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SOME EFFECTS OF COBALT HYDROXIDE UPON THE ELECTROCHEMICAL BEHAVIOUR OF NICKEL HYDROXIDE ELECTRODES

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Summary

The effects of cobalt addition upon the behaviour of the nickel hydroxide electrode have been studied using linear potential sweep, EDAX, scanning electron microscopy, and X-ray analysis. Thin film, homogeneous electrodes prepared by cathodic deposition from nitrate solutions containing 0 - 100% cobalt were examined and were found to exhibit a change in oxidation level achieved by the nickel along with a change in film structure.

The nickel component reached a maximum oxidation level of (IV) when around 50% cobalt was present and the electrode capacity was also maximised at this level of additive.

Evidence of a two-step oxidation process was observed over a 25% - 75% cobalt range, and the changes in electrode behaviour have been shown to be related to the film morphology.

X-ray analysis showed that the addition of cobalt stabilised the alpha- and gamma-phases of the active material.

Zusammenfassung

Die Einflusse des Kobaltzusatzes bei der Nickelhydroxidelektrode wurden mit linearer Potentialvariation, EDAX sowie SEM untersucht. Homogene Dunnschichtelektroden (durch Kathodenablagerung ans Nitratloosungen, 0 - 100% Kobalt, dargestellt) wiesen eine Nickeloxidationstufenanderung zusammen mit einer Anderung der Schichtstruktur vor.

Bei einen 50%-Kobaltzusat erreichte der Nickelkomponent seine maximale Oxidationsstufe von IV; unter diesen Umstanden wurde auch die Elektrodenkapazitat maximiert.

Im Bereich 25 - 75% Kobalt wurde ein zweistufiger Oxidationsprozess beobachtet. Die Wandlingen der Elektrodeneigeneschaften hangen mit der Schichtstruktur zusammen.

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Introduction

Over the years there has been considerable discussion about the mechanism of the redox process undergone by the nickel hydroxide electrode of the nickel–cadmium and nickel–iron battery systems [1]. In particular, the range of oxidation states through which the active material passes during cycling has been in some doubt. This confusion is compounded when additives such as lithium [2] or cobalt [3] are used.

This present work is concerned with cobalt addition to the electrode; however, whereas most previous studies have been confined to compositions up to 15% cobalt, this work examines the entire cobalt/nickel range in an attempt to elucidate the reaction processes occurring. Most researchers have not exceeded the 15% cobalt level due to the relatively high cost of the additive when compared with that of the active component. Indeed, battery manufacturers typically add just a few per cent of cobalt, except in special cells for military or space applications where high performance is required [4].

Earlier workers have observed increases in electrode capacity and in the oxygen overpotential when cobalt is added to the nickel hydroxide but have not clearly shown the nature of the capacity increases. The improved performance has been explained as being due to (i) increased charging efficiency as a result of reduced oxygen evolution during oxidation [5], or (ii) due to better conductivity through the active material [5] giving rise to greater utilisation, or possibly (iii) due to an increased oxidation state range (as indicated by our earlier work [6]).

By examining the complete nickel/cobalt composition range we have found evidence for the formation of large amounts of Ni(IV) species when cobalt is present above 25%. We have also observed that the oxidation of the active material occurs in two well-defined steps. The trends in electrode performance across the composition range are associated with alterations in the film morphology and a change in the relative stability of the nickel hydroxide phases present.

Experimental

Electrode substrates were prepared from 2×2 cm square, thin sheets of nickel, to which a nickel wire was spot welded to provide electrical contact. A nickel hydroxide, a homogeneous nickel and cobalt hydroxide, or a cobalt hydroxide film, was electrodeposited onto this substrate by cathodic polarisation at 1 mA cm^{-2} for 10 min from a 0.05 M nickel nitrate, a 0.05 M nickel and cobalt nitrate, or a 0.05 M cobalt nitrate solution, respectively. This produced a thin film deposit of hydrated α-phase material. The electrodes were then given a single constant current charge and discharge in 5 M KOH at 0.2 mA cm^{-2}, to oxidise any cobalt present to the Co(III) state. To convert this now dark brown or black hydrate to the β-phase usually found

in normal working cells, the electrodes were placed in a PTFE vessel containing 5 M KOH or 5 M KOH saturated with cobalt and stored for 120 h at a temperature of 40 °C.

A three-compartment glass cell was used for the experimental measurements. 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 with a Luggin capillary in the region of the working electrode. They were made up in the same 5 M alkali solution as that used in the working electrode cell.

Linear potential sweep experiments were performed using a potentiostat and waveform generator controlled by a microcomputer. Sweep rates from 1 mV s^{-1} down to 0.01 mV s^{-1} were used and electrodes were given several forming cycles before slow-sweep data were recorded.

EDAX, digital mapping and scanning electron micrograph results were obtained and specimens were prepared by critical-point drying with CO_2 (T_c = 304 K and P_c 73 atm) [7].

X-ray powder photographs were obtained for electrodes in various states of charge using Fe Kα radiation.

Solutions were prepared from AnalaR reagents and triple-distilled water.

Results

Figure 1 shows some typical linear potential sweep curves for β-phase electrodes of low, medium, and high cobalt content (as determined by EDAX). At low cobalt levels, or when cobalt is absent from the system,
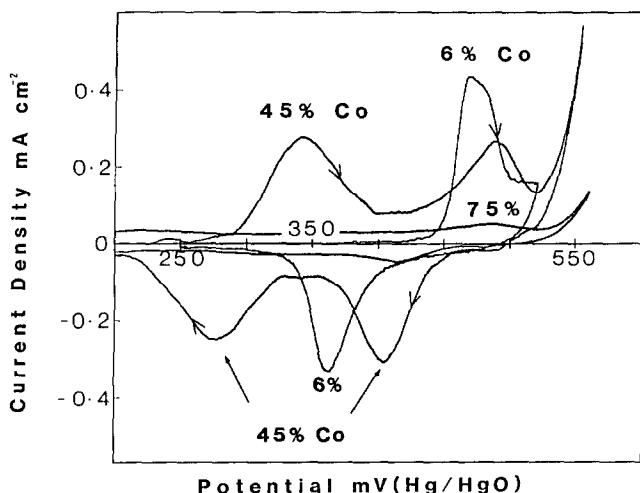

Fig. 1. Linear potential sweep curves for β-phase thin film electrodes containing 6, 45 and 75% cobalt, after a few cycles at 0.1 mV s^{-1}.

linear potential sweep experiments revealed a single oxidation peak around 480 mV (Hg/HgO) upon charging, followed by oxygen evolution above 520 mV and a single reduction maximum around 360 mV during discharge. At higher levels of cobalt, 25 - 75%, however, the experiments showed two oxidation maxima and two distinct reduction maxima. The oxidation peak separation increased with cobalt content until the peak magnitudes decreased below a measurable level; a similar trend was observed between the reduction maxima. The linear potential sweep curves are complementary to the small discontinuities in constant current charge/discharge curves observed at high cobalt levels in our earlier work [6].

It may also be noted that as the cobalt content increases, the potential range over which charge may be accepted, or returned, by the electrode, was extended. This complements the observation of steeper charging and discharging regions during constant current cycling [6].

Figure 2 shows how the electrode capacity derived from linear sweep experiments compares with constant current charging data obtained earlier [6]. These results show a marked increase in electrode capacity, reaching a maximum around 50% cobalt and diminishing as more cobalt is added, illustrating the electrocatalytic nature of the additive. The data suggest that the utilisation of the nickel component is increased up to a 2 Faraday per mole level, as shown by the higher of the two theoretical, solid, lines on the diagram. Thus the pairs of oxidation and reduction maxima observed during linear sweep experiments on high cobalt content electrodes may be due to a Ni(II)/Ni(III), Ni(III)/Ni(IV) reversible reaction process. This concept is
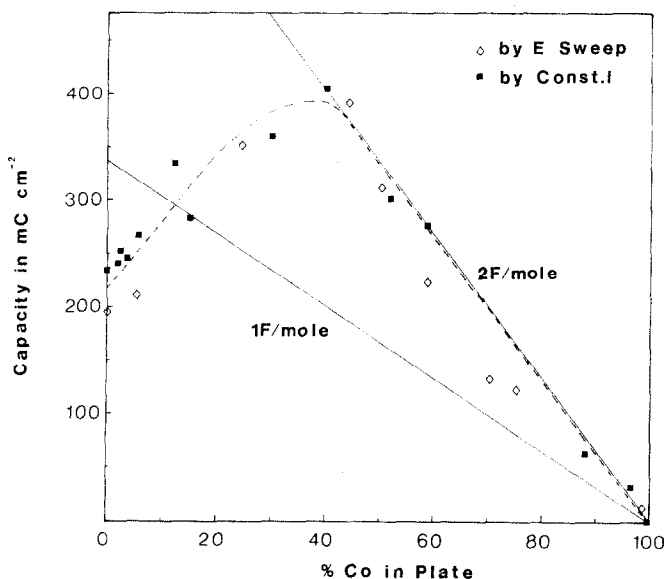

Fig. 2. Graph of electrode capacity *vs.* cobalt content obtained from linear potential sweep and constant current charging experiments.

supported by the observation of the Co(II)/Co(III) redox maxima near 170 mV, which is of a small magnitude. The apparent irreversibility of the oxidation of Co(II) compared with the Ni(II)/Ni(III) redox has been observed by several researchers and it has been suggested that resistive filming of the species prevents reduction of the Co(III) initially formed [8].

The possibility of one of the redox processes being related to a cobalt reaction may be discounted, because each component of the oxidation, or reduction, curve is of approximately the same integrated area across a considerable range of Co/Ni compositions. Had the cobalt been cycled between redox states, then the proportion of additive would have been related to the individual maxima capacity ratios.

Another interesting feature of the data is the apparent stability of the Ni(III) species; instead of observing a simple one-step process between Ni(II) and Ni(IV), a clearly defined intermediate state is seen.

Phase changes giving rise to multiple peak, oxidation or reduction, linear potential sweep curves have been recorded by several researchers working on the nickel hydroxide electrode [9], although they are often transitory features. The peaks have been related to α-, β- or γ-phase growth. The peak separation in these experiments has generally been less than 100 mV and often nearer 50 mV, whereas the current work has resulted in peak separations of up to 200 mV at high cobalt levels. These results, in this case, strengthen the designation of the peaks to various oxidation states rather than to different phases.

Finally, EDAX digital mapping of the electrode surface showed the films to be homogeneous, with no evidence of Ni/Co phase segregation which might have resulted in double peak linear sweep curves.

The role of cobalt in producing such a marked change in the utilisation of the active component can be partially explained by the electron micrographs shown in Fig. 3. Micrograph 3(a) shows a pure nickel hydroxide electrode film after ageing and several constant current charge/discharge cycles. The structure observed is thought to more closely resemble that of the film when immersed in electrolyte, due to the application of a critical-point drying technique whereby the film is preserved without significant contraction or cracking of the surface. Previous workers have published electron micrographs which exhibit cracking or crazing of the electrode film [10]. In micrograph 3(a), the film is seen to be essentially nodular, which was confirmed by stereoscopic pictures of the surface, with small quantities of inter-nodular filaments. The nodules were approximately 0.6 μm in diameter and displayed some surface features of a net-like nature. In comparison with earlier, unpublished, studies the film appeared, generally, to be more open and porous.

As cobalt was added to the system a gradual change in morphology occurred, the film becoming increasingly more net-like with the nodules decreasing in size until, at approximately 50% cobalt, structure 3(b) was observed. Some small, slightly angular, nodules which are less than 0.3 μm dia. can still be seen in these samples. This very open, net-like film presents
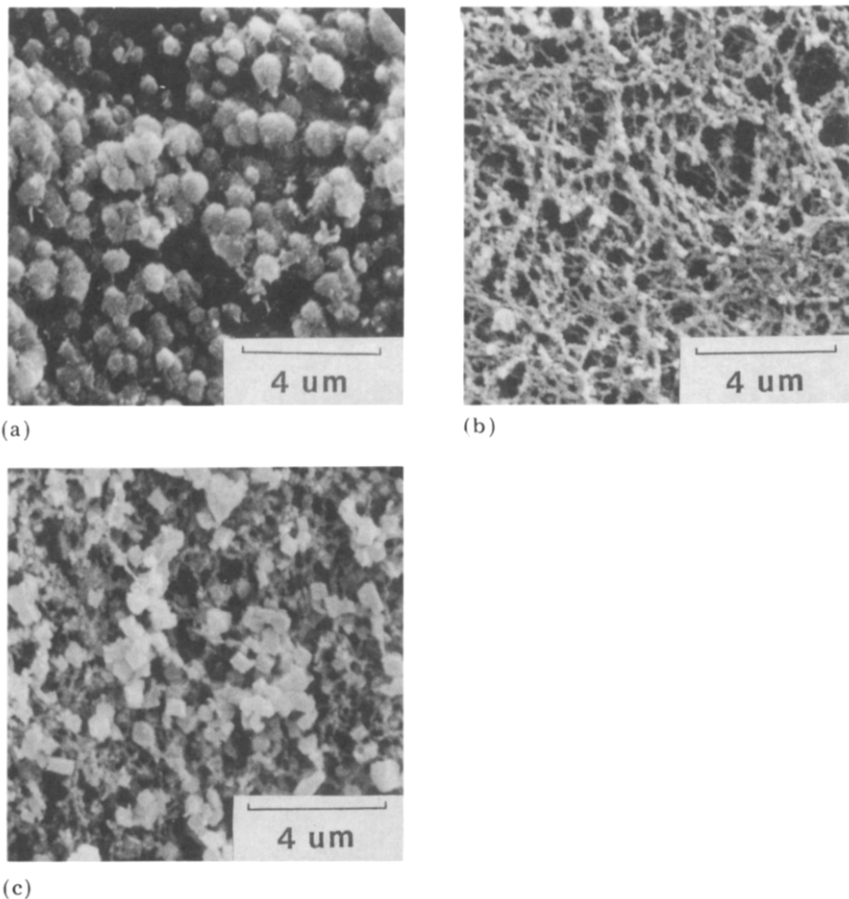
Fig. 3. Electron micrographs of typical β-phase electrode films after several cycles (magnification $\times 7500$): (a) nickel hydroxide electrode; (b) 45% cobalt electrode; (c) cobalt hydroxide electrode.

a much larger surface area to the electrolyte than it does in the absence of cobalt, which will undoubtedly improve the ease of charge and discharge of the material; the structure observed is reminiscent of sintered plaque electrode surfaces [11]. It should be noted that such structural alterations may have greater significance in thicker films and commercial electrodes.

Beyond the 50% cobalt level the film structure becomes more dense, with an increasingly flaky appearance. Angular nodules develop, growing in size and number until the 100% level is reached, as shown in Fig. 3(c). Stereoscopic pictures revealed that the particles were essentially cubic and of a similar size to the nickel hydroxide nodules in Fig. 3(a). The cubic structures have a relatively smooth surface and are inter-connected by filaments in a similar manner to that observed for the nickel hydroxide material. As mentioned earlier, the Co(III) species will not readily reduce, and thus the

essentially Co(III) structure observed in Fig. 3(c) might well differ from the predominantly Ni(II) film shown in Fig. 3(a). Previous SEM studies have revealed no structural changes due to cobalt addition because they generally have not exceeded the 10% Co level below which the structure is essentially nodular, with only slight indications of net-like features [12]. Wang *et al.* [13], however, report the growth of needle-like crystals on 7.6% cobalt electrodes during cycling, which may be related to the structure observed in these experiments.

A brief study of the morphology of α-phase electrodes was performed which revealed similar results to those already described. However, some caution in the interpretation of such data is required because β-phase nickel hydroxide is basically dehydrated α-phase material, and this transformation may have occurred in such a thin film during critical-point drying.

The two-step oxidation and reduction processes, along with the two Faraday per mole capacity data when large amounts of cobalt are present, indicate a reaction process where almost complete reduction of the active material to Ni(II) and nearly total oxidation to Ni(IV) occurs. The extent to which these reaction processes go to completion may well be related to the structural alteration of the film, in that large surface area changes occur. It may also be noted that the cathodic deposition processes used to prepare electrodes are themselves a subject of study [14] and that, depending upon the mechanism accepted, some margin of error may exist between the quantity of material thought to be deposited onto the electrode and that actually found. The presence of considerable amounts of Ni(IV) species, however, is still required to account for the results, probably in the form of a complex, or as $NiO_2 \cdot nH_2O$, or perhaps even in a more elaborate structure such as that proposed by Jungner at the turn of the century [1].

X-ray analysis of 45% Co, aged electrodes, showed a 7 - 8 Å d-spacing which is indicative of α-phase material, containing intercalated water layers. Cobalt thus appears to stabilise the α-phase which, in the absence of the additive, readily transforms to the β-phase structure. Electrodes which were charged also gave a high spacing in their X-ray patterns due to γ-phase intercalated water. The larger electrode capacity of α-phase nickel hydroxide compared with β-phase material has long been known [15] and this observation is consistent with the increases in capacity we have found.

Discussion

The clear evidence of an α- to γ-phase redox process at high cobalt levels, as determined by X-ray examination of 45% Co electrodes in various conditions of charge and discharge, is in agreement with the observations of Pickett and Maloy who examined 10% Co electrodes [14]. These α- and γ-lattice structures with a large c-axis spacing enable easy access of ions to the active material and thus the structure will oxidise to the Ni(IV) state more readily than β-phase material. At commercial levels of cobalt these effects

will be less pronounced. To explain the gradual changes in performance observed in this work, however, it must be concluded that the presence of even small amounts of cobalt introduces α- and γ-phase nickel hydroxide species which coexist with the β-phase material and undergo redox in a similar way.

The changes in electrode capacity and utilisation of the active material with cobalt content can be related to the morphological alterations of the films up to the 50% cobalt level. Beyond 50% cobalt content, however, the utilisation remains at a maximum, while the electrode capacity falls due to the decrease in active material present, and this cannot be explained by the morphological changes observed. It is proposed that, as the cobalt content rises, the conductivity of the film during discharge is improved and this results in more efficient charge return from the active material, as indicated previously [6], even when the surface area of the film is decreasing at these high cobalt levels.

Finally, it is apparent from the data obtained that the basic nickel hydroxide/oxyhydroxide redox reaction so often referred to in texts is a simplification of the true situation, especially when foreign ions such as cobalt are present.

Conclusions

(i) Significant additions of cobalt result in a two-step oxidation and reduction process for the active material, where large amounts of Ni(IV) are formed upon oxidation.

(ii) The presence of cobalt permits a deeper discharge of the active material.

(iii) Cobalt content greatly alters the film morphology, producing a very porous structure at the 50% level.

(iv) Addition of large amounts of cobalt stabilises the α-/γ-phase redox process of the active material, which, at lower additive levels, gradually reverts to the more commonly observed β-phase redox reaction.

Acknowledgements

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