Studies on the effect of cobalt addition to the nickel hydroxide electrode

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$Ni(OH)_2$ electrodes are known to take up potassium and lithium ions from electrolytes on cycling. The present study revealed lower levels of adsorption of potassium and lithium in the case of cobalt co-deposited β-nickel hydroxide electrodes although similar uptake patterns were clearly visible. At room temperatures, addition of cobalt has also been found to be advantageous in so far as the electrode performance on repeated cycling in 1 M LiOH + 4 M KOH is concerned. In pure KOH, however, cobalt addition has been found to have a detrimental effect on the life of the electrode although an easier charging process is observed in the initial stages. Increase in the end-of-charge potential in lithiated electrolyte was found to be a direct consequence of lithium adsorption by the cobalt co-deposited β-nickel hydroxide electrodes.

1. Introduction

The use of cobalt as an additive to the nickel hydroxide electrodes of relevance in Ni/Cd batteries has been known for some time [1]. It is generally believed that the presence of cobalt inhibits γ-phase formation [2, 3] thereby allowing for lower values of potassium absorption during the charging process [4]. Cobalt is also believed to be responsible for reducing the oxygen overvoltage and improving the performance of the nickel hydroxide electrodes [5–7]. The present study was directed at observing the effect of cobalt co-deposition on the nickel hydroxide electrodes by measuring the maximum charge potential, lithium and potassium ion uptake and the changes in the performance of the electrodes on repeated cycling in lithiated/non-lithiated electrolytes. Constant current charge/discharge studies, atomic absorption/emission spectroscopy, X-ray and cyclic voltammetry were used in this study in parallel to the earlier study conducted on the pure nickel hydroxide electrodes [8].

2. Experimental details

The experimental set-up, the method of making nickel electrode substrates and the α- and β-nickel hydroxide electrodes are the same as described in the previous study [8]. Cobalt co-deposited α-nickel hydroxide electrodes were electrodeposited onto the cleaned nickel electrode substrates from a nickel nitrate bath containing 5% cobalt nitrate (10 ml 0.05 M $Co(NO_3)_2$ + 190 ml 0.05 M $Ni(NO_3)_2$) by passing a cathodic current of 1 mA cm^{-2} for 10 min. α-Electrodes were then aged in 5 M KOH at 40° C for 5 days thereby giving the cobalt co-deposited β-nickel hydroxide electrodes. The β-electrodes were analysed by atomic absorption and were found to have a Co/Ni atomic ratio between 0.12 and 0.14. Constant current experimentation, atomic absorption/emission studies,

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Table 1. Maximum charging potential of pure and cobalt co-deposited nickel hydroxide electrodes in different electrolytes

Electrode	Electrolyte	Potential (mV)
β-Ni(OH)$_2$	5 M KOH	560
β-Ni/Co hydroxide	5 M KOH	555
β-Ni/Co hydroxide	1 M LiOH + 4 M KOH	580
α-Ni/Co hydroxide	5 M KOH	540

X-ray analysis and cyclic voltammetric studies were carried out as detailed previously [8]. All experiments were conducted at a room temperature of 22 ± 2° C. Hg/HgO electrodes in the same solution as that under investigation were used as the reference electrodes.

3. Results

Constant current charge/discharge cycle results for different electrodes in lithiated and non-lithiated electrolytes are shown in Table 1. The actual shape of the curves is shown in Fig. 1. It is observed that the addition of cobalt to β-Ni(OH)$_2$ electrodes lowers the maximum charge voltage very marginally by 5 mV when the electrolyte is 5 M KOH, but the presence of lithium in the electrolyte more than compensates
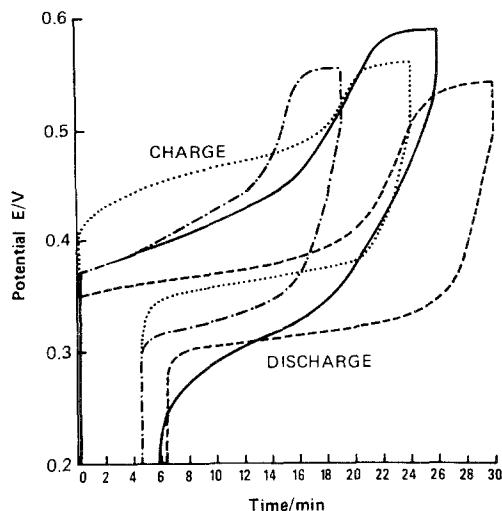

Fig. 1. Constant current charge/discharge curves (cycle 3) of nickel hydroxide and Ni/Co hydroxide electrode at 22° C versus Hg/HgO reference electrode. . . . . ., β-nickel hydroxide in 5 M KOH; — · —, β-Ni/Co hydroxide in 5 M KOH; ——, β-Ni/Co hydroxide in 4 M KOH + 1 M LiOH; — —, α-Ni/Co hydroxide in 5 M KOH.

the loss by increasing the maximum charge voltage from 555 mV to 580 mV. The results are in general agreement with observations of other authors [5, 6]. The cobalt co-deposited α-Ni(OH)$_2$ electrodes are fully charged at 540 mV. There is, however, no sign of γ-phase formation or lithium nickelates in the X-ray diffraction patterns taken for the charged β-electrodes.

Atomic absorption results are shown in Figs 2–5. It is seen that the concentrations of potassium and lithium decrease with increasing washing time to a final stabilization level. The stabilization of the concentration of these foreign ions indicates that they are absorbed/adsorbed by the electrodes during the charge/discharge process. The initial fall, however, is attributed to the washing away of the surplus electrolyte adhering to the surface of the electrodes. Fig. 2 shows that potassium is taken up in greater amounts by pure nickel hydroxide electrodes as compared with the cobalt co-deposited electrodes in both the charged as well as the discharged states in 5 M KOH; this is in agreement with other observations [4]. Furthermore, charged states have a higher potassium concentration than the discharged states. Fig. 3 shows that in lithiated potassium hydroxide electrolyte the potassium uptake by pure and cobalt co-deposited nickel hydroxide electrodes is almost the same level for the charged and discharged states, respectively. This indicates compensation by lithium hydroxide for the losses observed in potassium uptake effected because of cobalt impregnation as shown in Fig. 2. Similar results for the lithium uptake in Fig. 4 corroborate this view. Fig. 5 shows that cobalt co-deposited nickel hydroxide electrodes have a marked preference for lithium over potassium
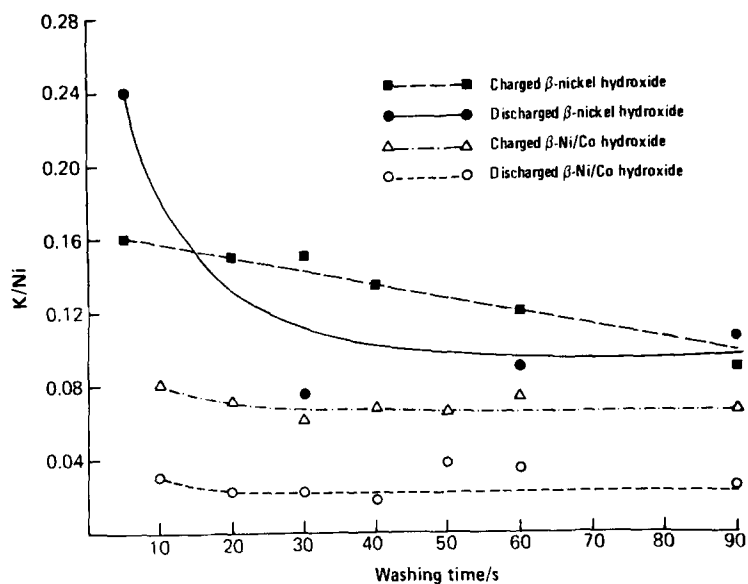
Fig. 2. K/Ni atom ratios of nickel hydroxide and Ni/Co hydroxide in 5M KOH as a function of washing time.

with respect to their original ratio in the electrolyte.

Table 2 gives the anodic peak current potentials of β-Ni/Co hydroxide electrodes along with those of the β-nickel hydroxide electrodes in lithiated and non-lithiated electrolytes. Cyclic voltammograms in Figs 6 and 7 present the pure and the cobalt co-deposited nickel hydroxide electrode cycles in 5 M KOH. It is observed that the addition of cobalt increases the anodic peak current initially, but on repeated cycling the peak current decreases in cobalt co-deposited electrodes as compared with an increase in the case of pure nickel hydroxide electrodes.

Furthermore, it is seen from Table 2 that the β-Ni/Co hydroxide electrodes have an anodic peak current potential 20 mV lower than that of the β-nickel hydroxide electrodes in 5 M KOH, thereby suggesting that the presence of cobalt accounts for an easier charging process in the initial stages. However, a comparison of their 100th cycle results suggests that the presence of cobalt in the β-electrodes results in a more difficult charging process on repeated cycling in 5 M KOH. These are in general agreement with the observations of other authors [6, 7].

Figs 8 and 9 show the cyclic voltammograms of the pure and the cobalt co-deposited β-nickel
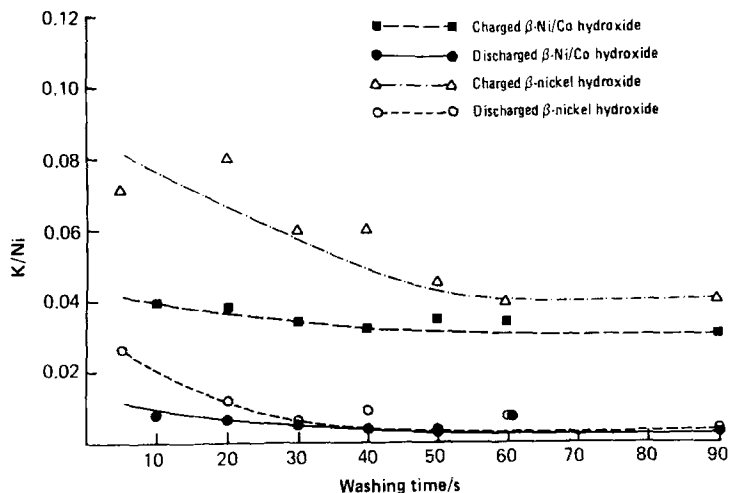

Fig. 3. K/Ni atom ratios of nickel hydroxide and Ni/Co hydroxide in 1M LiOH + 4M KOH as a function of washing time.
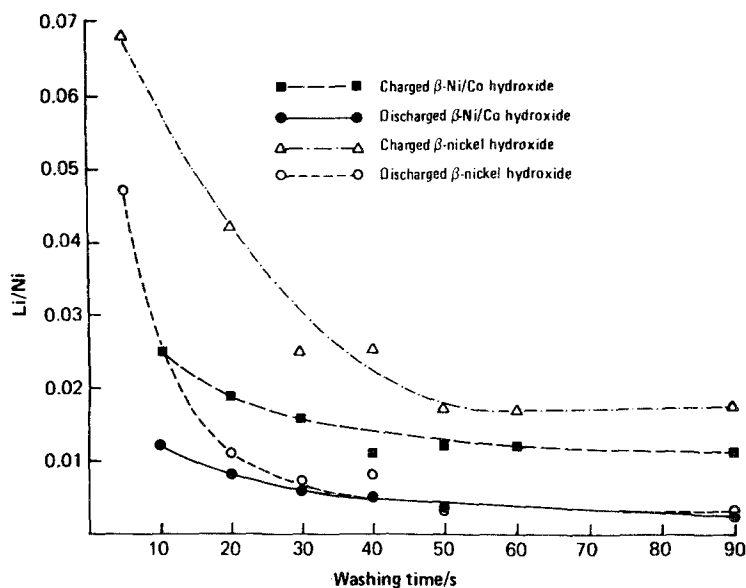
Fig. 4. Li/Ni atom ratios of nickel hydroxide and Ni/Co hydroxide electrodes in 1 M LiOH + 4 M KOH as a function of washing time.
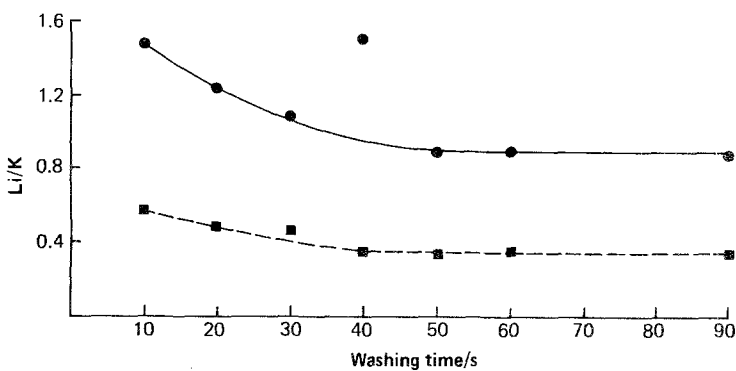
Fig. 5. Li/K atom ratios of β-Ni/Co hydroxide electrodes (■---■, charged; ●—●, discharged) in 1 M LiOH + 4 M KOH as a function of washing time.

Table 2. Anodic peak current potentials of β-nickel hydroxide and β-Ni/Co hydroxide electrodes in different electrolytes at 22 ± 2° C

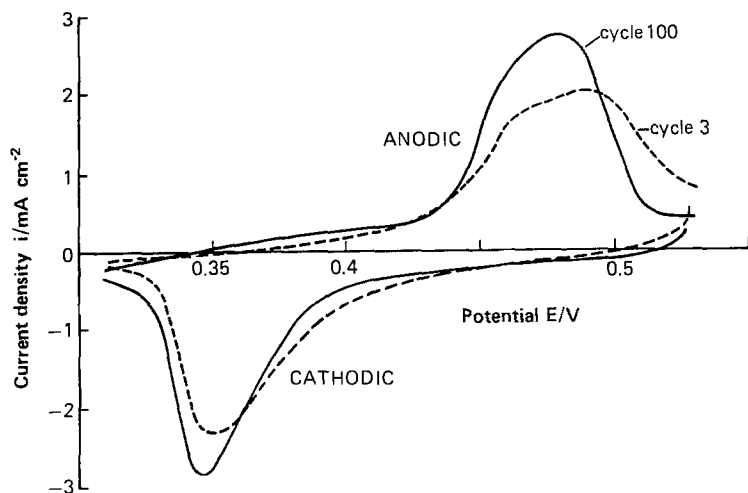| Electrode	Electrolyte	Potential (V)	
		Cycle 3	Cycle 100
β-Ni(OH)$_2$	5 M KOH	0.49	0.48
β-Ni/Co hydroxide	5 M KOH	0.47	0.50
β-Ni(OH)$_2$	1 M LiOH + 4 M KOH	0.47	0.48
β-Ni/Co hydroxide	1 M LiOH + 4 M KOH	0.44	0.46
β-Ni/Co hydroxide	Saturated LiOH	0.46	0.465

Fig. 6. Cyclic voltammograms of charge/discharge cycle of β-nickel hydroxide electrode in 5 M KOH. Sweep rate $1\,\mathrm{mV\,s^{-1}}$.

hydroxide electrodes in 1 M LiOH + 4 M KOH. It is observed from the actual contours and also Table 2 that the presence of cobalt results in a 30 mV easier charging process of the β-electrodes in the initial stages of cycling in the lithiated electrolytes. The 100th cycle anodic peak current potential values of the β-Ni/Co hydroxide electrodes still reflect an easier charging process compared to the corresponding 100th cycle values of β-nickel hydroxide electrodes, thereby suggesting an increased useful life of the electrodes due to the presence of cobalt.

Lower anodic peak current potentials for the β-Ni/Co hydroxide electrodes in 1 M LiOH + 4 M KOH as compared to those in 5 M KOH are observed in Fig. 10, reflecting an easier charging

process due to the presence of a lithiated surface. However, similar anodic peak current values are observed in both the contours. Furthermore, the anodic peak current potential decrease of 30 mV in the initial cycles due to the addition of lithium hydroxide to the electrolyte in the case of β-Ni/Co hydroxide electrodes as compared with the corresponding 20 mV decrease observed for the pure β-nickel hydroxide electrodes, reflects a pronounced beneficial effect of the lithiated surface in the case of β-Ni/Co electrodes due to the presence of cobalt. Fig. 11 shows that high concentrations of lithium do not show any appreciable change in the anodic peak current potentials after repeated cycling, although the electrode becomes more reversible. It is observed
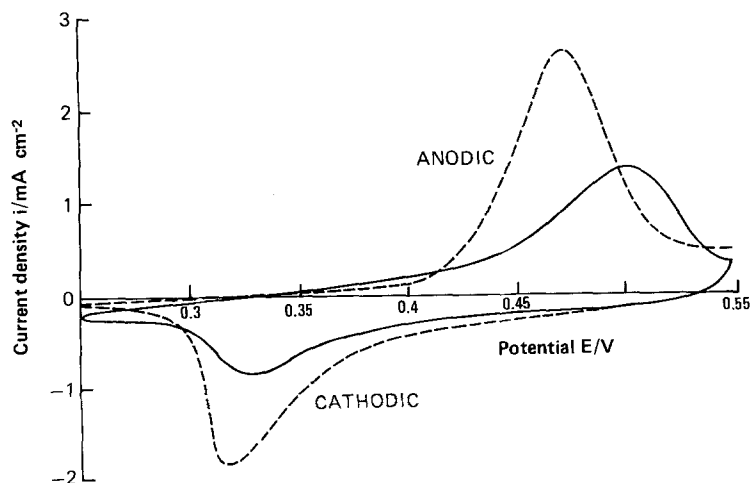

Fig. 7. Cyclic voltammograms of β-Ni/Co hydroxide electrode in 5 M KOH. Sweep rate $1\,\mathrm{mV\,s^{-1}}$. ---, cycle 3; ——, cycle 100.
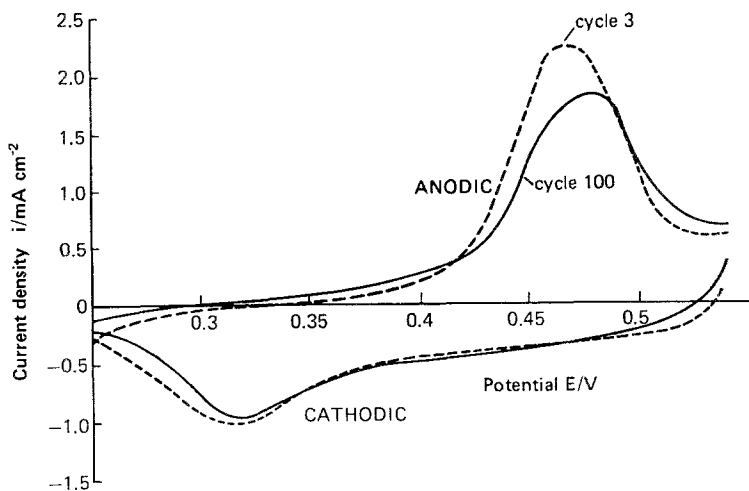
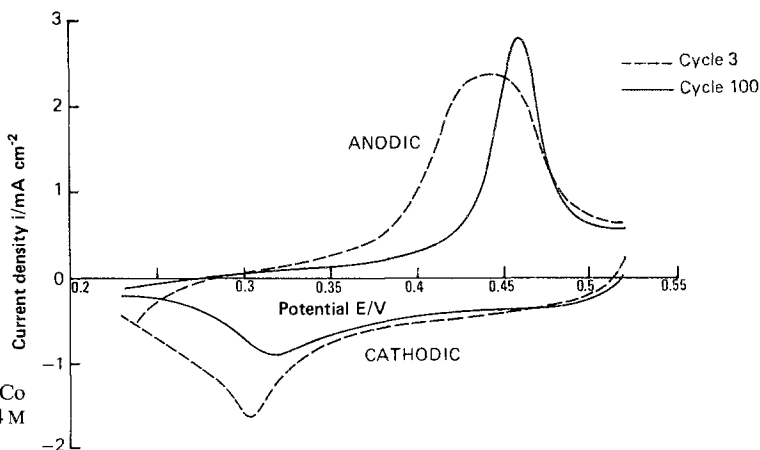Fig. 8. Cyclic voltammograms of β-nickel hydroxide electrode in 1 M LiOH + 4 M KOH. Sweep rate 1 mV s⁻¹.

Fig. 9. Cyclic voltammograms of β-Ni/Co hydroxide electrode in 1 M LiOH + 4 M KOH. Sweep rate 1 mV s⁻¹.
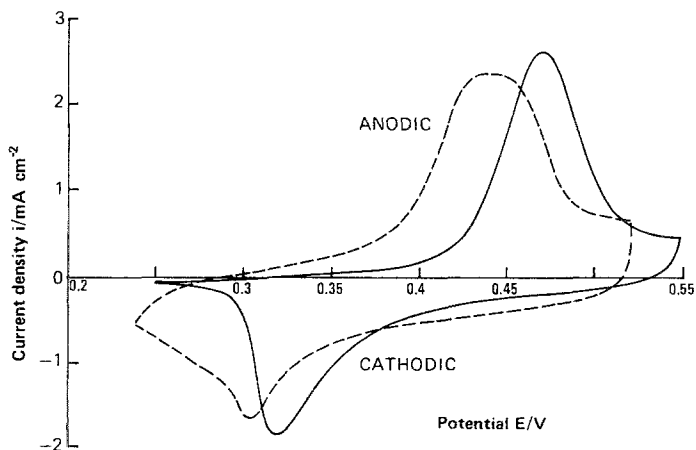
Fig. 10. Cyclic voltammograms (cycle 3) of β-Ni/Co hydroxide electrodes in 5 M KOH (———) and 1 M LiOH + 4 M KOH (– – –). Sweep rate 1 mV s⁻¹.
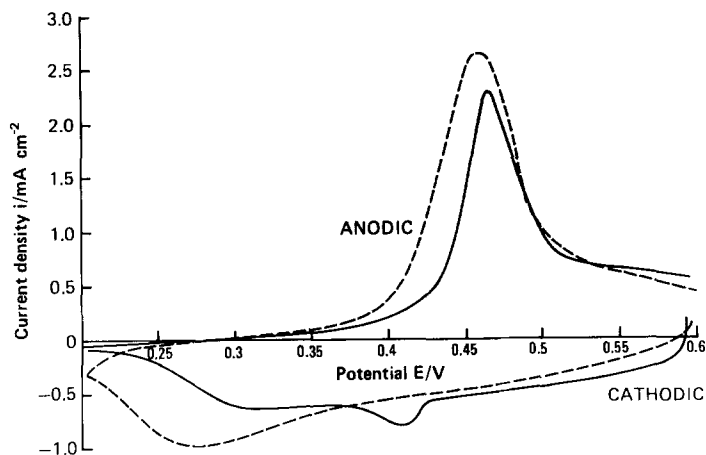
Fig. 11. Cyclic voltammograms of β-Ni/Co hydroxide electrode in saturated LiOH. Sweep rate $1\,mV\,s^{-1}$. ---, cycle 3; ——, cycle 100.

from Table 2 that the increased lithium concentration results in a shift in the anodic peak current potential to values higher than those in $1\,M$ LiOH $+ 4\,M$ KOH, thereby resulting in a more difficult charging process in saturated LiOH.

Since the 100 cycles were completed in each case in a relatively short span of around 17 h, any effects on account of ageing of the electrodes during repeated cycling were not observed.

4. Discussion

The study shows that lithium and potassium ions are taken up and retained firmly by the charged/discharged cobalt co-deposited nickel hydroxide electrodes. In the absence of any evidence of γ-phase availability, which is known to have lattice space to take up lithium and potassium ions, it is reasonable to believe that such ions are surface adsorbed by the β-phase materials. A lower concentration of potassium in cobalt co-deposited nickel hydroxide electrodes as compared to the pure nickel hydroxide electrodes in $5\,M$ KOH is attributed to the lower availability of the nickel hydroxide surface for adsorption due to the presence of $Co(OH)_2$ on the surface of the electrodes.

The constant current charge/discharge studies suggest that in lithiated electrolytes the cobalt co-deposited electrodes show increased oxygen overvoltage compared with pure nickel hydroxide electrodes, which may be due to a lithiated surface as suggested in the case of β-nickel hydroxide electrodes [8]. Cyclic voltammetric

results prove conclusively that the presence of cobalt in nickel hydroxide electrodes improves the performance and life of the electrodes in lithiated electrolytes. This also corroborates the results of constant current cycling.

Acknowledgements

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