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Studies concerning charged nickel hydroxide electrodes. VIII. The relative potentials of the β-/γ-nickel oxy hydroxide reduction processes

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In this communication it is demonstrated that a partly charged β-$Ni(OH)_2$/β-NiOOH couple can oxidize α-$Ni(OH)_2$ to the γ-phase. This observation is in accordance with the order of the reversible potentials and illustrates the greater stability of the γ-phase in 7 mol dm^{-3} KOH. Contrary to several claims in the literature β-NiOOH undergoes reduction over a range of potentials from 400 to 300 mV wrt Hg/HgO/KOH whilst the γ-phase containing Ni^{4+} species undergoes reduction usually at less positive potentials (below 300 mV).

Internal oxidation/reduction reactions between various α/γ and β/β-phase couples can be expected to take place in partly charged electrodes during open circuit stand periods in addition to oxygen evolution. Ageing of oxidized phases may also lead to changes in free energies. Both types of process may lead to shifting of peaks after open circuit stand periods.

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1. Introduction

There appears to be considerable misunderstanding in the literature with respect to the relative potentials at which β-NiOOH and the γ-phase $K_{0.33}NiO_2 0.67H_2O$ (commonly written γ-NiOOH), undergo reduction during cyclic voltammetry. It is often mistakenly assumed that the γ-phase containing quadrivalent nickel is always less stable than β-NiOOH and reduces at less negative potentials [1–5]. In practice the γ-phase can be more stable than the β-phase in alkali concentrations in the range 1–10 mol dm^{-3} [6–8].

Oxidation/reduction potentials have been proposed for species such as Ni_3O_4, Ni_2O_3 and NiO_2 on the basis of dubious thermodynamic cycles. Accordingly potential–pH diagrams based on such estimates must be viewed with caution. Recently [9] an attempt has been made to recompile a revised potential–pH diagram for nickel, however, there still appears to be a reluctance to accept the presence of quadrivalent nickel compounds such as $K_{0.33}NiO_2 \cdot 0.67H_2O$ which are now well established [6–8, 10].

In the case of oxide/hydroxide layers only a few molecules thick, there may be some doubt as to the chemical identity of the species present [3–5], nevertheless, in the case of moderately thick films and sintered plate electrodes the identity of the species can be established with some certainty [11, 12].

Paszkiewicz and Walas [1] have reported voltammetric studies for sintered plate electrodes. According to these workers the least cathodic reduction peak at 400 mV was ascribed to unstable NiO_2 whilst the most cathodic peak at 300 mV was assumed to be due to reduction of the more stable β-NiOOH. The instability of NiO_2 was claimed to have been demonstrated by the fact that the peak at 400 mV diminished with storage time. As will be demonstrated in this communication an alternative explanation can be given for the decay process. Arvia *et al.* [3–5] using thin film electrodes have also considered the peaks at most positive potentials to be due to reduction of the γ_1, and γ_2-phases described by Bode *et al.* [17]. These assignments like those of Paszkiewicz and Walas [1] follow earlier assignments by Malandin *et al.* [2]. No attempt was made in any of the above investigations to estab-

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lish the identity or oxidation state of the species present at the various points in the voltammograms by independent means. These assignments are at variance with the reversible potential and X-ray diffraction evidence [11, 12].

As will be shown in this communication it is possible to use a β-$Ni(OH)_2$/β-NiOOH couple to oxidize α-$Ni(OH)_2$ to the γ-phase clearly demonstrating the greater stability of the latter.

2. Experimental procedure

A sample of sintered plate electrode (1 cm × 1 cm) containing ~ 0.09 g of well crystallized β-$Ni(OH)_2 0.25 H_2O$ was first pre-charged galvanostatically in 7 mol dm^{-3} KOH such that the heterogeneous emf composition region had been reached [13]. This pre-charged electrode containing β-NiOOH was then coupled electronically through an external resistor to a second electrode containing a similar weight of α-$Ni(OH)_2 0.67 H_2O$ residing in the same electrode compartment as the pre-charged electrode. The voltage developed across the standard resistor (proportional to the current flow) was monitored on one channel of a Linseis 12-channel chart recorder. Potentials of the individual electrodes were also monitored (using an Hg/HgO/7 mol dm^{-3} KOH reference electrode) on other channels over a 1 h period.

Cathodic linear sweep voltammograms were

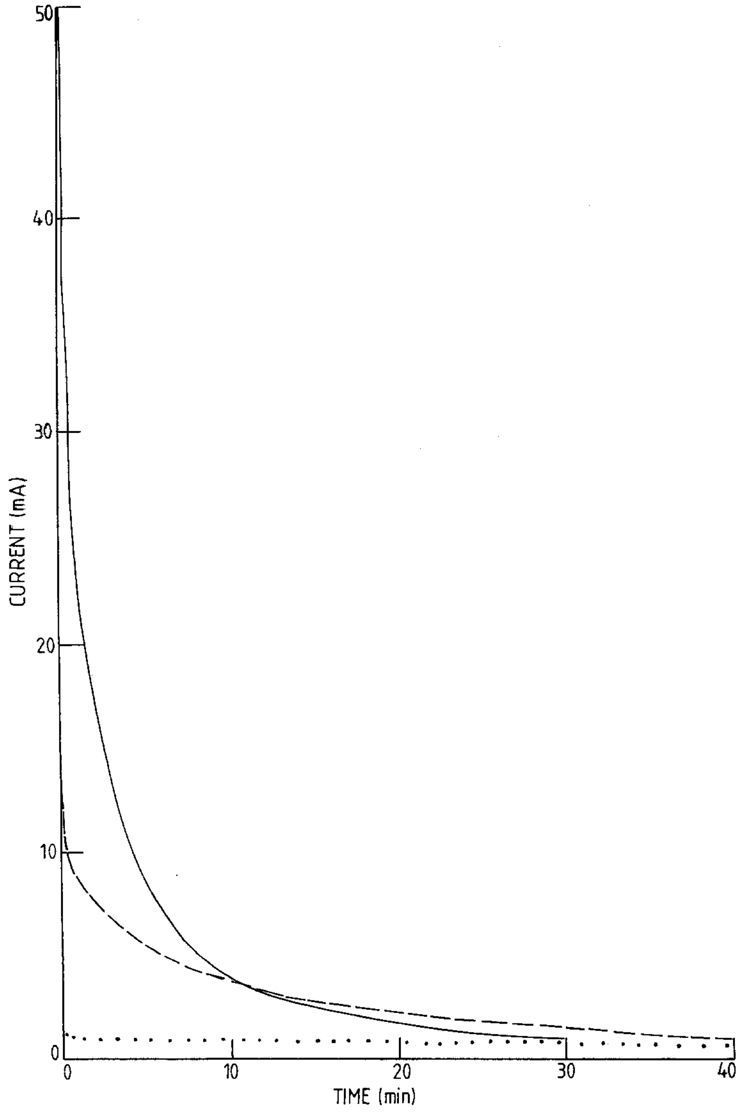

Fig. 1. Current–time curve for an α-$Ni(OH)_2$/γ$K_{0.33}NiO_2$/ 7 mol dm^{-3} KOH/β-$Ni(OH)_2$/ β-NiOOH cell discharged through different resistive loads. ———, 1 Ω; — — — —, 10 Ω; . . . . , 100 Ω.

also recorded as described previously [11, 12] using samples of β-$Ni(OH)_2$ which had been precycled and then charged to an average oxidation state of 3.0. Several electrodes were allowed to stand for various periods of time (up to 16 h) before conducting cathodic scans.

3. Results and discussion

An 'ordered' β-phase, $Ni(OH)_2/NiOOH$ or U_β^D/V_β^D couple having an E_r value [6] of 427 mV wrt Hg/HgO/7 mol dm^{-3} KOH will oxidize electrochemically precipitated α-$Ni(OH)_2$ to the γ-phase because of the lower potential of the U_α^A/V_γ^A couple (340 mV). A cell constructed between U_α^A/V_γ^A and U_β^D/V_β^D couples has an open circuit potential of $\sim$ 130 mV and is unusual in as much as the couple containing Ni^{4+}/Ni^{2+} species provides the negative pole of the cell whilst the lower valent Ni^{3+}/Ni^{2+} combination provides the positive pole.

The overall cell reaction (1) can be written thus:

$$1.54\,\text{Phase } V_\beta^D + 0.70\,\text{Phase } U_\alpha^A + 0.19\,KOH \rightleftharpoons 1.54\,\text{Phase } U_\beta^D + 0.70\,\text{Phase } V_\gamma^A + 0.16\,H_2O \qquad (1)$$

where the coexisting phases [13] have the following compositions:

$$V_\beta^D = [0.9\,NiOOH\cdot 0.1\,Ni(OH)_2]\cdot 0.21\,H_2O \cdot 0.033\,KOH$$

$$U_\beta^D = [0.25\,NiOOH\cdot 0.75\,Ni(OH)_2]0.25\,H_2O$$

$$V_\beta^A = [0.833\,NiO_2\cdot 0.16Ni(OH)_2]\cdot 0.35\,H_2O \cdot 0.33\,KOH$$

$$U_\alpha^A = [0.125\,NiO_2\cdot 0.875Ni(OH)_2]0.67\,H_2O.$$

Figure 1 illustrates the current–time behaviour for an experimental cell of type 1 above coupled through different resistive loads (1, 10 and 100 Ω), whilst Fig. 2 shows corresponding potential–time behaviour for each electrode. The cell on load eventually takes up a mixed potential between the

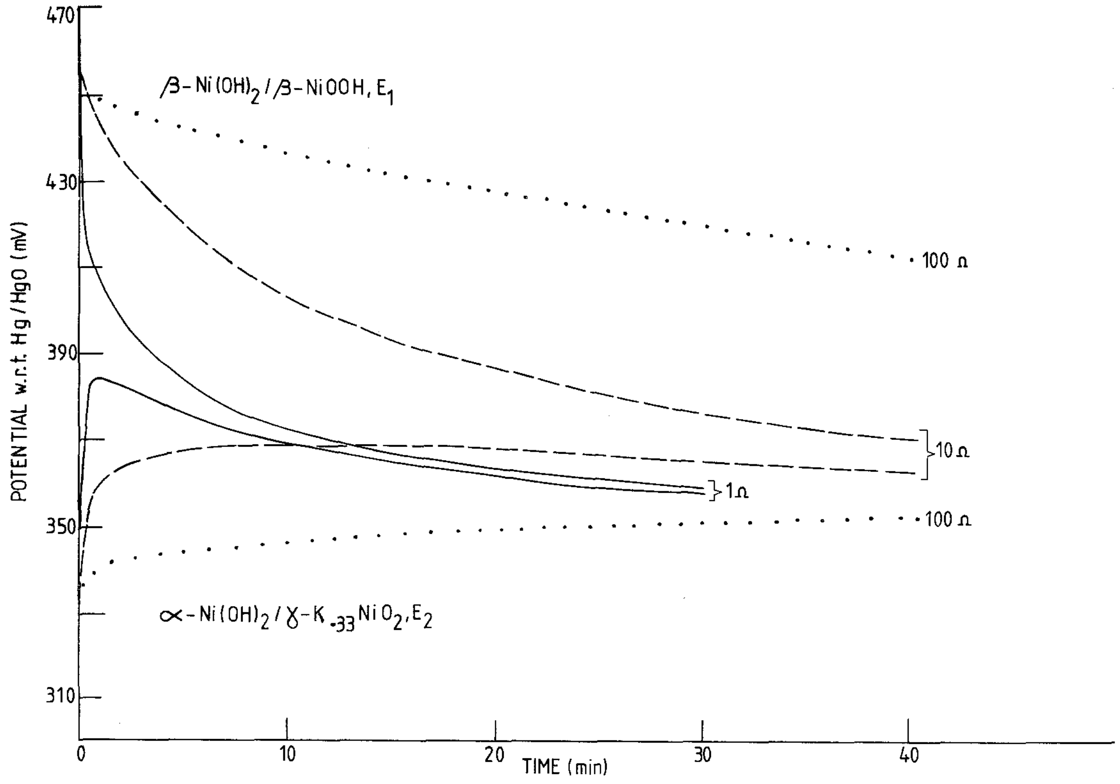

Fig. 2. Potential–time curves for each couple (wrt Hg/HgO/7 mol dm^{-3} KOH) in the α-$Ni(OH)_2/\gamma$-$K_{0.33}NiO_2$/7 mol dm^{-3} KOH/β-$Ni(OH)_2/\beta$-NiOOH cell discharged through different loads. ———, 1 Ω; — — — —, 10 Ω; . . . . , 100 Ω.

equilibrium potentials of the U_β^D/V_β^D and U_α^A/V_γ^A couples.

It should be noted that because the potential of the β-phase couple depends on the degree of order/disorder in the parent lattice in some instances, the reversible potentials for the α/γ and β/β-couples can be identical [6]. Clearly under these circumstances the β-phase couple would be unable to oxidize α-$Ni(OH)_2$.

Formation of the γ-phase appears to be dependent on the ease with which alkali cations and water may be admitted to the interlayers in the $Ni(OH)_2$ lattice. It appears to be energetically more favourable to form Ni^{4+} species directly within the expanded hydrated α-$Ni(OH)_2$ structure rather than convert well crystallized β-NiOOH to the γ-phase. Aleshkevich *et al.* [14, 15] have pointed out from the considerations of the energy to remove a proton from an OH^- group attached to the nickel cation that kinetic factors tend to favour formation of Ni^{4+} rather than Ni^{3+}. The ability of protons attached to quadrivalent nickel entities to undergo ion exchange with K^+ or other alkali cations to form $K_{0.33}NiO_2 0.67 H_2O$ provides an additional means of stabilizing higher valent nickel species. Indeed, provided suitable ligands are available Ni^{4+} can form several well characterized co-ordination compounds usually having a spin-paired d^6 electron configuration. Comparatively few complexes are known for Ni^{3+} [16].

The observations of Figs. 1 and 2 suggest that the decline in magnitude of the reduction peak at 400 mV with time observed by Paskiewicz and Walas might have arisen because a phase of the type V_β^D giving rise to the highest potential was being consumed during the oxidation of phases such as U_α^A or U_α^C [12] to the γ-phase. Such a process does not require the flow of an external current and would represent an open circuit decay process.

The relatively long time scale over which the decay process was observed by Paszkiewicz and Walas [1] would, however, require relatively high resistance paths to be present between the two couples in the electrode.

Fig. 3 shows a sequence of cathodic linear sweeps performed on samples of pre-cycled β-$Ni(OH)_2$ charged to a nickel oxidation state of 3.0 and stored at ambient temperature for various periods of time up to 16 h in the charged

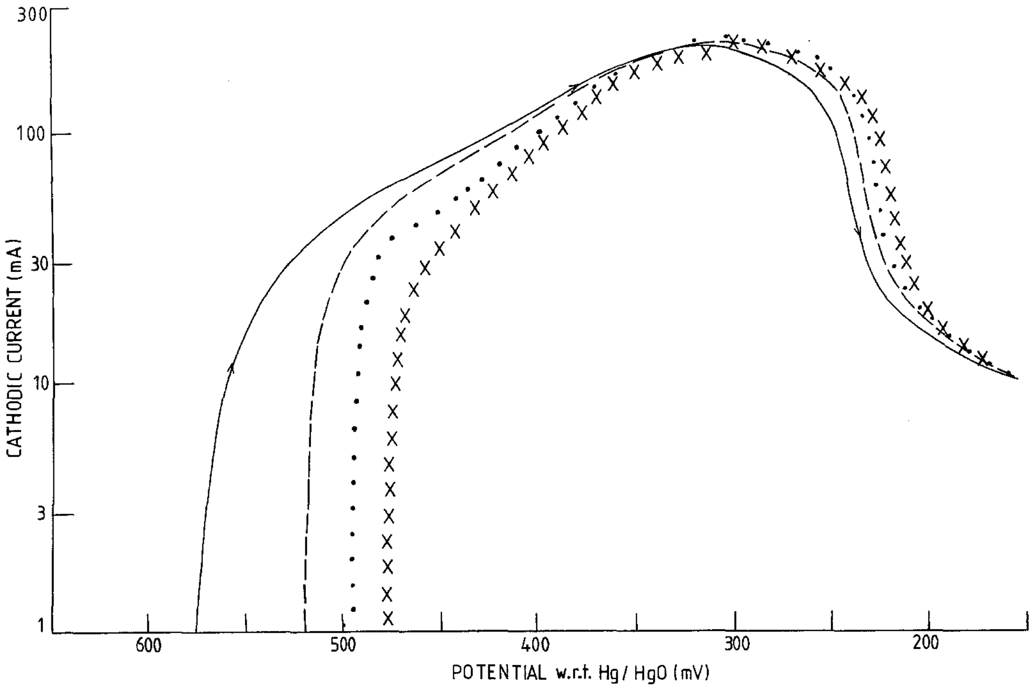

Fig. 3. Cathodic linear sweep voltammogram for precycled and precharged β-$Ni(OH)_2$ samples (Nickel oxidation state, 3.0) after various open circuit stand periods. ———, 0 h; — — — —, 40 min; · · · · · · ·, 2 h; X X X X, 16 h. Sweep rate 40 mV min^{-1}.

state. Even at an oxidation state of 3.0, the oxidized product contains some γ-phase in addition to predominantly β-phase materials [11, 12]. A shift in potential and decrease in height of the broad shoulder at ~ 400 mV with time together with a slight increase in size of the main peak at 300 mV is observed. The overall results are similar although not as pronounced as those observed by Paszkiewicz and Walas [1]. In the present case where only small amounts of α-phase materials are present, the most likely explanation for the peaks shifting with time would be changes in free energy for the oxidized β-phase materials during aging leading to a fall in E_0' and reduction potential.

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References

[1] M. Paszkiewicz and I. Walas, *Electrochim. Acta* **24** (1979) 629.

[2] O. G. Malandin, P. D. Lukoutsev and T. S. Tikhonova, *Elektrokhimiya* **7** (1971) 655.

[3] R. S. Schrebler-Guzman, J. R. Vilche and A. J. Arvia, *J. Electrochem. Soc.* **125** (1978) 1578.

[4] *Idem, J. Appl. Electrochem.* **9** (1979) 183.

[5] *Idem, ibid.* **9** (1979) 321.

[6] R. Barnard, C. F. Randell and F. L. Tye, *J. Appl. Electrochem.* **10** (1980) 109.

[7] *Idem, ibid.* **11** (1981) 517.

[8] R. Barnard, C. F. Randell and F. L. Tye, 'Nickel Electrode Symposium', Denver, Colorado Meeting of the Electrochemical Society 1981.

[9] D. C. Silverman, *Corrosion* **37** (1981) 546.

[10] J. F. Jackovitz and J. Seid el, 'Nickel Electrode Symposium', Denver, Colorado Meeting of the Electrochemical Society 1981.

[11] R. Barnard and C. F. Randell, 'Electrochemical Energy Storage 1981', *J. Power Sources* in press.

[12] *Idem, J. Appl. Electrochem.* in press.

[13] R. Barnard, C. F. Randell and F. L. Tye, *J. Electroanal. Chem.* **119** (1981) 17.

[14] S. A. Aleshkevich, E. J. Golovchenko, V. P. Morozov and L. N. Sagoyan, *Soviet Electrochem.* **4** (1968) 530.

[15] *Idem, ibid.* **4** (1968) 1117.

[16] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', Interscience, New York (1962) p. 744.

[17] H. Bode, K. Dehmelt and J. Witte *Z. Anorg. Allg. Chem.* **366** (1969) 1.