates which in turn may lower the cycle life.

Key words: Cyclic voltammetry, nickel oxyhydroxide, carbonation

INTRODUCTION

Carbonate is the most common contaminant in alkaline electrolytes. Studies on Ni–Cd cells [1] enlisted the specific effects of carbonate and excessive amount of carbonates as detrimental to the performance of Ni–Cd cells. In order to understand the effect of carbonation on the positive electrode (nickel) in alkaline batteries detailed study was carried out on pure nickel and electrodeposited NiOOH in 0.1 to 10.0M KOH solutions containing carbonates. An attempt has also been made to find the effect of LiOH in the presence of these carbonates.

EXPERIMENTAL

The nickel electrode surface preparation and the electrodeposition of nickel oxyhydroxide have been given earlier [2]. Triangular potential sweep experiments for these electrodes were carried out in Bio-analytical-systems- 100A, USA using a conventional three electrode cell assembly of nickel as working electrode, platinum as counter and Hg/HgO as reference electrodes respectively.

KOH solutions were prepared from analytical chemicals using triple distilled water. Solutions of KOH [0.1M < x > 10.0M] containing [0.1M < y > 1.0M] Na₂CO₃ were used. 6M KOH + 0.5M Na₂CO₃ solutions containing [0.1M < z > 0.3M] LiOH were also used for experimentation. The solutions were deoxygenated using nitrogen. The area of the electrode was 0.2 sq.cm.

Voltammetric sweep rates were varied from 2 to 500 mV.s⁻¹. In the case of pure nickel the switching potentials were between -1.3V to +0.6V while for NiOOH, it varied from 0.0V to 0.6V vs Hg/HgO.

E - log i plots were also obtained for the oxygen evolution reaction in pure nickel and electrodeposited NiOOH in all these solutions.

RESULTS

Electrochemical behaviour of nickel

During the forward scan, a broad anodic peak at -0.602V (I) and a passivation region from -0.300V to +0.100V are observed. A sharp peak appeared at 0.472V(II) followed by oxygen evolution. The reverse scan exhibited a sharp cathodic peak at +0.358V(III) which may be due to the reduction of Ni⁺³ to an intermediate

oxidation state of +3 and +2. Peak (III) was followed by a shoulder around +0.280V (IV) (Fig.1).

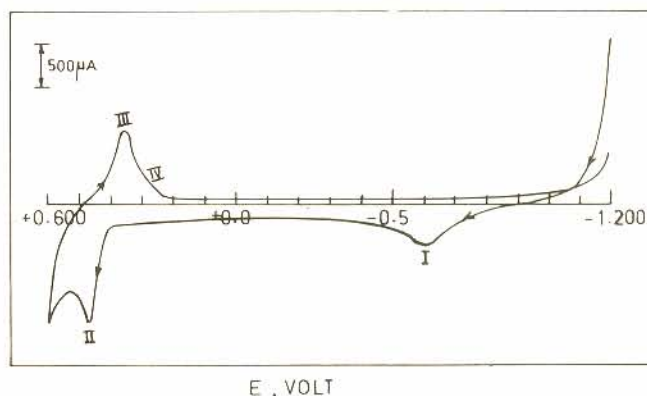


Fig. 1: Cyclic voltammogram for nickel in 6.0M KOH solution
 $E_{\lambda,c} = -1.2V$; $E_{\lambda,a} = +0.6V$; $v = 200mV.s^{-1}$

Presence of carbonate in KOH solutions does not modify the electrochemical spectrum. The forward scan exhibits two anodic peaks one at -0.650V(I') and another at 0.48V(II') respectively. In the reverse scan there is a sharp peak at 0.37V(III') followed by a shoulder at 0.28V(IV') (Fig. 2). The first anodic peak potential shifted to more active values suggesting carbonate ions favour the dissolution of nickel. However, the peak currents and Q_a decrease with carbonate ion concentration. The second anodic peak potential shifts to more noble values suggesting the oxidation of divalent nickel becomes difficult in the presence of carbonate. Increase in carbonate concentration decreased i_{pa} (II) and Q_a (II).

In the reverse scan, a constant current region is observed from +0.2V to -0.7V and hydrogen evolution starts earlier. The cathodic peak (IV') appears in all carbonate solutions and merges into a single peak above 100 mV .s⁻¹. The cathodic peak potential (III') becomes more active with the addition of carbonate suggesting that the desorption of oxygen is hindered while Q_c and $i_{p,c}$ decrease with carbonate concentration.

Variation of alkali concentration with a constant carbonate concentration also does not bring out any change in the electrochemical spectrum of nickel. However, in higher alkali, the two cathodic peaks appear distinctly at all scan rates (Fig. 3).

Oxygen evolution is found to be favoured at an optimum

concentration of LiOH. In 0.12M and 0.36M LiOH, the zero current crossing potential (ZCCP) in the reverse scan occurs at 0.495V and 0.485V respectively. In 0.24M LiOH, ZCCP occurs at 0.42V. At all concentrations, a constant current region is observed from -0.5V to 0.1V (Fig. 4).

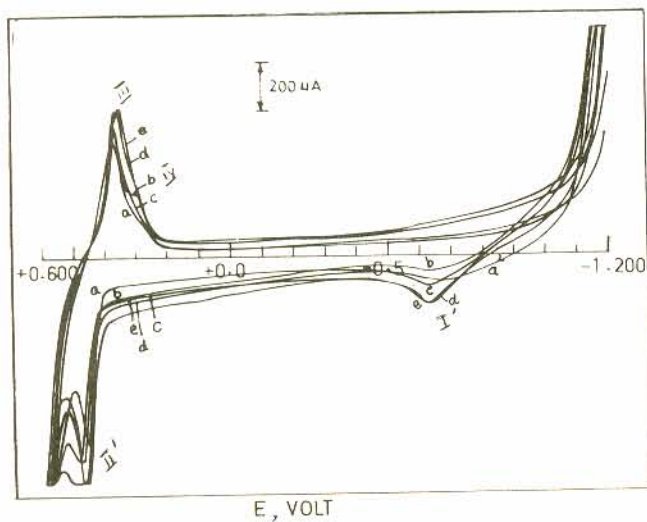


Fig. 2: Cyclic voltammogram for nickel in 6.0M KOH + different Na_2CO_3 solutions. (a) 0.1M (b) 0.2M (c) 0.3M (d) 0.5M (e) 1.0M Na_2CO_3 . $E_{\lambda,e} = -1.2\text{V}$; $E_{\lambda,a} = 0.6\text{V}$; $\nu = 100 \text{ mV.s}^{-1}$

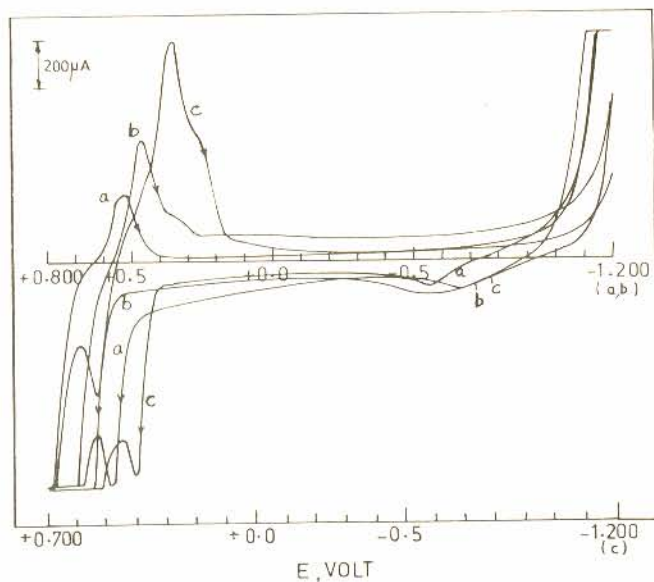


Fig. 3: Cyclic voltammogram for nickel in 0.5M Na_2CO_3 + different KOH solutions. (a) 0.1M (b) 1.0M (c) 10.0M KOH. $E_{\lambda,e} = -1.2\text{V}$; $E_{\lambda,a} = 0.6\text{V}$; $\nu = 100 \text{ mV.s}^{-1}$

In the presence of carbonate, Li^+ ion favours the dissolution of nickel (perhaps by a pH rise) while Q_a (I) decreases suggesting the dissolution and diffusion of HNiO_2^- away from the electrode.

The presence of Li^+ favours the oxidation of divalent nickel as evidenced by the shift of E_{pa} (II) to more active values and enhances Q_a (II) values. The desorption of oxygen and reduction

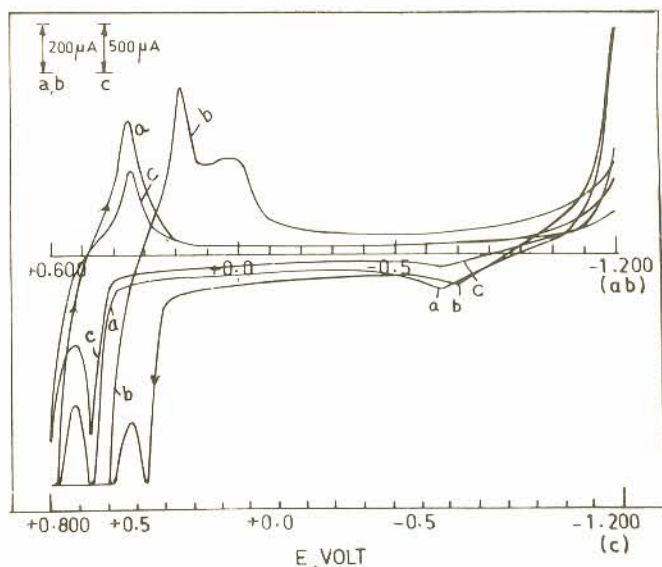


Fig. 4: Cyclic voltammogram for nickel in 6.0M KOH + 0.5M Na_2CO_3 + different LiOH solutions (a) 0.12M (b) 0.24M (c) 0.36M LiOH. $E_{\lambda,e} = -1.2\text{V}$; $E_{\lambda,a} = 0.6\text{V}$; $\nu = 100 \text{ mV.s}^{-1}$

of higher valent nickel oxides are not influenced by the presence of Li^+ ion in carbonate solutions.

Electrochemical behaviour on electrodeposited NiOOH

When polarised from 0.0V to 0.6V in 6M KOH containing 0.1M Na_2CO_3 solution, the cyclic voltammogram exhibits a single predominant peak at 0.397V (I) in the anodic scan while in the reverse cathodic scan, a sharp well defined peak at 0.269V (III) are obtained. Q under the peaks (Fig. 5) increases with V.

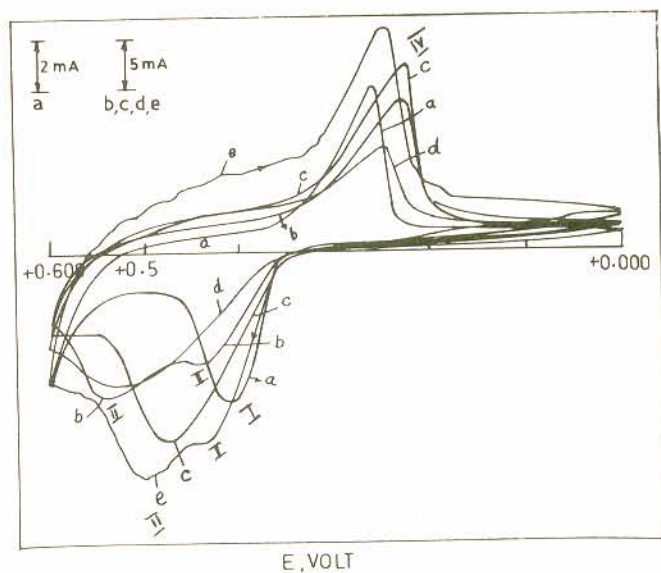


Fig. 5: Cyclic voltammogram of electrodeposited NiOOH in 6.0M KOH + different carbonate solutions (a) 0.1M (b) 0.2M (c) 0.3M (d) 0.5M (e) 1.0M Na_2CO_3 . $E_{\lambda,e} = 0.0\text{V}$; $E_{\lambda,a} = 0.6\text{V}$; $\nu = 100 \text{ mV.s}^{-1}$

With increase in Na_2CO_3 concentration from 0.1M to 0.2M, the cyclic voltammogram exhibits an additional anodic peak at 0.485V (II) at 50 mV.s^{-1} which disappears at higher V. With increase

in concentration above 0.3M Na₂CO₃, the second anodic peak disappears. In 1.0M Na₂CO₃, the second anodic peak disappears. In 1.0M Na₂CO₃, the Q under peak (II) increases while that of (I) decreases. E_{pa}(I) shifts to more positive values while E_{pc}(III) to more negative values.

In 0.1M KOH the electrochemical spectrum reveals an anodic peak at 0.6V (I') and a cathodic peak at 0.398V (IV) (Fig. 6, curve a). Increase of KOH concentration to 1.0M produces a sharp anodic peak at 0.529V (I) and a cathodic peak at 0.367V (IV) preceded by a shoulder at 0.45V (III).

In a 6M KOH solution, there are two anodic peaks at 0.395V (I) and at 0.48V (II) respectively. A single cathodic peak appears at 0.287V (IV) (Fig. 6, Curve c). 10.0M KOH solution (Fig. 6, Curve d) exhibits interesting features. There is a sharp anodic peak at 0.318V (I) and a small broad peak at 0.458V (II) accompanied by a shoulder at 0.56V (II'). In the cathodic scan a single sharp peak appears at 0.214V (IV). At $v > 50 \text{ mV.s}^{-1}$, Q under the peaks at 0.318V and 0.214V increases, suggesting that increase of OH⁻ ion favours the reaction occurring around the peaks.

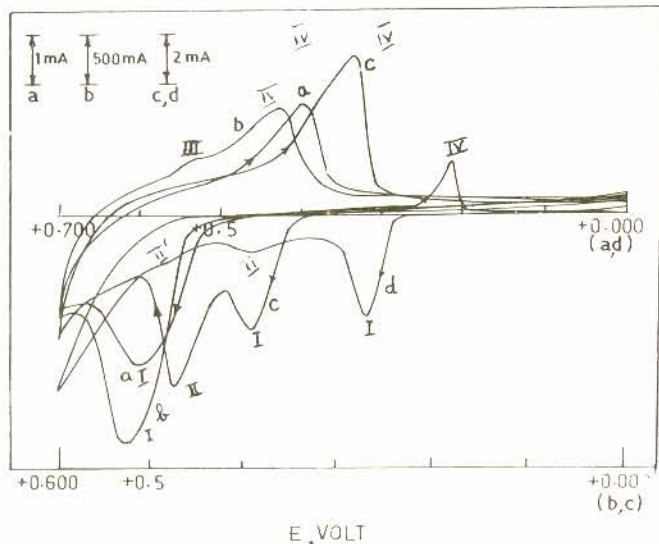


Fig. 6: Cyclic voltammogram of electrodeposited NiOOH in 0.5M Na₂CO₃ + different KOH solutions (a) 0.1M (b) 1.0M (c) 6.0M (d) 10.0M KOH E_{λ,c} = 0.0V; E_{λ,a} = 0.6V; $v = 10 \text{ mV.s}^{-1}$

The introduction of Li⁺ ion (0.12M) causes the electrochemical spectrum to exhibit two anodic peaks at 0.393V (I) and 0.526 (II) while in the reverse scan, a single cathodic peak at 0.257V appears. With further increase of Li⁺ ion, the second anodic peak merges with oxygen evolution (Fig. 7).

Oxygen evolution reaction

Pure nickel

In order to follow the oxygen evolution reaction, polarisation has been made from 0.3V to 0.6V at 100 mV.s⁻¹ and E - log i curves are obtained. A decrease in current is observed with potential till a minimum value is reached at 0.44V and a current is found to rise again (Fig. 8). Lithium and carbonate additions do not change the overall spectrum; however, the reversible potential of oxygen evolution reaction is found to be affected. Anodic Tafel slope of about 40 mV. decade⁻¹ is observed which becomes high with carbonate concentration. Exchange current increases with carbonate ion concentration [$> 0.3 \text{ M}$] (Table I).

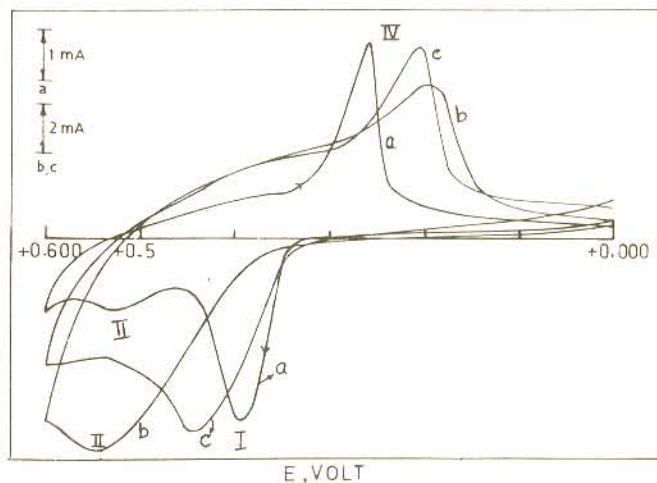


Fig. 7: Cyclic voltammogram of electrodeposited NiOOH in 0.5M Na₂CO₃ + 6M KOH + different LiOH solutions (a) 0.12 (b) 0.24 (c) 0.36M LiOH E_{λ,c} = 0.0V; E_{λ,a} = 0.6V; $v = 100 \text{ mV.s}^{-1}$

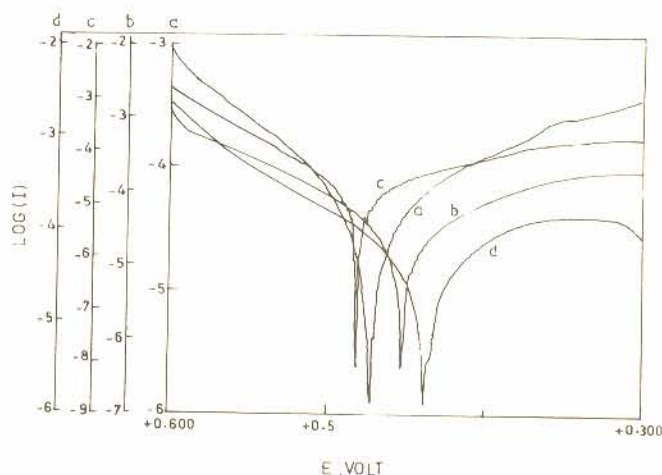


Fig. 8: E-log i plot for oxygen evolution reaction on nickel at 6.0M KOH + different carbonate solutions (a) 0.0M (b) 0.1M (c) 0.2M (d) 0.5M Na₂CO₃; $v = 100 \text{ mV.s}^{-1}$

Electrodeposited NiOOH

When polarised from 0.3V to 0.6V, the E - log i plot exhibits a decrease in current upto 0.49V and starts rising to 0.49V in 6.0M KOH solutions (Fig. 9). Lithium and carbonate ions do not markedly vary the overall behaviour. The minimum current-potential is influenced by these ions. An anodic Tafel slope of 40 mV. decade⁻¹ is observed and i_0 for oxygen evolution reaction is found to decrease with Li⁺ ions in carbonate solutions while carbonates enhance the rate (Table I).

DISCUSSION

In alkali solutions the initial portion of the anodic E - i curve is assigned to the steady electrodisolution of nickel and the passivation state depends on the solubility of Ni(OH)₂. Before the formation of the anodic peak, the initial surface oxidation takes place. The participation of water and OH⁻ ions by adsorption on the metal [3] can be given as



TABLE-I: Effect of carbonate, hydroxyl ions and lithium ions on the exchange current of oxygen evolution reaction.

Solution	Exchange current (μA)	
	Nickel	Electrodeposited NiOOH
6.0M KOH	10	6
6.0M KOH + 0.1M Na ₂ CO ₃	6.7	36
6.0M KOH + 0.2M Na ₂ CO ₃	6.2	50
6.0M KOH + 0.3M Na ₂ CO ₃	12.3	70
6.0M KOH + 0.5M Na ₂ CO ₃	45.3	100
0.5M Na ₂ CO ₃ + 0.1M KOH	3.9	26
0.5M Na ₂ CO ₃ + 1.0M KOH	—	10
0.5M Na ₂ CO ₃ + 10.0M KOH	80	8
0.5M Na ₂ CO ₃ + 6M KOH + 0.12M LiOH	10	24
0.5M Na ₂ CO ₃ + 6M KOH + 0.24M LiOH	10	31
0.5M Na ₂ CO ₃ + 6M KOH + 0.36M LiOH	10	10

Anodic Tafel slope { Nickel = $40 \pm 5 \text{ mV.decade}^{-1}$
Electrodeposited NiOOH = $42 \pm 5 \text{ mV.decade}^{-1}$

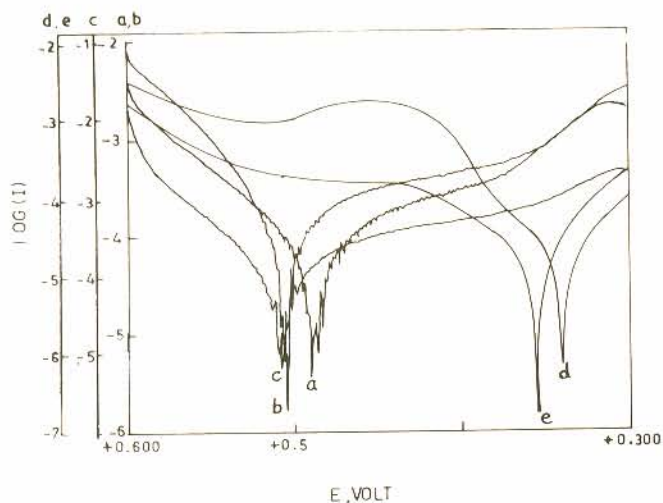
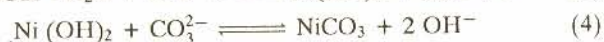
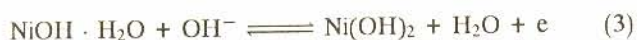
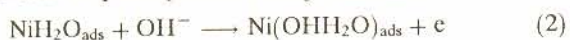


Fig. 9: E-log *i* plot for oxygen evolution reaction on electrodeposited NiOOH in 6M KOH + different Na₂CO₃ solutions (a) 0M (b) 0.2M (c) 0.3M (d) 0.5M (e) 1.0M Na₂CO₃ ($\nu = 100 \text{ mV.s}^{-1}$)

The dependency of $E_{pa}(I)$ with $\log [\text{CO}_3^{2-}]$ concentration (Fig. 10) reveals the participation of CO_3^{2-} ions and



In higher alkali ($> 6\text{M KOH}$) the

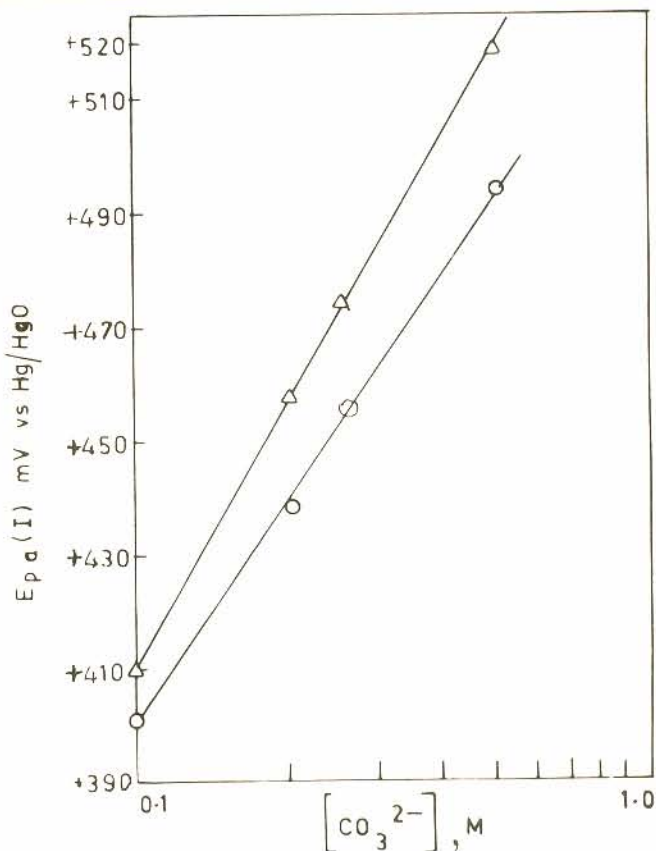
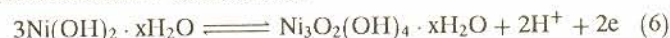


Fig. 10: Variation of anodic peak potential (*I*) with log carbonate ion concentration of 6.0M KOH (1) 75 mV.s^{-1} (2) 100 mV.s^{-1}

From the dependence of anodic peak potential on V and OH⁻ concentrations it is shown that



In carbonate solutions, the coverage of the surface by NiCO₃

prevents the divalent hydroxide the undergo oxidation. The proton diffusion which is assisted by the electric field is hindered by the presence of carbonate adsorption of nickel. On anodic polarisation, the partially hydrated intermediate undergoes a structural rearrangement along with an electron transfer.

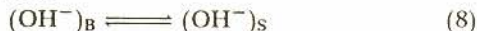


If the above reaction is a reversible conjugated electrochemical system with monolayer formation, the corresponding anodic and cathodic current peaks must occur at the same potentials. Since there is no cathodic peak corresponding to the anodic peak in the same potential region, the above conjugated reaction is not simple. One can visualise the formation of NiOOH from the hydrated stable $\text{Ni}_3\text{O}_2(\text{OH})_4 \cdot x\text{H}_2\text{O}$. Carbonate decreases the $Q_a(\text{II})$ suggesting that the oxidation of $\text{Ni}_3\text{O}_2(\text{OH})_4 \cdot x\text{H}_2\text{O}$ is hindered, while the increase of OH^- ion concentration favours the reaction.

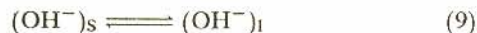
The appearance of a shoulder accompanied by the broad cathodic peak on the reverse scan indicates that the species formed on the forward scan undergo successive reduction. Some of the oxygen atoms from the oxide that is formed alters the ratio of Ni/O from 0.5 to 0.66. The appearance of a broad cathodic peak is due to the formation of $\text{Ni}_3\text{O}_2(\text{OH})_4 \cdot x\text{H}_2\text{O}$ further reduction of which is not possible on electrodeposited NiOOH. The earlier appearance of anodic peaks with OH^- ion concentration suggests that oxide formation, oxygen adsorption and oxygen evolution are favoured by OH^- ion. The appearance of peak III in 1.0M KOH is due to the desorption of oxygen and is favoured by OH^- ion concentration.

The cathodic peak (IV) is due to the reduction of higher valent oxides to lower oxidation states of 2 to 3. Increase of carbonate ion concentration postpones the appearance of peak (I) thereby hindering the formation while its reduction is favoured.

On anodic polarisation, OH^- ions move towards the film/solution interface as



where B is the bulk of the solution and S is the surface of the film. Depending on the local electrical field and thickness of diffusion of OH^- ions from the surface to some site in the interior of the film



occurs. The oxidation of divalent hydroxide releases the proton which diffuses away from the electrode to a site in the oxide where it combines with an OH^- ion to form water.



where 'n' is the neutralisation site. As oxidation proceeds, the neutralisation site moves towards the solution side and the progress of the neutralisation site ceases as it reaches the solution phase. This explains the presence of water concentration gradient in the film and the variation in the electrochemical activity with changes in water activity in the solid phase.

In presence of carbonates on electrodeposited NiOOH, the anodic peak current (II) and cathodic peak current (III) are found to vary with \sqrt{v} in 6.0M KOH solutions [Figs. 11 and 12]. The cathodic peak potential (IV) is found to vary with $\log [\text{CO}_3^{2-}]$ concentration suggesting the participation of carbonate ions [Fig. 13].

At higher anodic potentials, carbonate ion can diffuse in the solid phase and compete with the OH^- ion to meet the protons. The diffusion of protons as well as OH^- ions is hindered by the presence of carbonate thereby decreasing the water content which is responsible for electrochemical activity. At still higher anodic

potentials, water molecules in contact with the oxide liberate oxygen. This dual type of transport of H^+ ions from the interior

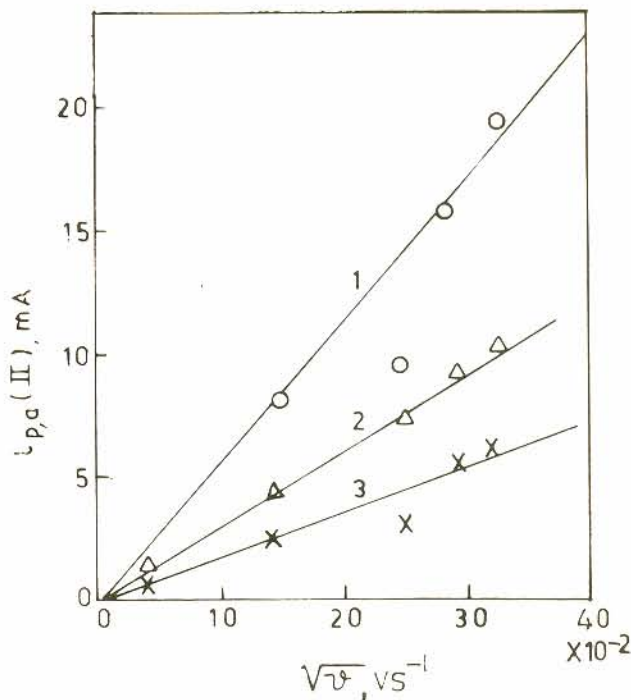


Fig. 11: Variation of anodic peak current (II) with \sqrt{v} in 6.0M KOH and different carbonate solutions (1) 0.0M (2) 0.3M (3) 0.5M Na_2CO_3

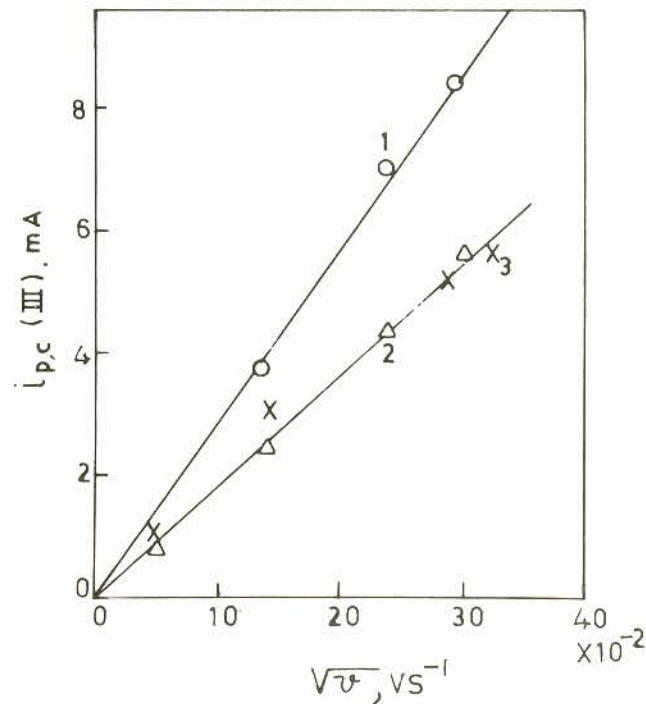


Fig. 12: Variation of cathodic peak current (III) with \sqrt{v} in 6.0M KOH and different carbonate solutions (1) 0.0M (2) 0.3M (3) 0.5M Na_2CO_3

and OH^- ions from the solution into the solid phase depends on the interlayer distance and the presence of 'free' and bound water [4].

Near oxygen evolution, the presence of Ni^{4+} species has been

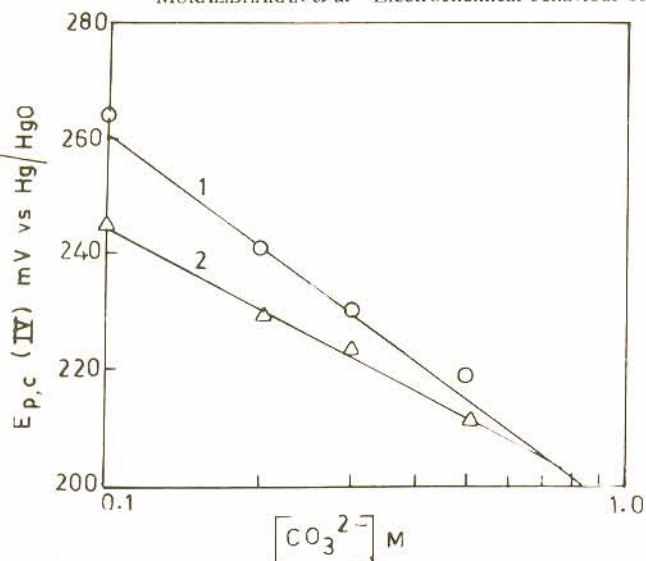


Fig. 13: Variation of cathodic peak potential (IV) with log carbonate concentration in 6.0M KOH containing different carbonate solutions (1) 50 mV.s⁻¹ (2) 75 mV.s⁻¹

proposed [5 - 11]. The evidence for Ni⁵⁺ is based mostly on coulometric data or determinations of active oxygen by titration with iodide or arsenious oxide. The limited X-ray absorption data do not appear to support a valence of four for nickel [12].

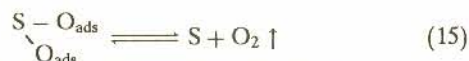
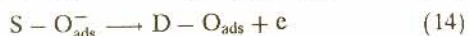
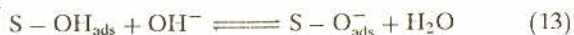
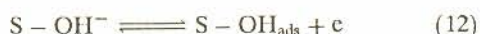
The Q_a (I) decrease by carbonate is not affected by the presence of Li⁺ ions. Increase of Q_a (II) with Li⁺ ion concentration even in presence of carbonate is due to existence of anionic species either as nickelate or nickilite to account for the presence of firmly incorporated alkali metal cations in the oxidised hydrated materials. In presence of CO₃²⁻, diffusion of lithium is favoured while that of H⁺ ion is hindered. The desorption of oxygen molecules and reduction of higher valent oxides in the reverse scan are hindered by carbonates. The conversion of lower valent oxides is not affected by the presence of Li⁺ ions in alkaline carbonate solutions.

The dependence of ZCCP in the reverse scan on Li⁺ ion concentration suggests the penetration of Li⁺ ion on the crystal lattice as an exchange between Li⁺ and H⁺ ion. In the LiOH concentration used, lithium nickelate may be formed which may stabilise the higher valent oxides.

Oxygen evolution reaction

Oxygen evolution occurs on nickel oxide electrodes throughout charge, on overcharge and on standby. Studies on the nickel surface earlier revealed the method of electrode preparation and the past history of the electrode affecting the results [13,14]. On thin anodically formed films, there are two Tafel regions for oxygen evolution, one with a slope of 39-44 mV decade⁻¹ at lower current density and above 0.6V, the slope smoothly changes to 58- 65 mV decade⁻¹ [15]. The low Tafel slope region is coupled with an appreciable pseudo-capacitance of the intermediates. This implies that an electrochemical desorption step is rate controlling with the coverage by intermediates dependent on the potential. The proposed intermediates in the low current density region are Ni(IV) sites on the nickel oxide surface with relatively low coverages.

The observed Tafel slope of 40 mV decade⁻¹ in the present study on nickel suggests that



where S is Ni(III)O - OH and D is Ni(IV) - O - O. In presence of carbonate upto 0.3M in 6.0M KOH, decrease in exchange current density is due to the blocking of the active sites on the oxide by carbonate ion. Enhanced oxygen evolution above 0.4M is due to the adsorption of O⁻ on the carbonate surface which enhances the second electron transfer. Lithium ion in carbonate solution facilitates the formation of nickel (IV) oxides in preference to oxygen evolution. Hence a decrease in exchange current density is obtained.

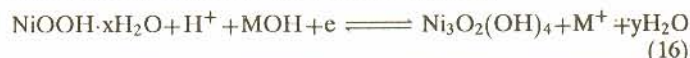
On electrodeposited NiOOH, addition of Li⁺ ion to solution hinders the desorption of O_{ads}⁻ by shifting the oxygen evolution potential to more noble values suggesting that O⁻ competes for the active sites with OH⁻ ion on NiOOH surface. Carbonate ion favours desorption of O_{ads}⁻ and enhances the oxygen evolution reaction.

Application to battery

The battery consists of electrodes of the second kind and electron transfer reactions at each of the electrodes may be



where O and R are oxidant and reductant respectively in the solid state. Studies on pure nickel revealed the step,



and the overall reaction [16,17] may be [0.833NiO₂ · 0.167 Ni(OH)₂] 0.35 H₂O · 0.33 MOH to [0.125 NiO₂ · 0.875 Ni(OH)₂] 0.67 H₂O.

This process involves protonation and dehydration. The appearance of the anodic (I) and the cathodic peak (IV) on electrodeposited NiOOH is due to this redox couple. The peak potential separation between these peaks is a measure of irreversibility. The greater the value of ΔE_p, the more is the irreversibility. Since ΔE_p varies linearly with v (Fig. 14), ΔE_p $v \rightarrow 0$ is used to evaluate the electrode reversibility. In general, carbonate OH⁻ ion (> 1M) and Li⁺ (> 0.23M) favour reversibility [Table II].

TABLE-II: Effect of addition of carbonates, hydroxyl ions and lithium ions on the reversibility of charge storage reaction

Solutions	(ΔE _p) _{v→0} (mV)
6.0M KOH	127.5
6.0M KOH + 0.1M Na ₂ CO ₃	87.5
6.0M KOH + 0.2M Na ₂ CO ₃	95.0
6.0M KOH + 0.3M Na ₂ CO ₃	77.5
6.0M KOH + 0.4M Na ₂ CO ₃	115.0
6.0M KOH + 0.5M Na ₂ CO ₃	75.0
0.5M KOH + 0.1M KOH	200
0.5M KOH + 1.0M KOH	115
0.5M KOH + 6.0M KOH	110
0.5M KOH + 10.0M KOH	90
0.5M Na ₂ CO ₃ + 6M KOH + 0.12M LiOH	132.5
0.5M Na ₂ CO ₃ + 6M KOH + 0.24M LiOH	115.0
0.5M Na ₂ CO ₃ + 6M KOH + 0.36M LiOH	112.5

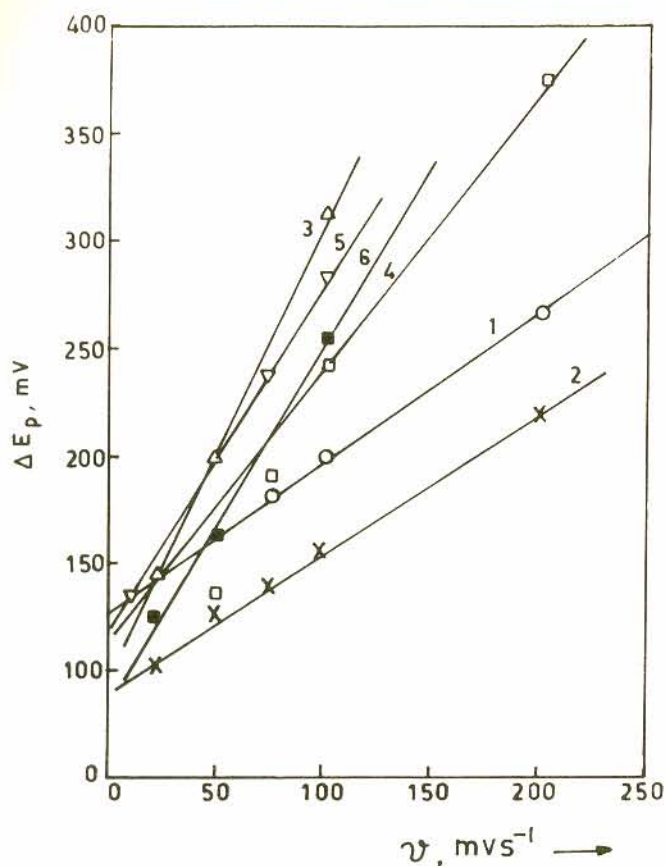


Fig. 14: Typical (ΔE_p) vs ν plot for electrodeposited NiOOH in 6.0M KOH containing different concentrations of carbonate
(1) 0.0M (2) 0.1M (3) 0.2M (4) 0.3M (5) 0.5M (6) 1.0M Na_2CO_3

CONCLUSION

In alkaline carbonate solutions, nickel carbonate formed prevents the oxidation of divalent hydroxides. The diffusion of protons away from the oxide and OH^- ion toward the electrode are hindered. The charge storage reaction is thereby marginally influenced. The oxygen evolution reaction and self discharge are enhanced in the presence of carbonate which in turn may lower the cycle life.

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