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# Some effects of the addition of cobalt to the nickel hydroxide electrode

R. D. ARMSTRONG, G. W. D. BRIGGS, E. A. CHARLES

*Electrochemistry Research Laboratories, Department of Physical Chemistry, Bedson Building, University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, UK*

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The action of cobalt upon the characteristics of the nickel hydroxide electrode has been investigated by constant current, linear potential sweep and EDAX methods. It was found that cobalt raises the oxygen overpotential and promotes greater utilization of the active material, although major additions of cobalt were observed to lower the working potential of the electrode. It was also found that cobalt prevented any significant loss of electrode capacity when the system was poisoned with iron.

## 1. Introduction

Since Edison [1] patented the addition of cobalt hydroxide to the positive plate material of nickel–cadmium as well as Ni–Fe cells in 1914, there have been numerous studies concerning the role of cobalt in such batteries [2, 3, 4]. This research has produced some conflicting results, probably due to the various types of electrodes and cells used in the studies. As commercial nickel hydroxide is of higher purity than formerly ($< 0.5\%$ Co at the present time), many battery manufacturers are now having to buy and add increased quantities of cobalt separately to their electrodes. It is thus desirable for economic reasons to know the optimum amount of cobalt necessary to maximize the performance of the electrode. There has been a general increasing interest in cobalt, particularly in Japan and several patents have been obtained recently upon nickel–cadmium positive plates [5, 6, 7].

It is known that, after initial oxidation, cobalt remains in the (III) state within a nickel hydroxide lattice [8] and that, as a result, it does not contribute through the Co(II)/Co(III) couple to the capacity of the electrode. The additive allows the nickel to reach a higher oxidation state upon charging, which is similar to the effect of using a lithiated electrolyte in the cell, where nickel(IV) species can be formed as indicated by Tuomi [9]. Barnard and Randell [10], among others, also refer to the existence of Ni(IV) species in the $\gamma$ phase active material, although there is still some controversy about the possible oxidation state range. In this paper we have examined thin film electrodes and have found evidence for the formation of substantial amounts of Ni(IV) in the oxidized active material. We have also looked at the effectiveness of cobalt as an antidote to iron poisoning [11].

## 2. Experimental details

Electrodes were prepared from $2 \times 2$ cm square, thin sheets of nickel, to which a nickel wire was spot welded to provide electrical contact. A nickel hydroxide or homogeneous nickel and cobalt hydroxide film was electrodeposited onto this substrate by cathodic polarization at $1\,\mathrm{mA\,cm^{-2}}$ for 10 min from a 0.05 M nickel nitrate solution or a 0.05 M nickel and cobalt nitrate solution respectively. This produces a thin film deposit of hydrated green alpha phase material. The electrodes were then given a single constant current charge and discharge in 5 M KOH to oxidize any cobalt present to the Co(III) state. To convert this, now black, hydrate to the beta phase, usually found in normal working cells, the electrodes were placed in a PTFE container containing 5 M KOH or 5 M KOH saturated with cobalt and stored for 120 h at a temperature of 40° C.

For the experimental measurements a three-compartment glass cell was used. Two platinum counter electrodes were placed in the side chambers and the working electrode was positioned in the centre. Hg/HgO reference electrodes were used for all the measurements, made up in the same 5 M alkali solution as that used in the working electrode cell.

For the constant current tests a cycle current of $0.2\,\mathrm{mA\,cm^{-2}}$ was used and electrodes were cycled until they reached a stable condition (usually in six cycles).

Linear potential sweep experiments were made using a potentiostat and waveform generator controlled by an Apple II microcomputer. A sweep rate of $1\,\mathrm{mV\,s^{-1}}$ was used and electrodes were cycled until the shape of the voltammogram became constant.

EDAX measurements were carried out using a JEOL JSM35 scanning electron microscope.

Solutions were prepared using Analar reagents and the iron saturated solution was prepared by boiling fresh ferric hydroxide with alkali and filtering the resulting solution to remove any solids. The concentration of iron in this freshly prepared solution was estimated to be approximately $5 \times 10^{-5}$ M [12].

## 3. Results

Fig. 1 shows the percentage cobalt established to be in

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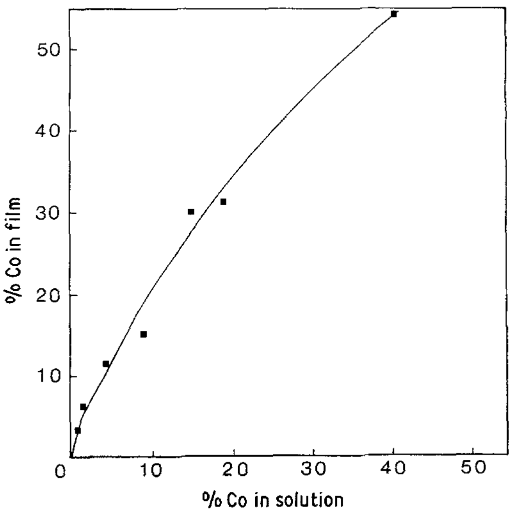

Fig. 1. Percentage cobalt found in cathodically deposited thin films, as determined by EDAX, over half the composition range.

the thin film by EDAX plotted against the percentage cobalt in the deposition solution. It can be seen that cobalt is preferentially deposited onto the substrate across the cobalt range and that at low percentages the cobalt level in the film is roughly double that in the solution. Using this information, a series of electrodes containing cobalt at various levels from 0 to 100% were prepared for testing.

Fig. 2 shows typical constant current charge and discharge curves for 0 and 12% cobalt electrodes. The 12% cobalt electrode exhibits a higher oxygen overpotential, a greater capacity, a slightly increased gradient across the charge and discharge potential plateau region and a general depression of the plateau potential. These trends were observed up to approximately 45% Co where the capacity begins to drop, as would be expected if the cobalt does not contribute to discharge.

The increase in the top of charge potential is shown clearly in Fig. 3 where data from several electrodes have been averaged for each cobalt level studied. It can be seen that there is a complex relationship between cobalt content and the oxygen evolution potential but that the general trend is to increase the potential and hence increase the oxidation level of the nickel. This series of results does not agree with the limited work of Sood [13] who examined a 12% cobalt electrode.

The corresponding electrode capacity results are shown in Fig. 4 along with the theoretical capacities for a one- or two-electron exchange reaction in the nickel component of the material, the latter being represented by solid lines. The figure shows that the maximum possible oxidation change occurs in electrodes with more than 40% cobalt present, for which the observed capacities require a conversion from Ni(IV) to Ni(II).

Beyond 40% Co the plot indicates that the nickel species are reaching a deeper average level of discharge than usually observed [14], possibly due to the conductivity of the cobalt(III) material. During discharge, nickel(II) species accumulate at the hydroxide/electrolyte interface. These species are insulating and consequently prevent discharge of the crystallite core; however, the presence of Co(III) may maintain the current path allowing more complete discharge of the core material. The capacity data is in reasonable agreement with the work of Januszkiewicz [15] who found a 50% capacity improvement in batteries containing between 20 and 40% cobalt.

Fig. 5 shows typical linear potential sweep curves for electrodes exposed to iron-saturated electrolyte. It can be seen that cobalt-containing electrodes maintain a larger capacity and it has also been observed that they reach a maximum in capacity within a lower number of cycles than pure nickel hydroxide electrodes under the same conditions. EDAX studies of the cycled electrodes indicate that iron is incorporated into the active material whether cobalt is present or not, which is similar to the behaviour of lithiated systems [16].

From constant current experiments it was found

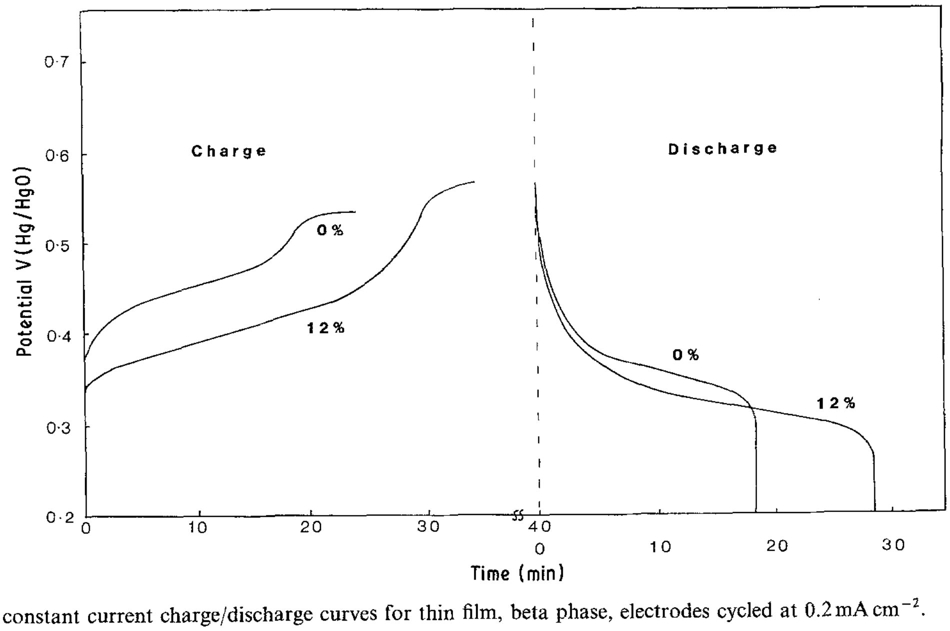

Fig. 2. Typical constant current charge/discharge curves for thin film, beta phase, electrodes cycled at 0.2 mA cm$^{-2}$.

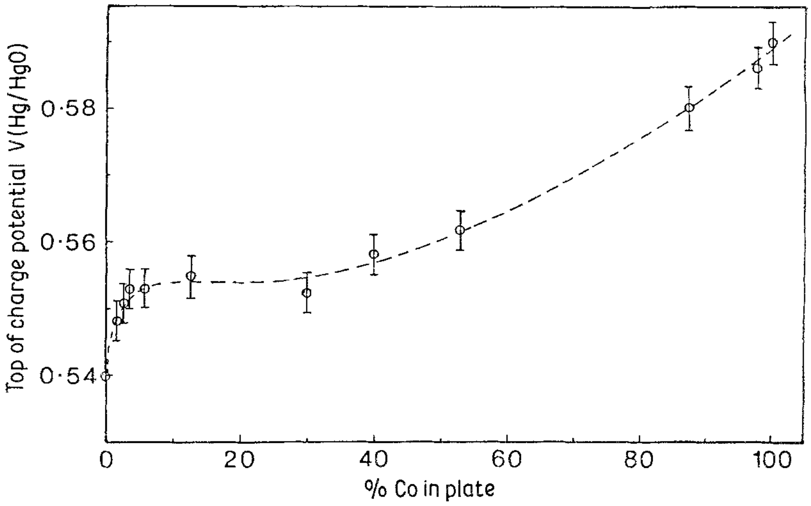

Fig. 3. Variation of top of charge potential with cobalt content from constant current cycles at 0.2 mA cm$^{-2}$ of thin film, beta phase, electrodes.

that the presence of iron depressed the oxygen overpotential by some 50 mV, but that electrodes containing cobalt suffered a smaller drop in overpotential of approximately 30 mV. The capacity data were in good agreement with the linear sweep results observed.

## 4. Discussion

The results clearly illustrate the main action of cobalt in the nickel hydroxide electrode. The most beneficial aspects are (i) the raising of the oxygen overpotential; (ii) the apparent increase in the depth of discharge and (iii) the nullification of the effect of iron poisoning which is closely related to the oxygen overpotential. Several possible mechanisms for oxygen evolution at the electrode surface have been proposed but most begin with the step

$$\mathrm{OH}^-_{\mathrm{aq}} \longrightarrow \mathrm{OH}_{\mathrm{ads}} + e^-$$

possibly followed by

$$\mathrm{OH}_{\mathrm{ads}} + \mathrm{OH}^-_{\mathrm{aq}} \longrightarrow \mathrm{O}^-_{\mathrm{ads}} + \mathrm{H_2O}$$

$$\mathrm{O}^-_{\mathrm{ads}} \longrightarrow \mathrm{O}_{\mathrm{ads}} + e^-$$

$$2\mathrm{O}_{\mathrm{ads}} \longrightarrow \mathrm{O}_2\uparrow$$

as suggested by Bronoel and Reby [17]. In this process either the adsorption of hydroxide ions or the oxidation of $\mathrm{O}^-_{\mathrm{ads}}$ can be the rate determining step, depending upon the potential.

The action of cobalt here is likely to be a surface effect where the additive alters the enthalpy of chemisorption. It is known that such reactions involving an adsorbed intermediate exhibit 'volcano-type' characteristics when reaction current is plotted against $\Delta G^{\ddagger}_{\mathrm{ads}}$ [18]. The change in thermodynamics thus alters the kinetics of the process. Whether cobalt increases or decreases the enthalpy of adsorption is not known;

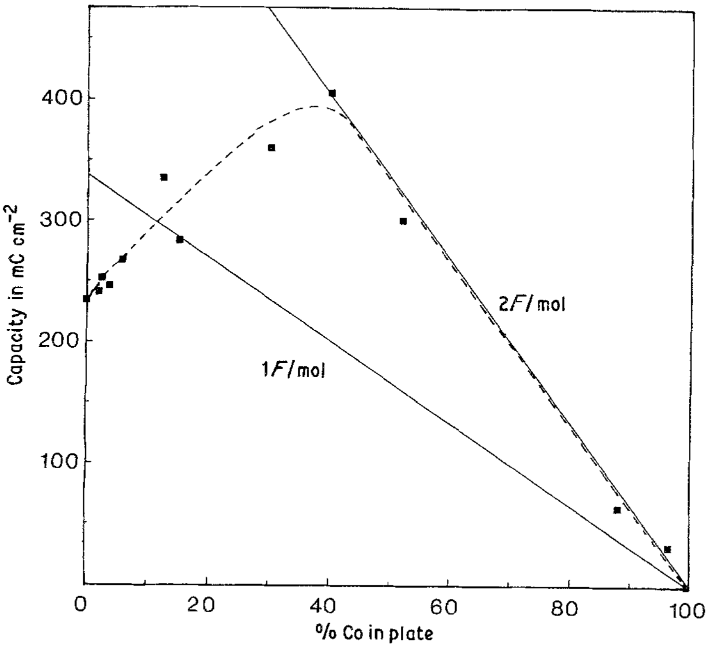

Fig. 4. Comparison of theoretical and actual capacity results obtained by constant current cycling of thin film, beta phase, electrodes at 0.2 mA cm$^{-2}$.

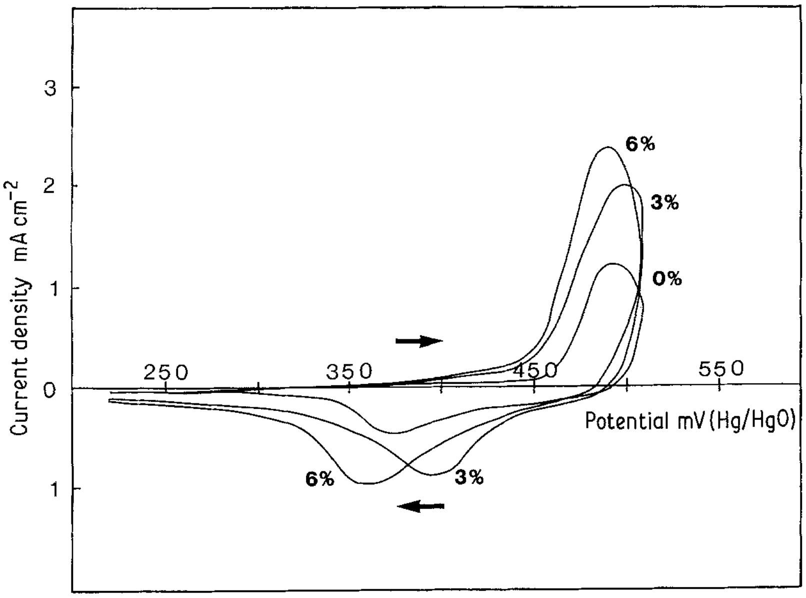

Fig. 5. Typical linear potential sweep curves for thin film, beta phase, electrodes after 150 cycles at 1 mV sec$^{-1}$ in iron poisoned 5 M KOH.

however, it is apparent that iron(III) exhibits the opposite influence.

This benefit, when coupled with the decrease in the oxidation potential of the active material in the presence of cobalt, produces a considerable overpotential, as shown in Table 1. The depression of the charge and discharge potentials is generally considered detrimental as the cell operating voltage is lowered. However, for high temperature applications, where the oxygen evolution potential normally begins to merge with the oxidation potential, it may be beneficial in maintaining the charging efficiency.

For comparison with the data in Table 1, it may be noted that the top of charge potential is increased by approximately 20 mV when a 1 M LiOH/4 M KOH electrolyte is used, in the absence of cobalt.

The action of cobalt in this system is clearly complex; however, this study indicates improvements in electrode performance up to 40% cobalt. Because of the relatively large cost of this additive it is envisaged that it will only be used at such levels in special application batteries.

## 5. Conclusions

(1) Cobalt increases the oxygen overpotential, thus allowing further oxidation of the nickel species.

(2) The utilization of the nickel species increases up to 40% cobalt current, where a Ni(II) to Ni(IV) reaction occurs which is a much larger oxidation state range than usually achieved in the electrode.

*Table 1. Changes in overpotential from constant current experiments in 5 M KOH electrolyte*

| *% cobalt in the film* | *Top of charge* *E*, mV (Hg/HgO) | *Half charge* *E*, mV (Hg/HgO) | *Overpotential in* mV |
|---|---|---|---|
| 0 | 540 | 474 | 66 |
| 2 | 548 | 472 | 76 |
| 4 | 552 | 455 | 97 |
| 6 | 554 | 452 | 102 |
| 12 | 555 | 428 | 127 |

(3) Cobalt decreases the effect of iron poisoning of the system to a level similar to that observed in lithiated electrolyte.

(4) These effects can be detected even with quite small additions of cobalt where it is economically feasible for commercial use.

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## References

[1] T. A. Edison, US Patent 1 083 356 (6 June, 1914).

[2] W. R. Scott and D. W. Rusta, 'Sealed-Cell Nickel–Cadmium Battery Applications Manual', NASA reference publication, 1052 (Dec., 1979).

[3] O. G. Malandin, A. V. Vasev, P. N. Bityutskii, I. S. Shamina and G. V. Suchkova, 'Effect of cobalt on the chemical and phase composition of nickel oxide electrodes', *Soviet Electrochem.* **14** (1977) 74.

[4] R. N. Turner, 'An electroanalytical study of the ageing of nickel hydroxide and related electrodes', Ph.D. thesis, Newcastle University (July, 1982).

[5] Sanyo Electric Company, Japanese Patent JP 59 163 753 (14 Sept., 1984).

[6] H. Yasuda, Japanese Patent JP 60 170 161 (3 Sept., 1985).

[7] M. Oshitani, Japanese Patent JP 61 124 061 (11 June, 1986).

[8] R. G. Gunther and S. Gross, 'The Nickel Electrode', Proceedings of the Symposium, The Electrochem. Soc. (1982).

[9] D. Tuomi, 'The forming process in nickel positive electrodes', *J. Electrochem. Soc.* **112** (Jan., 1963) 1.

[10] R. Barnard and C. F. Randell, 'Studies concerning charged nickel hydroxide electrodes VIII', *J. Appl. Electrochem.* **13** (1983) 97.

[11] D. A. Corrigan, 'The catalysis of the oxygen evolution reaction by iron impurities in thin film nickel oxide electrodes', *J. Electrochem. Soc.* **134** (1987) 377.

[12] C. F. Baes and R. E. Mesmer, 'The Hydrolysis of Cations', Wiley Interscience (1976).

[13] A. K. Sood, 'Studies of the effect of cobalt addition to the nickel hydroxide electrode', *J. Appl. Electrochem.* **16** (1986) 274.

[14] C. W. Tobias, 'Advances in Electrochemistry and Electrochemical Engineering', Vol. **5**, Wiley Interscience (1967).
[15] S. Januszkiewicz, 'Addition of Cobalt to Nickel–Cadmium Batteries', Proceedings of the 13th Annual Power Sources Conference, USA (May, 1959).
[16] R. D. Armstrong, G. W. D. Briggs and M. A. Moore, 'The effect of lithium in preventing iron poisoning in the nickel hydroxide electrode', *Electrochim. Acta* **31** (1986) 25.
[17] G. Bronoel and J. Reby, 'Mechanism of oxygen evaluation in basic medium at a nickel electrode', *ibid.* **25** (1980) 973.
[18] Southampton Electrochemistry Group, 'Instrumental Methods in Electrochemistry', Ellis Horwood Pub. (1985).