

## STRUCTURAL AND ELECTROCHEMICAL CHARACTERISTICS OF PLASTIC (PTFE) BONDED NICKEL HYDROXIDE ELECTRODES

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### Summary

The performance and structural characteristics of PTFE bonded nickel hydroxide electrodes have been studied as a function of electrolyte composition, temperature, and overcharge. The results demonstrate that crystal growth and the relative stability of the  $\beta$ -NiOOH and  $\gamma$ -NiOOH oxidised phases are highly dependent on these parameters. The ways in which these relationships are reflected in electrode performance are discussed.

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### Introduction

The technological importance of nickel hydroxide electrodes is reflected in the extensive literature relating to their study, but recent reviews [1, 2] highlight areas in which ambiguity still exists. In particular, the mechanisms of the redox processes and the influence of parameters such as electrolyte composition, overcharge, etc., on the structural characteristics of the charged electrode are in doubt. Much of the confusion may be attributed to the lack of structural characterisation of electrode materials for which electrochemical data have been presented. Of fundamental importance is the detailed phase composition of the oxidised material — which may comprise  $\gamma$ -NiOOH,  $\beta$ -NiOOH or a mixture — and whether the reduced material is of the  $\alpha$ -Ni(OH)<sub>2</sub> or the  $\beta$ -Ni(OH)<sub>2</sub> type. The electrochemical differences of the possible redox couples have been considered in detail by Barnard *et al* [3, 4]. In order that electrochemical and physicochemical measurements can be meaningful, it is imperative that as much structural information as possible is available for the materials under investigation, and, consequently, the value of many studies has been limited by doubts concerning the precise redox processes examined.

Detailed studies of Ni(OH)<sub>2</sub> electrodes have hitherto been largely devoted to pocket or sintered constructions which hinder reliable structural examination of the active materials. The development of plastic bonded

electrodes [5], although prompted primarily by financial considerations, has important consequences from a research viewpoint since it has provided a means of electrode fabrication which enables reliable electrodes to be constructed rapidly and reproducibly from well-characterised active materials. Moreover, effective structural examination is possible during electrode cycling since interference from the current collector/support is minimal

Notwithstanding the problems of accurate crystallographic work on materials with inherently small crystal sizes, an examination of the effects of electrolyte composition, temperature, and overcharge on the active material structure in PTFE bonded electrodes has been undertaken using powder X-ray diffraction and thermal analysis. The role of  $\text{Co}(\text{OH})_2$  additives in relation to phase stability has been discussed previously [6]

## Experimental

A commercial grade  $\text{Ni}(\text{OH})_2$  ( $\beta$ - $\text{Ni}(\text{OH})_2$  structure, 1.48% coprecipitated Co) was treated with  $\text{CoSO}_4$  solution and  $\text{Na}_2\text{CO}_3$  solution [7] to precipitate additional cobalt (2.4%) on the surface. PTFE bonded electrodes were fabricated to contain 75% (by weight)  $\text{Ni}(\text{OH})_2 + \text{Co}(\text{OH})_2$ , 24% graphite (Foliac X2115, Rocol) and 1% PTFE (Fluon GP1 dispersion, I.C.I.). The electrodes, of nominal capacity 0.8 A h, were cycled between nickel mesh counter electrodes in excess electrolyte ( $400 \text{ cm}^3$ ) of various compositions ( $[\text{OH}^-] = 6 \text{ mole dm}^{-3}$ ) at temperatures of 4, 25, and 60 °C. Overcharges of 25, 50, and 100% were employed based on the nominal capacities. Charging was at the C/3 rate, followed immediately by discharging at C/2 to 0.0 V relative to Hg/HgO. Loss of electrolyte by evaporation and the absorption of atmospheric  $\text{CO}_2$  were minimised by a thin layer of liquid paraffin floated on the electrolyte.

Samples of electrode material were examined after one, three, and eight charges, and after the eighth discharge; they were dried as completely as possible between sheets of absorbent paper but not washed. Treated in this way, samples were demonstrated to suffer no structural changes prior to examination.

Differential thermal analysis (DTA) curves were recorded on a Stanton Redcroft STA 780 thermal analyser at a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  in static air. Powder X-ray diffraction data were obtained using a Philips PW 1050/70 vertical goniometer with  $\text{Cu K}\alpha$  radiation at a scan speed of  $1^\circ 2\theta \text{ min}^{-1}$ . The following characteristic X-ray diffraction peak positions ( $2\theta$ ) were used as a basis for phase identification:  $\beta$ - $\text{Ni}(\text{OH})_2$  — 19.2°, 33.2°, 38.7°;  $\beta$ - $\text{NiOOH}$  — 19°, 38° (note the absence of the 33.2° peak of the starting material);  $\gamma$ - $\text{NiOOH}$  — 12.6°, 25.5°. Accurate, quantitative determinations are not possible for such broad X-ray diffraction peaks, but in all cases the results were demonstrated to be consistent with DTA data.

## Results

Potassium hydroxide solution is the preferred electrolyte for alkaline cells due to its high conductivity and low temperature properties, but LiOH is a very common additive. In order to evaluate the effect of LiOH concentration on relative phase stabilities and electrochemical performance, electrodes were cycled in a range of electrolytes from 6M KOH to saturated LiOH (approximately 5.3M at 25 °C). All electrodes reached a stable capacity after two or three cycles, in accordance with the good forming characteristics of electrodes of this type. Under all conditions, the maximum utilisation (100%  $\equiv$  0.289 A h g<sup>-1</sup> Ni(OH)<sub>2</sub> + Co(OH)<sub>2</sub>) attained in pure KOH was higher than in pure LiOH; for example, at 25 °C and 50% overcharge the utilisation in KOH exceeded that in LiOH by 25%. For comparison, 6M NaOH electrolyte was examined and intermediate results were obtained (Fig. 1)

It is important to note that contrary to the simple implications of Fig. 1, in mixed KOH/LiOH electrolytes the utilisation did not decrease uniformly as the LiOH content increased. In fact, an initial increase was apparent to give a maximum at 1.5 - 8 mole% LiOH (in the electrolyte) for electrodes subject to 50% overcharge; this maximum occurred at higher LiOH levels at low temperature (Fig 2)

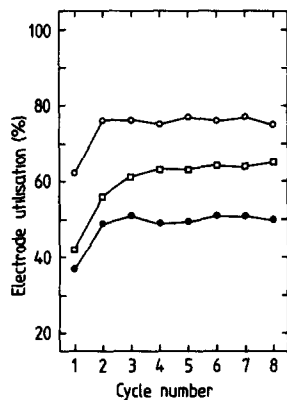


Fig 1 Electrode utilizations at 25 °C, 50% overcharge ○, in 6M KOH, □, in 6M NaOH, ●, in saturated LiOH

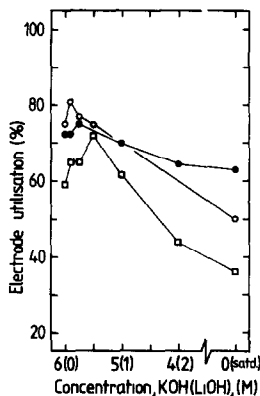


Fig 2 Electrode utilizations, 3rd cycle, 50% overcharge ●, at 60 °C, ○, at 25 °C, □, at 4 °C

Structural evidence from X-ray diffraction and DTA indicated that this electrochemical behaviour was related to the amounts of  $\beta$ -NiOOH and  $\gamma$ -NiOOH in the charged electrodes. There was some evidence to support the proposal [8] that the addition of small amounts of LiOH (<2% in this study) increased the amount of  $\gamma$ -NiOOH in the charged state. Such behaviour was surprising since higher LiOH concentrations were clearly shown to favour the

formation of  $\beta$ -NiOOH, with the amount of  $\gamma$ -NiOOH being correspondingly suppressed. Indeed, in pure LiOH no evidence was found for the formation of  $\gamma$ -NiOOH.

For those electrodes exhibiting the highest utilisations, X-ray diffraction (Fig 3) and DTA (Fig 4) implied complete discharge of small amounts of the highly oxidised  $\gamma$ -NiOOH in addition to the predominant  $\beta$ -NiOOH. This behaviour reflects the mean nickel oxidation states in  $\gamma$ -NiOOH (3.7) and  $\beta$ -NiOOH (3.0) [9]. Larger amounts of  $\gamma$ -NiOOH were not fully reduced under normal cycling regimes however, and a consequent decrease in utilisation was observed. The reversibility of the  $\beta$ -NiOOH  $\leftrightarrow$   $\beta$ -Ni(OH)<sub>2</sub> system is difficult to assess crystallographically due to the structural similarity of both phases. However, electrodes comprising only  $\beta$ -NiOOH in the charged state have been observed to give utilisations of approximately 100% [6, 10], which suggests a high degree of reversibility under favourable conditions. It is relevant to note that, in general, the  $\gamma$ -NiOOH content of charged electrodes increased with cycling.

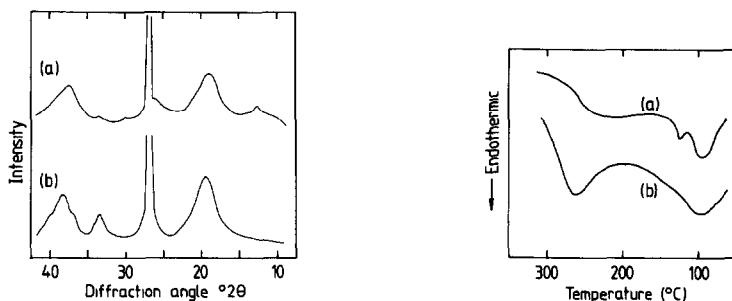


Fig 3 X-ray diffraction traces of electrodes exhibiting greatest utilisation at 25 °C, 50% overcharge after forming (a) charged, (b) discharged (the intense peak at 26.6°2 $\theta$  is due to graphite)

Fig 4 DTA traces of electrodes exhibiting greatest utilisation at 25 °C, 50% overcharge after forming (a) charged (endotherms at 100, 130, 230 °C correspond to surface water loss,  $\gamma$ -NiOOH,  $\beta$ -NiOOH), (b) discharged (endotherm at 265 °C corresponds to  $\beta$ -Ni(OH)<sub>2</sub>)

Tests at 4 °C and 60 °C implied that the ease of  $\gamma$ -NiOOH formation varied inversely with temperature. For example, for electrodes cycled at 60 °C with 50% overcharge, 4 mole% LiOH prevented  $\gamma$ -NiOOH formation after 8 cycles, and in pure KOH there was no evidence for  $\gamma$ -NiOOH on the first charge. At 4 °C and the same overcharge, however, 17 mole% LiOH was required to inhibit  $\gamma$ -NiOOH totally, and at a level of 8 mole% LiOH,  $\gamma$ -NiOOH was apparent even after the initial charge. These observations cannot simply be related to the results of chemical oxidations of  $\beta$ -Ni(OH)<sub>2</sub> which were found to produce the greatest amount of  $\gamma$ -NiOOH with powerful oxidising agents (e.g., Br<sub>2</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) in KOH or NaOH at high temperatures. Oxidations in LiOH, on the other hand, gave only  $\beta$ -NiOOH. An early report

[11], however, does imply that greater degrees of chemical oxidation may occur at low temperatures

A more important consequence of elevated temperature operation was a decrease in electrode utilisation on cycling, irrespective of the electrolyte (Fig. 5) This was shown to correlate with a morphological change in the reduced  $\beta\text{-Ni}(\text{HO})_2$  which, at cycle 8, was not only more crystalline than at lower temperatures (on the basis of X-ray diffraction peak widths), but also more crystalline than the starting material. This variation in crystal size was supported by DTA measurements (Fig 6), since it has been shown [6] that an increase in crystal size is associated with an increase in the decomposition temperature of  $\beta\text{-Ni}(\text{OH})_2$ . For electrodes cycled at 60 °C, the sharp endotherm corresponding to this transition occurred at a temperature higher than that for the starting material (278 °C), whereas cycling at 4 °C resulted in endotherms as low as 260 °C and consistent with crystal fragmentation

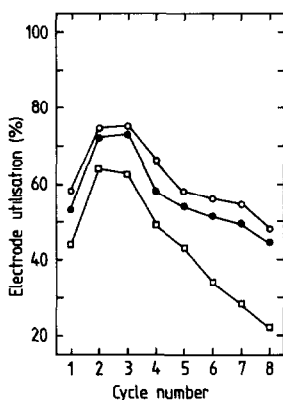


Fig 5 Electrode utilisations at 60 °C, 50% overcharge ●, in 6M KOH, ○, in 5.75M KOH/0.25M LiOH, □, in saturated LiOH

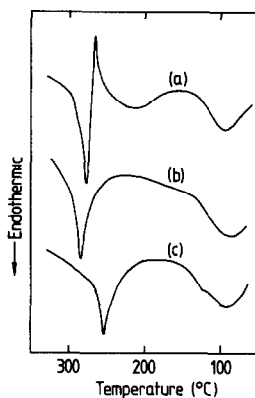


Fig 6 DTA traces (a) uncycled electrode, (b) electrode after 8 cycles at 60 °C (discharged), (c) electrode after 8 cycles at 4 °C (discharged) The exotherm at 260 °C in uncycled material is due to graphite

The relative amount of  $\gamma\text{-NiOOH}$  in charged electrodes was found to be proportional to the overcharge, except at 60 °C This effect was most marked at 4 °C where 100% overcharge produced detectable  $\gamma\text{-NiOOH}$  on the first charge even in 16 mole% LiOH. At 50% overcharge,  $\gamma\text{-NiOOH}$  was observed at LiOH levels below 8 mole% but for 25% overcharge no  $\beta\text{-NiOOH}$  formation occurred on the first cycle, irrespective of electrolyte composition At 4 °C, the electrolyte composition producing maximum utilisation was shifted to higher LiOH concentrations at high overcharge levels for 25% overcharge, pure KOH or 1.5 mole% LiOH; 50% overcharge, 8 mole% LiOH; 100% overcharge, 30 mole% LiOH. This is consistent with the above conclusion that maximum utilisation is achieved for electrodes containing *small* amounts of  $\gamma\text{-NiOOH}$

It is interesting to note that the only oxidised phases detected in the present study were  $\gamma$ -NiOOH and  $\beta$ -NiOOH, the phases initially observed by Glemser and Einerhand [12]. Contrary to earlier reports [13, 14], no evidence supported the formation of  $\text{LiNiO}_2$  or an isostructural phase, even in saturated LiOH at 60 °C. Aia [15] also failed to detect such a phase and considered hydrolysis of  $\text{LiNiO}_2$  during washing to be a possible explanation. However such a reaction appears to be slow [16], and its effects would therefore be expected to be insignificant during electrode washing. In the present study, the electrodes were not, in fact, washed. Chemically prepared  $\text{LiNiO}_2$  was also demonstrated to be electrochemically inactive under normal cycling conditions. Only after standing for 10 days in electrolyte was a very small utilisation observed (approximately 2%), which was attributed to the products of slow hydrolysis.

## Discussion

The correlation between  $\gamma$ -NiOOH formation and temperature may be associated with a variation, with temperature, in the relative electrochemical potentials for  $\gamma$ -NiOOH formation and oxygen evolution. In support of this view, X-ray diffraction data confirmed that self-discharge of  $\gamma$ -NiOOH to  $\beta$ -Ni(OH)<sub>2</sub> was enhanced at elevated temperatures. An additional factor, which may be relevant, is that  $\gamma$ -NiOOH formation may occur either directly from oxidation of  $\alpha$ -Ni(OH)<sub>2</sub> [3, 4], or from  $\beta$ -Ni(OH)<sub>2</sub> via  $\beta$ -NiOOH. The initial reduction product of  $\gamma$ -NiOOH has been suggested to be  $\alpha$ -Ni(OH)<sub>2</sub> [3, 4], which may then age to  $\beta$ -Ni(OH)<sub>2</sub> [17]. If such ageing is slow, e.g., at low temperatures, build up of  $\gamma$ -NiOOH may be expected due to the additional  $\gamma$ -NiOOH formed from the  $\beta$ -NiOOH during the overcharge period on each cycle. At elevated temperatures, however, rapid ageing would eliminate significant build up of  $\gamma$ -NiOOH by such a mechanism since the initial oxidation product of  $\beta$ -Ni(OH)<sub>2</sub> is  $\beta$ -NiOOH.

The poor performance of electrodes at 60 °C cannot be interpreted in terms of the stabilities of the phases involved, since the decrease in utilisation did not correlate with changes in phase composition. Also, the initial utilisations (cycles 1 - 3) were generally only slightly worse than at 25 °C, and in electrolytes of high LiOH content utilisations were actually better. The observed deterioration in performance can, however, be ascribed to the gradual recrystallisation of the reduced phase and concomitant increase in crystallite size; this is totally consistent with previous reports [6, 12, 17] which have associated high utilisations with reduced material of low crystallinity.

LiOH additions to KOH electrolyte produced marked effects in electrode performance, especially at low concentrations where an increase in utilisation was attributed to full discharge of small amounts of  $\gamma$ -NiOOH. This effect may reflect the higher oxygen evolution potential in lithiated electrolytes [2] resulting in increased  $\gamma$ -NiOOH formation. With respect to

structural considerations, LiOH clearly stabilises  $\beta$ -NiOOH relative to  $\gamma$ -NiOOH, since under all conditions X-ray diffraction and DTA indicated that the only oxidised phase present in pure LiOH was  $\beta$ -NiOOH. Although  $\beta$ -NiOOH has been reported [3] not to contain substantial quantities of alkali cations,  $\gamma$ -NiOOH is known to accept  $K^+$ ,  $Na^+$ ,  $Rb^+$  and, significantly,  $Li^+$  [4]. The incorporation of both  $K^+$  and  $Li^+$  into  $\gamma$ -NiOOH suggests that the structural effects observed are most likely to result from stabilisation of the  $\beta$ -NiOOH structure. In a previous publication [6], it was suggested that both Co and Li are required in order to prevent  $\gamma$ -NiOOH formation, and it was proposed that  $Li^+$  may prevent phase segregation of  $Co(OH)_2$  or  $CoOOH$  by forming charge compensated  $Li^+Co^{3+}$  defects in the  $\beta$ -Ni(OH) $_2$  structure, *i.e.*,  $Li_xCo_xNi_{1-2x}(OH)_2$ . In this respect it is important to emphasise that all electrodes in this study contained Co, and at exactly the same level.

No X-ray diffraction evidence was found for the formation of an  $LiNiO_2$  type phase (Fig 7). Such a phase has been reported [18] to form on the third cycle of an electrode at 20 °C in an electrolyte containing only 20 g  $dm^{-3}$  LiOH, and at 50 °C with 10 g  $dm^{-3}$  LiOH. In the present study, DTA traces of samples from electrodes cycled at 60 °C in pure LiOH displayed only an endotherm corresponding to  $\beta$ -NiOOH decomposition. Chemically prepared  $LiNiO_2$  shows no related peak and is thermally stable up to 800 °C. The suggestion that  $LiNiO_2$  is the only oxidised phase obtained in LiOH electrolytes [2] is clearly not applicable to the electrodes of this study, and if it forms at all in  $Ni(OH)_2$  electrodes, it may be of significance only for electrodes containing nickel with a high surface area such as sintered electrodes.

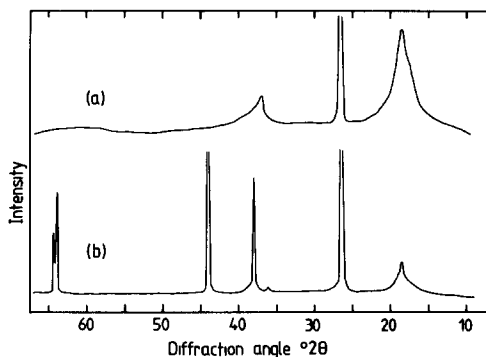


Fig 7 X-ray diffraction traces (a) electrode cycled in saturated LiOH at 60 °C, (b) electrode of chemically prepared  $LiNiO_2$  (intense peak at  $26.6^\circ 2\theta$  is due to graphite)

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