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Studies concerning charged nickel hydroxide electrodes. I. Measurement of reversible potentials

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Reversible potentials (E_R) have been measured for nickel hydroxide/oxyhydroxide couples over a range of KOH concentrations from 0·01–10 M. It is shown that the couples derived from the parent α- and β-$Ni(OH)_2$ systems can be distinguished by the relative change in KOH level on oxidation and reduction. In the case of couples derived from the α-class of materials a dependence of 0·470 moles of KOH per 2e change is found compared with 0·102 moles of KOH per 2e change for the β-class of materials. Couples derived from the α- and β-$Ni(OH)_2$ systems can be encountered in a series of 'activated' and 'de-activated' forms having a range of formal potentials E_0'. 'Activated' and 'de-activated' β-$Ni(OH)_2$/β-NiOOH couples are found to lie in the range 0·443–0·470 V whilst α-$Ni(OH)_2$/γ-NiOOH couples lie in the range 0·392–0·440 V w.r.t. Hg/HgO/KOH. It is demonstrated for 'de-activated', β-$Ni(OH)_2$/β-NiOOH couples that E_R is independent of the degree of oxidation of the nickel cation between states of charge of 25% and 70%. Similarly E_R is constant for states of charge between 12% and 60% for 'activated' α-$Ni(OH)_2$/γ-NiOOH couples. The constant potential regions are considered to be derived from heterogeneous equilibria between pairs of co-existing phases both containing nickel in upper and lower states of oxidation. Differences in E_0' between the 'activated' and 'de-activated' couples are considered to be related to the degree of order/disorder in the crystal lattice.

1. Introduction

The $Ni(OH)_2$/NiOOH electrode because of its use in the nickel–cadmium cell system has been the subject of numerous investigations, but its mode of operation still remains an enigma. Several reviews [1–4] are available giving the extensive background literature. There is still disagreement between the various workers as to the precise value of the equilibrium potential or whether the system can be regarded as 'reversible' in the thermodynamic sense [5]. This is due largely to the possibility of at least two distinct couples based on the α- and β-$Ni(OH)_2$ crystal structures interacting in the potential-determining reactions. This complication has not always been fully appreciated by previous workers [6–17].

Bode and collaborators [18, 19] showed that α-$Ni(OH)_2$ on oxidation was converted to γ-NiOOH at a lower potential than the corresponding oxidation of β-$Ni(OH)_2$ to β-NiOOH. Complicating features are that the unstable α-$Ni(OH)_2$ reverts to β-$Ni(OH)_2$ on standing in alkali, and β-NiOOH can be further oxidized to γ-NiOOH. The γ-phase differs structurally from the β-phase in having greater expansion along the *c*-axis due to the presence of additional water and alkali metal cations in the interlayer spaces [18, 19]. Although, not apparent from the commonly used formulation, the γ-phase has a higher average nickel oxidation state (3·3–3·7) compared with the β-phase owing to the presence of Ni^{4+}. Several groups of workers [20–22] have shown that the discharge potential for γ-NiOOH is lower than for β-NiOOH. This suggests differences in the standard potentials for the two systems.

The most detailed study of the reversible potential for essentially β-phase materials was conducted by Conway and co-workers [13–17]. They found the potential of the β-phase couple to be dependent on the KOH and H_2O activities of the electrolyte. Kornfeil [12] has also claimed such dependences, although different ones from those of Conway and Bourgault [13–15]. Whilst uptake

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of alkali cation is expected for the γ-phase as shown by several workers [1, 4, 18, 19, 22], this is not expected [18, 19, 22] for the pure β-phase. An important contribution made by Conway's group [13–17] was the realization that charged nickel hydroxide electrodes were above the reversible oxygen potential. Thus values obtained from simple open circuit potential measurements tend to be mixed rather than true equilibrium values. An extrapolation technique [13–17] enabled the removal of the influence of the oxygen evolution reaction. This approach has also been adopted in the present study.

Estimates of the potential of the α-Ni(OH)$_2$/γ-NiOOH system are considerably less numerous. MacArthur [23] attempted estimations from cyclic voltammetric measurements and found a dependence of e.m.f. with KOH activity (the water activity was not included). A stoichiometry was deduced from the Nernst relationship for the γ-phase in partial agreement with Bode *et al.* [18, 19]. As expected both the formal potential and dependence of the reversible potential on KOH activity differed considerably from that obtained by Conway and Bourgault [13–15].

The purpose of the present investigation was to redetermine the reversible potentials for the β-Ni(OH)$_2$/β-NiOOH and α-Ni(OH)$_2$/γ-NiOOH systems and establish the influence of KOH and H_2O activity. Previous studies [22] have drawn attention to the presence of large 'residual capacities' after discharge of sintered plate nickel hydroxide electrodes. By studying the change in reversible potential as a function of the degree of oxidation of the nickel, the type of discharge process likely to be involved has been deduced. Thermodynamic aspects of the proposed discharge model will be considered in more detail in the second paper of this series.

2. Experimental

2.1. *Electrode materials*

Measurements were made on four types of active material which will be designated; 'activated' and 'de-activated' β-Ni(OH)$_2$, together with 'activated' and 'de-activated' α-Ni(OH)$_2$. Test electrodes containing 'de-activated', β-Ni(OH)$_2$ were prepared by alternate impregnation of conventional nickel sinter plaques with nickel nitrate and sodium hydroxide solution [24]. The precipitation of active material was conducted at 90° C and this procedure gave a β-phase product as confirmed by X-ray diffraction [22]. The sample size was 1 cm x 1 cm (thickness 0·065 cm) and the electrodes contained ~ 0·09 g of Ni(OH)$_2$, giving a theoretical capacity for a 1 e change of 26 mA h.

In order to prepare a sample of 'activated', β-Ni(OH)$_2$ considerable care was taken to avoid contamination by unwanted phases, in particular γ-NiOOH. A suitable procedure consisted in charging 'de-activated' β-Ni(OH)$_2$ electrodes at 20 mA for 50 min in 7 M KOH so that about $\frac{2}{3}$ of the total capacity was utilized. The electrodes were then discharged at 20 mA to 0·15 V, and stored in 7 M KOH for over 24 h before measurements were taken. Diffraction patterns for the "activated", β-phase were found to be indistinguishable from the parent 'de-activated' material.

Electrodes incorporating 'activated' α-Ni(OH)$_2$ were prepared by electroprecipitation from 1 M nickel nitrate solution using a method similar to that described by Hausler [25]. A sample of sintered plate electrode having the dimensions 1 cm x 1 cm contained ~ 0·06 g Ni(OH)$_2$ and the theoretical capacity for a 1·67 e change was about 29 mA h. X-ray diffraction studies for this type of material frequently showed no diffraction lines other than those due to nickel sinter. In isolated cases extremely weak and diffuse patterns could be obtained showing the presence of the principal lines of α-Ni(OH)$_2$ [19, 26, 27]. This behaviour is indicative of a highly disordered layer lattice which is frequently encountered with the α-class of materials [26].

Samples of 'de-activated' α-Ni(OH)$_2$ were prepared by allowing samples of the freshly electroprecipitated material to stand in 7 M KOH at 22° C for over 16 h. As will become apparent later in this paper, this procedure did not result in full conversion to the more stable β-phase. In order to effect complete conversion of the α-structure to the β-structure a higher temperature and/or a longer period of contact with the alkali were required, e.g. 2–3 hours at 90° C in 6–9 M KOH [18]. Attempts to characterize the 'de-activated' α-phase by X-ray diffraction procedures have so far been unsuccessful.

2.2. *Measurement of equilibrium potentials* (E_R)

The indirect methods proposed by Conway and co-workers [13–17] were employed. Briefly, the technique involves measurement of the e.m.f. (E) as a function of time (t) after interruption of polarization at constant current. Although, the magnitude of the current is arbitrary in relation to the E_R values, some care is needed in its choice to ensure that excessive levels of charge are not applied to β-phase materials which could otherwise result in γ-phase contamination. Plots of E against log $(t + \tau)$ are found to be linear at short times (< 100 s) for both anodic and cathodic polarization provided suitable values of the constant τ are chosen. The points of intersection of the lines correspond to the reversible potential E_R. This method of data processing to obtain E_R values from e.m.f. decay/recovery data will be discussed more fully later in Section 3.1.

2.2.1. *Modified procedure based on that of Conway and Bourgault* [13–15]. Sintered plate electrodes containing α- or β-phase nickel hydroxides were charged so as to produce predominantly γ- or β-NiOOH respectively. For example starting with 'de-activated' β-Ni(OH)$_2$ charging at 10 mA for 2 h gave mainly β-NiOOH but after prolonged charging (16 h) at the same rate γ-NiOOH resulted [22]. As it is known [18, 19, 23] that the α-phase oxidizes directly to the γ-phase, charging at 10 mA for 3 h was sufficient to produce γ-NiOOH, starting from 'activated' α-Ni(OH)$_2$. During charging the current was interrupted at regular intervals (about 10 min). The e.m.f. fall versus time measurements were taken at 5 s intervals for up to 100 s. The electrode was the then discharged at 20 mA and the current interrupted at the same relative charge points as those on charge. The e.m.f. rise versus time relationship was again noted.

Reversible potentials (E_R) were evaluated directly from the E versus t data for readings between 5 and 25 s by means of a programmable calculator. A copy of the calculator programme is available from the authors (Texas Instruments TI 58). The constant τ was estimated (± 0·5 s) automatically by the calculator using an iterative procedure such that the value of τ gave a correlation coefficient close to unity for a straight line describing the E versus log $(t + \tau)$ data. The points of intersection of the anodic decay and cathodic recovery lines (described by a pair of simultaneous equations) were similarly processed by the calculator to give E_R.

During the investigation it became apparent that the unmodified procedure of Conway and Bourgault [12–15] was not entirely satisfactory because it always required the use of an initially fully charged electrode. As will be shown later, in the case of β-Ni(OH)$_2$ it was difficult to avoid the presence of some γ-NiOOH even if the charge input was restricted to 1 F mole^{-1}. This caused serious errors in the measured potentials. In the case of activated α-phase materials these became progressively de-activated on immersion in alkali and the unmodified procedure was again unsatisfactory because of the length of time required to fully charge the electrodes. In order to avoid fully charging the electrodes the modified approach was used or another procedure based on Conway and Gileadi [17] was employed (Section 2.2.2).

2.2.2. *Procedure based on that of Conway and Gileadi* [17]. Electrodes containing α- or β-Ni(OH)$_2$ were partially charged at a current i for t s. The current was interrupted and the E versus t relationship noted. The electrode was then recharged at a current i for a further t s, the current interrupted and the decay process observed as before. Discharging at a current $-i$ for t s was then performed and the recovery relationship noted. The E_R values were computed as described previously. By this procedure E_R could be obtained at increments of it, $2it$, $3it$, etc. (in Coulombs) respectively. The current i was typically 10 mA. Reversible potentials were recorded using both 'aged' and 'activated' forms of α- and β-Ni(OH)$_2$ over the alkali concentration range 0·01–10 M.

2.3. *Electronic equipment*

E.m.f. against time measurements were made manually using a Bradley 173B digital voltmeter (input impedance ~ 10^{12} Ω) internally calibrated against a Weston standard cell. The sample/hold facility on the DVM proved to be particularly useful. A chart recorder was not used because a resolution of at least ± 0·1 mV was required for accuracy.

Constant currents were supplied by simple transistorized units, values being displayed by a digital multimeter (Solartron 1242).

2.4. *Test cell*

The test cell consisted of a PTFE beaker (100 ml) which contained a cylindrical nickel grid counter electrode, $Ni(OH)_2$ working and Hg/HgO/KOH reference electrodes. The nickel support connecting the working electrode and also the reference electrode were kept in position near the centre of the beaker by means of a 'push-fit' through the PTFE lid. A distance of ~ 3 mm was maintained between the tip of the Luggin capillary (glass) and the test electrode face (1 cm x 1 cm). The electrolyte was pre-saturated with nitrogen and a nitrogen blanket was maintained over the surface of the electrolyte to minimize ingress of CO_2 from the atmosphere. The reference electrode always contained electrolyte of the same concentration as used in the test cell and all measurements were made at 25 ± 1° C. Unless otherwise stated all potentials are referred to Hg/HgO/KOH.

2.5. *Electrolyte*

Potassium hydroxide solutions in the concentration range 0·1–7 M were made up from AR grade pellets and triply-distilled water. The solutions were pre-electrolysed between large areas of nickel sinter for several days before use to remove impurities (mainly trace quantities of iron).

3. Results and discussion

3.1. *Interpretation of E versus t data*

Fig. 1. depicts typical E versus log t and E versus log $(t + \tau)$ plots for electrodes containing initially 'activated' α-$Ni(OH)_2$ in 1 M KOH. The anodic decay line is in two parts; the second higher slope region II when extrapolated to the point of intersection with the corresponding cathodic recovery line III has been ascribed to a mixed potential E_m between the nickel hydroxide/oxyhydroxide and the oxygen evolution reaction [13–17]. In order to obtain the true reversible potential, E_R, it is necessary to extrapolate the first part of the anodic decay line I to its point of intersection with the cathodic recovery line III.

Explanations for the change in slope of the anodic decay lines for essentially β-phase materials have been proposed at length by Conway *et al.* [13–17] in terms of the various steps in the oxygen evolution reaction on the charged electrode surface.

The slopes of the decay lines are considered by Conway *et al.* [13–17] to be identifiable with the negative of the Tafel Slope parameter b. It is interesting to note that the cathodic recovery lines show no corresponding change in slope. The initial portions of the E versus log t curves (up to $t \sim$ 100 s) appear to be controlled by capacitative decay/recovery processes which can be used to evaluate the reversible potential. Calculation is accomplished by using a factor τ to make plots of E versus log $(t + \tau)$ linear. The factor τ is defined [13–17] as the time required for the electrode to decay from infinite positive potential to the potential at zero time, and can be used to calculate the value of the surface pseudo-capacitance C_s using the relationship:

$$\tau = \frac{bC_s}{2{\cdot}303i} \tag{1}$$

Equation 1 implies that a plot of τ versus $1/i$ should be linear. This is illustrated in Fig. 2 for a fully charged plate containing the γ-phase. Values of C_s are found to be about 220 F/g $Ni(OH)_2$. This behaviour has been well established by Conway and co-workers [13–17].

Superficially the anodic decay and cathodic recovery lines show a resemblance to the behaviour which might have been expected if the e.m.f. was controlled by diffusion of species (e.g. protons) within the solid phase. Thus it could be argued that the data processing could be made using equations derived from diffusion theory analogous to those proposed by Scott [28] for MnO_2. Diffusion equations could in principle be applied to the cathodic recovery line, III, on the E versus log $(t + \tau)$ plot given in Fig. 1. However, it is difficult to reconcile the regions I and II having distinct slopes of 13·2 mV/decade and 29·2 mV/decade, for the anodic decay process with a single diffusion process (see Fig. 1). Furthermore, the low values and non-constant slopes obtained in the initial regions at various states of charge can only be understood in terms of unusual and varying dif-

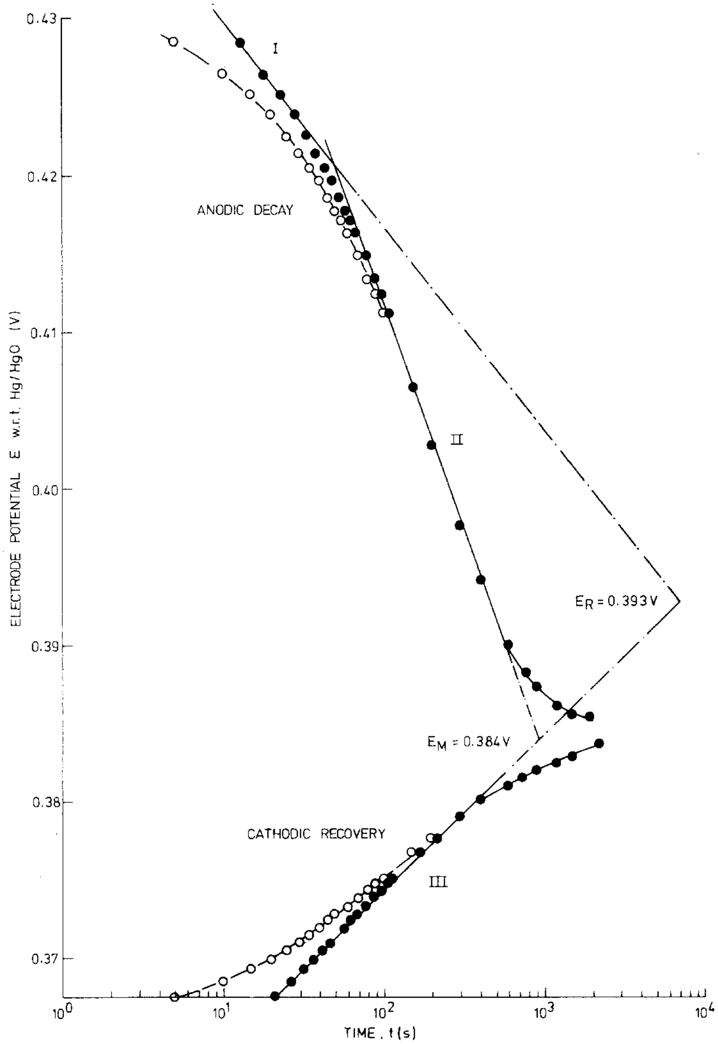


Fig. 1. Potential E against log t data for an 'activated' α-Ni(OH)$_2$/γ-phase couple in 1 M KOH. ○ E versus log t; ● E versus log $(t + \tau)$.

fusion laws having a time dependence from $t^{1/7}$ to $t^{1/4}$. Most diffusion processes obey a $t^{1/2}$ dependence, which would in turn give a slope for the E versus log $(t + \tau)$ line of 29 mV/decade. In view of the fact that the diffusion law must similarly change to compensate for the non-constant slope this description is inadequate. It might also be thought that the factor τ could be identified with an arbitrary constant depending on the boundary conditions used to establish the diffusion equations. In this case it is difficult to understand why τ is proportional $1/i$ (Equation 1).

The conclusion to be reached is that the e.m.f. data can be described most accurately by a simple capacitative decay/recovery model in agreement with that proposed by Conway *et al.* [13–17]. Even though the interrelation between the components in the equivalent circuit and the electrochemical processes involved is open to considerable speculation it does provide a foundation for understanding the E versus t data. As pointed out by Milner and Thomas [1] the assumptions in the method of Conway *et al.* for obtaining E_R values do require a symmetry in the charge/discharge processes and a total invariance of the pseudocapacitance with e.m.f. Even though these conditions may not be strictly met the method when carefully applied can give reproducible results and

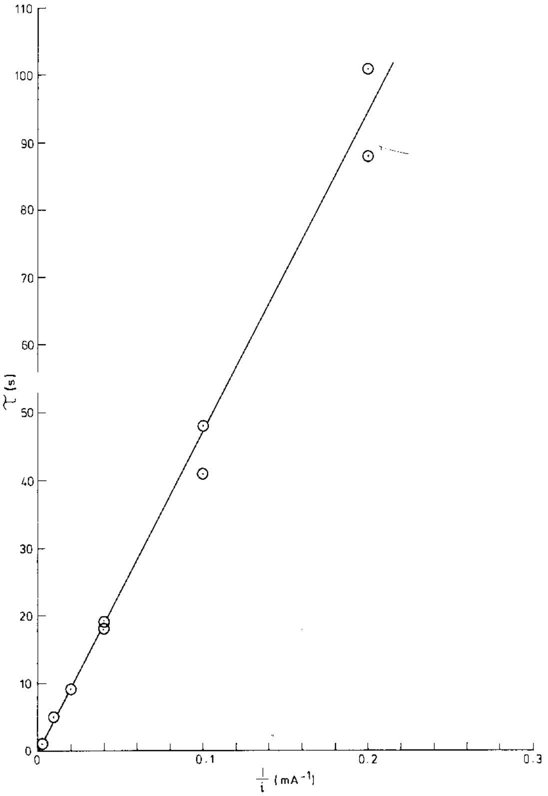


Fig. 2. Plot of τ (s) against i^{-1}(mA^{-1}) for a fully charged γ-phase material in 1 M KOH.

the values obtained can be used to gain considerable insight into the nickel oxyhydroxide electrode system.

3.2. *Variation of E_R with the state of oxidation of the nickel*

Figs. 3a–c show the variation of reversible potential E_R at various states of discharge for electrodes subjected to only low levels of total applied charge [< 10%, based on the $Ni(OH)_2$ content]. Fig. 3a compares the results obtained for electrodes containing initially 'de-activated' β-$Ni(OH)_2$ with those containing 'activated' α-$Ni(OH)_2$ for various KOH concentrations in the range 0·01–10 M. Figs. 3b and c show similar data for 'de-activated' α-$Ni(OH)_2$ and 'activated' β-$Ni(OH)_2$ respectively. In all cases it can be clearly seen that E_R is essentially independent of the state of charge of the electrode for each alkali concentration chosen.

Fig. 4 compares plots of E_R as a function of the state of charge of the electrode in terms of the total $Ni(OH)_2$ content for the 'de-activated' β-$Ni(OH)_2$/β-NiOOH and 'activated' α-$Ni(OH)_2$/γ-NiOOH system, respectively, in 1 M KOH. Data for the β-phase system were obtained using the method in Section 2.2.2 whilst data for the α-phase system were obtained using the method in Section 2.2.1. The mole fractions of $Ni(OH)_2$, X, used in Fig. 4 were calculated assuming an upper nickel oxidation state of Ni^{3+} in the β-phase system and Ni^{4+} in the α/γ-phase system. The mole fractions of nickel hydroxide, X, used in Fig. 4 are not known precisely since this would have required analytical measurements to determine the state of charge for each working electrode. The oxidation states are inferred from supplementary experiments using identical electrode materials and analytical procedures as described previously [22]. The mole fractions are considered to be known within ± 0·05. Considering first the results for the β-phase system it is clear over the range X from 0·75–0·30 that the potential remains constant within experimental error (± 4 mV). At values of X below 0·30 the potential falls gradually. Conway Gileadi [17] observed similar behaviour. The deviation at high states of oxidation in the β-phase system, was considered [17] to be caused by interference from an alternative oxygen evolution process. We consider that the depression in potential arises from γ-phase contamination. As is clear from Fig. 4 the α-$Ni(OH)_2$/γ-NiOOH system has a lower E_0 value than for the corresponding β-$Ni(OH)_2$/β-NiOOH system and depression of the potential for the contaminated β-phase system is to be expected. The independence of the potential with degree of oxidation was found to be the case over significant ranges of X for all alkali concentrations, but the precise limits were not determined in every case.

Because of the instability of 'activated' α-$Ni(OH)_2$ (i.e. a tendency to revert to a 'de-activated' α-phase) it proved to be extremely difficult to obtain meaningful data for the variation of E_R with X except in dilute alkali. For this reason only data in 1 M KOH have been presented in Fig. 4. As in the case of the β-phase system it is clear that the potential remains constant between the limits of X from 0·88 to 0·40. In 7 M KOH the 'flat region' was found to extend only between the limits 0·85 to 0·80. The upward deviation in potential is considered to be caused

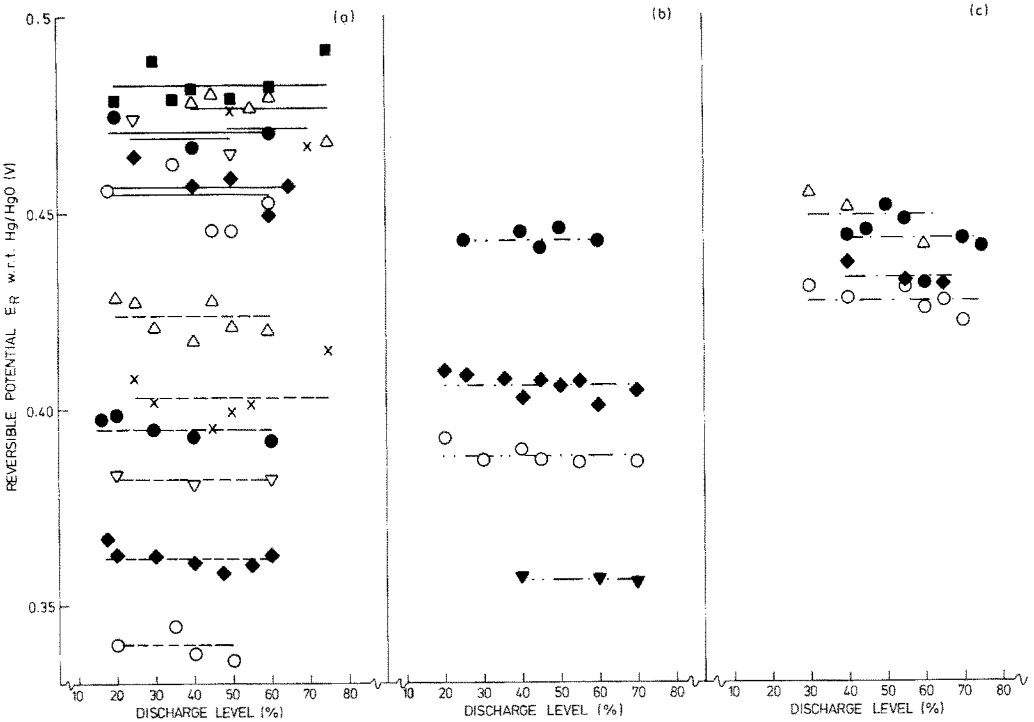


Fig. 3. Variation of reversible potential E_R at various states of discharge for electrodes subjected to low levels of applied charge (< 10%). Couples investigated: (a) ——— 'de-activated' β-Ni(OH)$_2$/β-NiOOH; (a) - - - - - - - 'activated' α-Ni(OH)$_2$/γ-NiOOH; (b) ··—··—··—'de-activated' α-Ni(OH)$_2$/γ-NiOOH; (c) —·—·—·— 'activated' β-Ni(OH)$_2$/β-NiOOH. Alkali concentrations (M): ■ 0·01; △ 0·1; × 0·5; ● 1·0; ▽ 2·0; ◆ 5·0; ○ 7·1; ▼ 10·4.

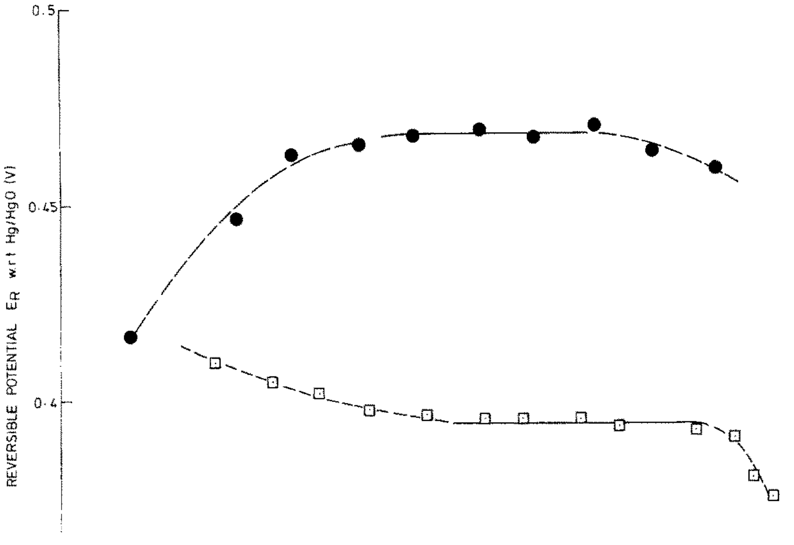


Fig. 4. Variation of reversible potential E_R as a function of the state of charge of the electrode expressed in terms of the total Ni(OH)$_2$ content. ● 'de-activated' β-Ni(OH)$_2$/β-NiOOH couple in 1 M KOH; ⊡ 'activated' α-Ni(OH)$_2$/γ-NiOOH couple in 1 M KOH.

by contamination by phases having higher E'_0 values than for that based on the 'activated' α-Ni(OH)$_2$ system (i.e. 'de-activated' α- or β-phase contaminants). Because the conversion of α-Ni(OH)$_2$ to more stable species is both time and alkali concentration dependent [18, 27] the precise point at which the upward potential excursion is noted depends largely on the experimental procedure employed. Clearly it is desirable to make E_R measurements after as short a time as possible necessitating small charge inputs. This is feasible provided the constant potential region is first located as in Figs. 3a–c. For example, if E_R is measured after removing 50% of the applied charge it is possible to obtain constant E_R values with states of total charge as little as 5%. This is a direct consequence of the non-uniform charging characteristics of the sintered plate electrode and implies that at low states of charge (5–10%) only the active material closest to the current collector becomes charged. The limits suggested by the mole fractions of nickel hydroxide shown in Fig. 4 must therefore be viewed with caution. These are empirical quantities dictated largely by the type of electrode fabrication employed. Nevertheless because both systems show apparently 'heterogeneous discharge' behaviour over wide nickel oxidation ranges, as seen in Figs. 3 and 4, it becomes feasible to examine the dependence of E_R with alkali and water activity.

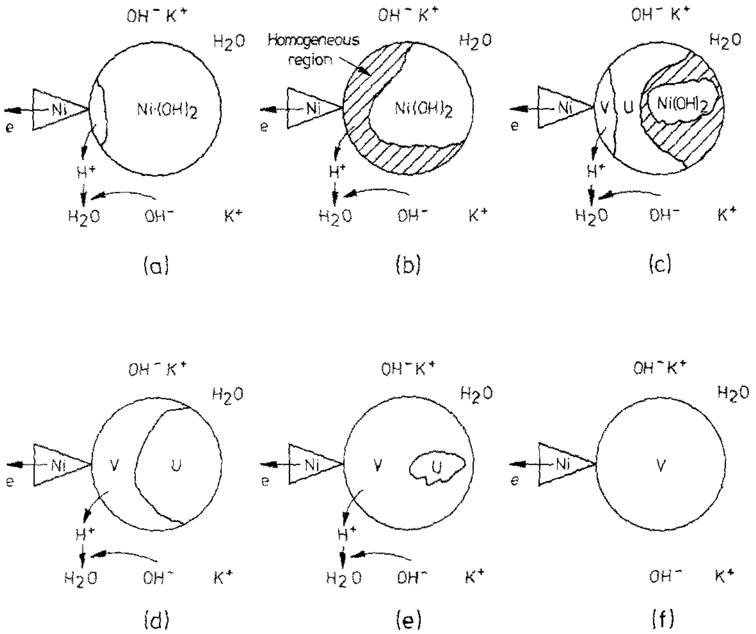
3.3. *Nature of the potential-determining processes*

Conway and Gileadi [17] suggested that the potential of the charged nickel hydroxide electrode remained constant for states of charge between 20% and 50% because its potential was controlled by a surface phase of constant composition, superimposed on a bulk phase of varying degree of oxidation but not potential determining. The heterogeneous model was dismissed because for states of charge up to 20% the potential was a function of nickel oxidation state. X-ray diffraction measurements were considered to show that oxidation took place in a homogeneous phase over the whole of the charge process. In agreement with Conway and Gileadi [17] a hypothetical totally heterogeneous reaction is unlikely to be involved. However, a system which shows small regions of apparent homogeneity towards both high and low limits of nickel oxidation state but with a heterogeneous region between the limits is possible. In order for a cathode to function efficiently by such a mechanism both oxidized and reduced phases should possess adequate electronic as well as ionic conductivity [29]. There is evidence [30–32] to suggest that both α- and β-Ni(OH)$_2$ are reasonable proton conductors. On the other hand both materials in the pure state are low conductivitiy p-type semiconductors [32–35]. On charging, n-type conductivity can be developed [34] by oxidation of Ni^{2+} cations to Ni^{3+} or Ni^{4+}. In the case of the β-phase material the reaction can be written simply as:

$$\mathrm{Ni(OH)_2} \rightleftharpoons \mathrm{NiOOH} + \mathrm{H^+} + \mathrm{e}. \qquad (2)$$

The charge/discharge processes for a single grain of active material are depicted by the diagrams of Fig. 5a–i. It is logical that charging must take place initially at a tri-phase boundary of Ni/Ni(OH)$_2$/KOH (i.e. close to the Ni current collector). Charging could not start at a place on the nickel hydroxide surface remote from the electron sink because the potential drop across the poorly conducting Ni(OH)$_2$ would be prohibitive. The proposition can be verified readily by direct experimental observation where blackening (oxidation of the green nickel hydroxide) only takes place adjacent to the current collector. Once electronic conductivity has been initiated for example in β-Ni(OH)$_2$ this is readily propagated most probably around the surface of the grain as in Fig. 5a. This initial homogeneous solid solution of Ni^{3+} ions in a Ni(OH)$_2$ matrix continues to grow by charge transfer and diffusion until a phase U of fixed nickel ion composition $Ni^{2+}_x \cdot Ni^{3+}_{(1-x)}$ is reached at which stage phase separation occurs thereby providing a means of reaching a stable point on the free energy composition curve. From elementary thermodynamic considerations [38, 39] phase V richer in the higher valence state must be simultaneously present as in Fig. 5c. If the potential–composition curve is assumed to be symmetrical then the phase V will have a composition $Ni^{2+}_{(1-x)} \cdot Ni^{3+}_x$. Once phases U and V are both present the potential remains invariant until phase U has been completely oxidized to phase V (Fig. 5f) or an alternative process becomes dominant. In spite of the apparent heterogeneity the oxidation process can still be considered to occur topochemically.

CHARGE PROCESS



DISCHARGE PROCESS

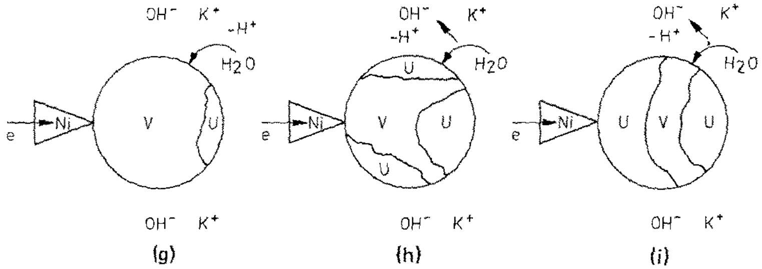


Fig. 5. Diagrammatic representation of the charging processes (a–f) and discharging processes (g–i) taking place in a single grain of active material.

The formation of a hypothetical boundary between the phases U and V poses the question as to the site of the charge transfer reaction. Whilst it could be proposed that the U/V phase boundary constitutes a charge-transfer interface, considerations of continuity of current would require that the proton (or some other equally mobile ionic species) must carry the charge from the solid/electrolyte interface to the U/V boundary. It seems more probable that the electron is the only entity which carries the current as such within the solid phase, the protons moving solely under the influence of concentration gradients (i.e. by diffusion). For this situation to prevail it is necessary to assume that the oxide/solution interface is the site of the charge transfer reaction. Although a visible distinction exists between uncharged green $Ni(OH)_2$ and the black partly charged phases U and V it is difficult to distinguish between phases U and V as such. Thus the movement of the U/V boundary cannot be used to elucidate on the type of discharge mechanism. In reality it is unnecessary for a single boundary to exist between phases U and V; these components probably being distributed as a mosaic within a crystallite. This is a consequence of phase separation [38] resulting entirely from the introduction of Ni^{3+} ions into the $Ni(OH)_2$ lattice, beyond the solubility limit. Furthermore, the movement of the U/V phase boundary need not relate to the site of the charge transfer reaction.

Figs. 5g–i show the behaviour of a grain of phase V on discharge. Because phase V is electronically conducting (more so than phase U) discharge is depicted not as starting close to the electron source but at other positions where a surface condition for electrolyte availability is favourable. When phase U covers the electronic contact in sufficient depth there is the possibility, due to its inadequate electronic conductivity, of premature termination of discharge even though some phase V remains (Fig. 5i). The efficiency of reduction of active material in a practical sintered plate electrode depends on the number and location of effective current collectors in relation to the active material. In general it is observed that the active material furthest from the current collector tends to remain undischarged. Conversely on the charge process the active material closest to the current collector tends to reach the highest state of oxidation.

The oxidation of α-$Ni(OH)_2$ to γ-NiOOH is considered to proceed in a similar manner to the oxidation of β-$Ni(OH)_2$, with the formation of co-existing phases U′ and V′ which contain Ni^{2+} and Ni^{4+} ions respectively. This choice will be discussed later. It is interesting to note that Briggs and Fleischmann [36] have made micrographic observations using thick α-$Ni(OH)_2$ films which provide possible evidence of phases U′ and V′. In cross-sections of partially charged electrodes they observed a zone of uncharged green α-$Ni(OH)_2$, a black central region and very significantly a thinner layer next to the current collector possessing a yellowish, metallic lustre. It is tempting to suggest that the black central region identifies with phase U′ whilst the yellowish metallic region relates to the more highly conducting phase V′. The apparent heterogeneity of the charge process for thick α-$Ni(OH)_2$ films was also confirmed by Briggs and Fleischmann [36] since two rising potentiostatic current–time transients characteristic of the nucleation and growth of distinct phases were observed. However, in the case of thin-film electrodes only one rising transient was observed. Accordingly Briggs and Fleischmann [36] concluded that the change of phase was coincidental in the case of the thick film electrode.

In a previous study [29] it was shown that oxidation of the β-phase in sintered plate electrodes invariably terminates at an average nickel oxidation state of ~ 2·75 after which oxidation to the γ-phase commences. This is also responsible for the fall in potential seen in Fig. 4 during oxidation of β-$Ni(OH)_2$. Whilst this reaction is in progress reproducible potentials cannot be obtained. In the review by Milner and Thomas [1] (their Fig. 3) it is apparent that a large number of investigators find an oxidation state of ~ 2·7 for the oxidized β-phase rather than the expected value of 3·0. Although, the existence of pure β-NiOOH is not disputed the equilibrium potential measurements suggest that this is difficult to achieve by anodic oxidation in concentrated alkali (e.g. 7 M). The preparative procedures described by Bode *et al.* for β-NiOOH generally employ dilute alkaline media (i.e. 0·1–1·0 M).

The materials with an oxidation state of ~ 2·75 and 2·25 could be identified with the compounds proposed by Glemser and Einerhand [37] of $Ni_3O_2(OH)_4$ and $4Ni(OH)_2 \cdot NiOOH$; we consider that it is better to regard the above as particular solid solution limits rather than as specific compounds. Nevertheless the fact that by carefully controlling the oxidation conditions such limits are found is significant. Glemser and Einerhand [37] considered that the secondary discharge step [22] was related to $Ni_3O_2(OH)_2$. However, as shown previously [22] this is unlikely to be the case but a material nearer in composition to $4Ni(OH)_2 \cdot NiOOH$ could be involved. Because the removal of Ni^{3+} or Ni^{4+} defects from phases U or U′ lead to diminishing electronic conductivity if the current is sufficiently large a barrier layer of Ni^{2+} can form between the charged active material and the electron source. It is considered that the inherent inefficiencies observed during discharge of nickel oxyhydroxide electrodes stem from this effect. Because of the intervention of semiconducting processes the secondary discharge stage is not related to an equilibrium process as will be discussed in more detail in the next paper [38].

It might be argued that the secondary discharge step arises as a result of proton diffusion limitations in the solid state or to a change in diffusion mechanism. However, this concept is inconsistent with the inability to remove further capacity when the electrodes are left to recover on open circuit [22]. Another objection is that the step is only observed during the discharge process and since the mechanism of proton diffusion should be independent of the direction of the externally applied electric field a corresponding step would be expected also on the charge process if proton diffusion limitations were involved. Conway and Bourgault [13–15] have shown using isotopic substitution methods that proton diffusion limitations are not responsible for the slow rate of e.m.f. decay of the nickel oxyhydroxide electrode on open circuit. Russian workers [32] similarly conclude that lack of electronic conductivity of the active material is more likely to be the cause of failure on discharge at high rates.

3.4. *Dependence of E_R with KOH and H_2O activities*

Table I gives the values of E_R for the α-Ni$(OH)_2$/γ-NiOOH and β-Ni$(OH)_2$/β-NiOOH systems determined in the horizontal regions shown in Figs. 3a–c at various alkali concentrations. Also listed are the logarithms of the activities of the KOH and H_2O species. These values have been calculated from the data of Akerlof and co-workers [40, 41]. It should be noted that some confusion arises in these papers [40, 41] in as much as a_{MOH} is used to denote both mean ionic activity and activity. The activity coefficients measured are in fact mean ionic activity coefficients $\gamma_\pm$ so that $a_{KOH} = (\gamma_\pm m)^2$. In this paper a_{KOH} denotes activity only. Fig. 6 shows plots of E_R versus $\log a_{KOH}$ for the 'activated' and 'de-activated' β-Ni$(OH)_2$/β-NiOOH and α-Ni$(OH)_2$/γ-NiOOH systems in addition to results obtained by previous workers [13–15, 23].

The dependence of reversible potential E_R on the alkali and water activities for the results in Table 1 can be fitted to an empirical equation at constant temperature (25° C) of the form:

$$E_R = E_0' - p \log a_{KOH} + q \log a_{H_2O} \qquad (3)$$

where E_0' is the formal potential and p and q are constants. The following equations, obtained by using a mean-square fitting procedure, can be shown to most accurately describe the experimental results for the four systems examined:

activated, α-Ni$(OH)_2$/γ-NiOOH

$$E_R^A = 0{\cdot}3919 - 0{\cdot}0139 \log a_{KOH} + 0{\cdot}0386 \log a_{H_2O} \qquad (4)$$

de-activated α-Ni$(OH)_2$/γ-NiOOH

$$E_R^B = 0{\cdot}4403 - 0{\cdot}0139 \log a_{KOH} + 0{\cdot}0470 \log a_{H_2O} \qquad (5)$$

activated β-Ni$(OH)_2$/β-NiOOH

$$E_R^C = 0{\cdot}4428 - 0{\cdot}0028 \log a_{KOH} + 0{\cdot}0315 \log a_{H_2O} \qquad (6)$$

de-activated β-Ni$(OH)_2$/β-NiOOH

Table 1. Dependence of reversible potential E_R *with KOH concentration for various nickel hydroxide/oxyhydroxide couples*

KOH concentration		*log* a_{KOH}	*log* a_{H_2O}	*Reversible potential* (E_R) *w.r.t. Hg/HgO/KOH* (V)			
Molarity (M)	*Molality* (*m*)			*α-phase/γ-phase*		*β-phase/β-phase*	
				'activated'	*'de-activated'*	*'activated'*	*'de-activated'*
0·01	0·01	−4·0877	−0·00015	–	–	–	0·483 ± 0·005
0·1	0·1	−2·2059	−0·0015	0·423 ± 0·004	–	0·449 ± 0·007	0·477 ± 0·004
0·5	0·5	−0·8808	−0·0075	0·403 ± 0·007	–	–	0·472 ± 0·006
1	1·01	−0·2448	−0·0158	0·395 ± 0·003	0·443 ± 0·002	0·443 ± 0·006	0·471 ± 0·004
2	2·05	+ 0·5083	−0·0360	0·382 ± 0·001	–	–	0·469 ± 0·006
5	5·36	+ 2·0071	−0·1331	0·362 ± 0·003	0·406 ± 0·002	0·433 ± 0·003	0·457 ± 0·006
7·1	7·97	+ 2·9441	−0·2451	0·340 ± 0·004	0·388 ± 0·003	0·427 ± 0·003	0·453 ± 0·007
10·4	12·65	+ 4·3563	−0·5052	–	0·356 ± 0·001	–	–

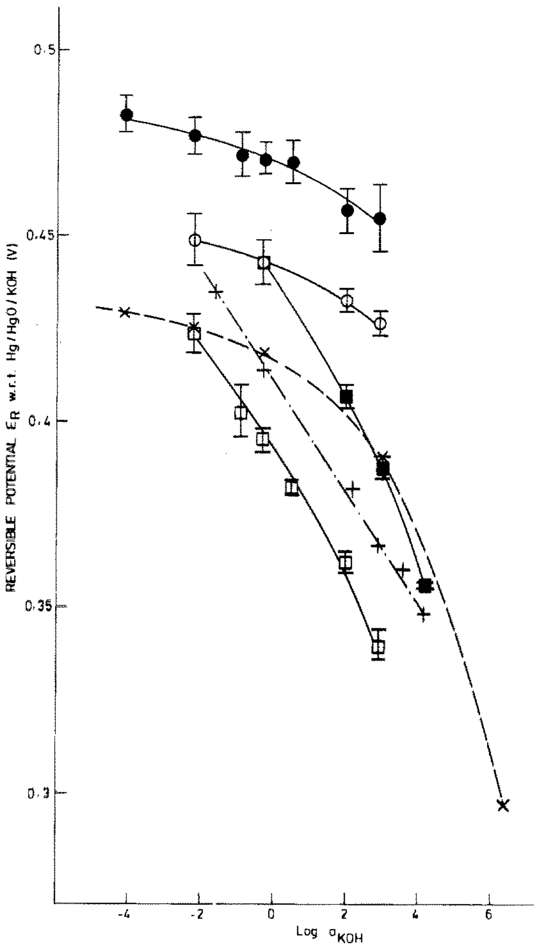


Fig. 6. Variation of reversible potential, E_R, as a function of log activity of KOH (log a_{KOH}) for various nickel hydroxide/oxyhydroxide couples: ● 'de-activated' β-$Ni(OH)_2$/β-NiOOH; ○ 'activated' β-$Ni(OH)_2$/β-NiOOH; ■ 'de-activated' α-$Ni(OH)_2$/γ-NiOOH; □ 'activated' α-$Ni(OH)_2$/γ-NiOOH; + data by MacArthur [18]; × data by Conway and Bourgault [10].

$$E_R^D = 0{\cdot}4701 - 0{\cdot}0032 \log a_{KOH} + 0{\cdot}0342 \log a_{H_2O}. \qquad (7)$$

Fig. 6 shows these lines. The overall generalized cell reaction for a $Ni(OH)_2$/NiOOH couple against a Hg/HgO/KOH reference electrode may be written thus:

$$(wU)y_1H_2O \cdot z_1KOH + (z_2 - z_1)\,KOH + HgO \rightleftharpoons (wV)y_2H_2O \cdot z_2KOH + (1 + y_1 - y_2)\,H_2O + Hg \qquad (8)$$

where U and V (or U′ and V′) denote the composition of the co-existing phases determining the equilibrium potential as discussed in Section 3.3. This approach differs from that of previous workers where fully oxidized and reduced species are considered. Accordingly the quantity w is defined as 2/number of electrons required to oxidize 1 mole of phase U (or U′) to phase V, (or V′) and depends on the composition of the pairs of co-existing phases, derived from the parent β or α-phase $Ni(OH)_2$. It should be noted that the co-existing phases [38] are solid solutions of the various ions having predetermined composition, and not simply mechanical mixtures of the two components. From Equation 8 the following Nernst equation can be derived:

$$E = E_0 + 2{\cdot}303\,\frac{wRT}{2F}\log\frac{a(\mathrm{V})}{a(\mathrm{U})} + 2{\cdot}303\,\frac{RT}{2F}\log\frac{(a_{H_2O})^{1+y_1-y_2}}{(a_{KOH})^{z_2-z_1}} \qquad (9)$$

The quantity E_0 is the standard potential; a(U), a(V), a_{H_2O} and a_{KOH} are the activities of the various species and R, T and F have their usual significance. It should be noted that because the nickel hydroxide electrode shows the same hydroxyl ion dependence as the Hg/HgO/KOH reference the a_{OH} terms cancel out and do not appear in Equations 8 or 9.

The reversible potentials for the four systems studied in this work have only been measured in the heterogeneous regions, i.e., where the e.m.f. is independent of the state of oxidation of the solid phase components as confirmed by Figs. 3a–c and Fig. 4. Consequently the terms a(U)/a(V) or a(U′)/a(V′) are constant and in fact unity if the e.m.f. – composition curves are symmetrical [38]. In keeping with the usual practice these terms can be conveniently incorporated in the E_0 terms and described as formal potentials E_0'.

By combining the empirical Equations 4–7 obtained for the four systems with Equation 8 the relative changes in KOH and H_2O content, i.e. $(z_2 - z_1)$ and $(1 + y_1 - y_2)$ on oxidation can be evaluated using the relationships:

$$p = 0{\cdot}0296(z_2 - z_1) \qquad (10)$$

and

$$q = 0{\cdot}0296(1 + y_1 - y_2) \qquad (11)$$

The results are summarized in Table 2.

From both Fig. 6 and Table 2 it is clear that

Table 2. Summary of e.m.f. data obtained for 'activated' and 'de-activated' nickel hydroxide/oxyhydroxide couples

System	*Formal potential* (E'_0)	*Change in KOH content* [($z_2 - z_1$) mean]		*Change in H_2O content* [($1 + y_1 - y_2$) mean]		*KOH content in oxidized phase* (V, V') (moles)	*H_2O content* (moles)	
							Reduced phase (U, U')	*Oxidized phase* (V, V')
'activated' α-phase/γ-phase	0·3919	0·470	0·470	1·304	1·446	0·33	0·67	0·35
'de-activated' α-phase/γ-phase	0·4403	0·470		1·588				
'activated' β-phase/β-phase	0·4428	0·095	0·102	1·064	1·110	0·026	0·25	0·22
'deactivated' β-phase/β-phase	0·4701	0·108		1·155				

only these couples derived from 'activated' and 'de-activated' α-Ni(OH)$_2$ show a marked change of E_R with a KOH, i.e. a change in KOH content on oxidation. A significant change in water content may also be deduced. In the case of couples derived from 'activated' and 'de-activated' β-Ni(OH)$_2$ the dependence of E_R with KOH activity is much smaller than for the α-phase materials and the changes in water activities are even smaller being only just within the limits of detection by the experimental method employed (note the relatively large error bars in Fig. 6 and in Table 1). Another striking feature of Fig. 6 and Table 2 is that whilst the values of E_0' for the 'activated' and 'de-activated' materials derived from the parent α- or β-Ni(OH)$_2$ differ noticeably the overall changes in KOH content $(z_2 - z_1)$ are, within experimental error, identical. Examination of the reversible potential as a function of alkali activity can therefore provide a means of distinguishing between the α- and β-crystal structures.

3.5. *Composition of the co-existing phases*

In order to use the measured changes in KOH and H_2O content further it is necessary to make assumptions regarding the likely compositions of the co-existing phases. If it is assumed that the fully oxidized product from both 'activated' and 'de-activated' α-Ni(OH)$_2$ is an identical γ-phase (i.e. phase V′) material then according to Bode *et al.* [19, 42] and Russian workers [43], this material is likely to have an oxidation state of 3·67 and a Ni/K ratio of 3·0. From the data of Table 2, it is clear that for a 2e transfer the change in KOH is 0·47 moles. This implies that the least oxidized co-existing phase (U′) has an oxidation state of 2·25 and if it is devoid of KOH giving a value for w of 1·41. As discussed previously it has been tentatively suggested on oxidation of β-Ni(OH)$_2$ ('activated' or 'de-activated') that co-existing phases (U and V) are found at nickel oxidation states of 2·25 and 2·75 respectively giving a value for w of 4·0. Again it is assumed that the least oxidized co-existing phase U is free from KOH. The overall changes in H_2O and KOH contents between the various phases can be determined from the ratios $(y_2 - y_1)/w$ and $(z_2 - z_1)/w$. By assuming that the phases U and U′ have the same water contents as the parent β- and α-Ni(OH)$_2$, respectively, namely 0·25 and 0·67 H_2O then the water contents of the oxidized phases V and V′ may also be calculated. These results are included in Table 2. Because the differences between the 'activated' and 'de-activated' systems in terms of relative H_2O or KOH content are small, average values have been taken. These values may then be used to write half-cell reactions for the couples derived from α- and β-Ni(OH)$_2$ as follows:

(a) 'activated' or 'de-activated' phase U′ ⇌ phase V′

$$[0{\cdot}125\,\mathrm{NiO_2}\cdot 0{\cdot}875\,\mathrm{Ni(OH)_2}]\,0{\cdot}67\,\mathrm{H_2O} + 0{\cdot}33\,\mathrm{KOH} + 1{\cdot}42\,\mathrm{OH^-} \rightleftharpoons [0{\cdot}833\,\mathrm{NiO_2}\cdot 0{\cdot}167\,\mathrm{Ni(OH)_2}]\,0{\cdot}35\,\mathrm{H_2O}\cdot 0{\cdot}33\,\mathrm{KOH} + 1{\cdot}74\,\mathrm{H_2O} + 1{\cdot}42\,e \tag{12}$$

(b) 'activated' or 'de-activated' phase U ⇌ phase V

$$(0{\cdot}25\,\mathrm{NiOOH}\cdot 0{\cdot}75\,\mathrm{Ni(OH)_2}]\,0{\cdot}25\,\mathrm{H_2O} + 0{\cdot}025\,\mathrm{KOH} + 0{\cdot}5\,\mathrm{OH^-} \rightleftharpoons [0{\cdot}75\,\mathrm{NiOOH}\cdot 0{\cdot}25\,\mathrm{Ni(OH)_2}]\,0{\cdot}22\,\mathrm{H_2O}\cdot 0{\cdot}025\,\mathrm{KOH} + 0{\cdot}53\,\mathrm{H_2O} + 0{\cdot}5\,e \tag{13}$$

3.6. *Comparison with other workers*

Considering first the data for the β-phase couples it is clear that the change in both KOH and H_2O on oxidation are small. These measurements are in keeping with the observations of Bode *et al.* [18, 19] in that the fully oxidized β-NiOOH is essentially free from alkali cation.

From Fig. 6 it may be seen that the results of Conway and Bourgault [13–15] show an apparently greater dependence of E_R with a_{KOH} towards the high alkali concentrations than is found in the present work. The part of the curve at low alkali activities (below 1 M) could indeed be considered to be derived from an 'activated' β-phase starting material. However, the departure at high alkali concentrations in the light of the present investigation is most probably caused by interference from additional α/γ-phases. This inevitably arises if the β-phase is fully charged and then discharged particularly in high alkali concentration. In order to account for this fall in e.m.f. at high alkali concentrations Conway and Bourgault [13–15] proposed an unusually high H_2O dependence, namely:

$$E_R = 0{\cdot}420 - 0{\cdot}004 \log a_{\mathrm{KOH}} + 0{\cdot}105 \log a_{\mathrm{H_2O}}. \tag{14}$$

This should be compared with Equation 6 of this work.

Conway and Bourgault [13–15] proposed a formula for the charged β-phase of (2NiOOH) 0·14 KOH. Alternative formulations have been proposed by other workers namely (2NiOOH) $2H_2O$ [6–8], (2NiOOH) 0·2 H_2O [9, 10] and (2NiOOH) 0·67 KOH · 1·16 H_2O [12]. Contamination by the γ-phase is particularly evident in the work of Kornfeil [12].

Bode *et al.* [19, 42] have proposed a formula for the γ-phase produced in NaOH as ($4NiO_2$ · 2NiOOH) $2H_2O$ · 2NaOH or $Na_{0{\cdot}33}NiO_2$ · 0·67 H_2O. Similarly Russian workers [43] have prepared various γ-phases by oxidation of Na NiO_2 single crystals in the appropriate alkali, namely $Li_{0{\cdot}3}Na_{0{\cdot}01}H_{0{\cdot}04}NiO_2$ · 0·5 H_2O, $Na_{0{\cdot}3}H_{0{\cdot}04}$ · NiO_2 · 0·6 H_2O and $K_{0{\cdot}3}Na_{0{\cdot}005}$ $H_{0{\cdot}04}NiO_2$ · 0·4 H_2O. The composition of the γ-phase (phase V′) used in Equation 12 is equivalent to $K_{0:33}NiO_2$ · 0·68 H_2O with the difference being that the required Ni oxidation state (3·67) has been achieved by using a mixture of Ni^{2+} and Ni^{4+} cations rather than Ni^{3+} and Ni^{4+} cations. The incorporation of Ni^{3+} and Ni^{4+} ions in the γ-phase suggested by Bode *et al.* [19] was made on the basis of the magnetic measurements of Labat [44] using chemically oxidized samples of $Ni(OH)_2$. Labat's measurements made *in situ* during the anodic oxidation of β-$Ni(OH)_2$ are less convincing because there is evidence that Ni^{4+} was present before production of Ni^{3+} was completed. There are several observations which reasonably suggest that the γ-phase could be equally formulated with Ni^{2+} and Ni^{4+} ions. Firstly α-$Ni(OH)_2$ can be oxidized directly to the γ-phase without obvious emergence of an intermediate trivalent stage. Furthermore oxidation of α-$Ni(OH)_2$ to the γ-phase occurs at a lower potential than the oxidation of β-NiOOH to 'γ-NiOOH'. Aleshkevich *et al.* [45] point out from considerations of the energy to remove a proton from an OH group attached to the nickel cation that kinetic factors tend to favour the formation of Ni(IV) rather than Ni(III). As far as the e.m.f. data are concerned the manner in which the Ni oxidation state is achieved is relatively unimportant but it is easier to rationalize the development of the co-existing phases in the α-$Ni(OH)_2/\gamma$-phase system in terms of only one higher valent species.

Whilst the dependence of E_R with a_{KOH} confirms a considerable uptake of K^+ ion on oxidation of 'activated' or 'de-activated' α-$Ni(OH)_2$, e.m.f. data alone cannot establish the composition of the γ-phase. The good correlation between the water contents in the γ-phase required by the e.m.f. data and that proposed by Bode *et al.* [19, 42] and by the Russian workers [43] is significant. The variation of e.m.f. with water activity for both the 'de-activated' and 'activated' α-$Ni(OH)_2/\gamma$-phase systems is greater than the experimental error and is more significant than obtained for the corresponding β-phase systems. A useful aspect of the measurements is to establish the likely oxidation state of the least oxidized co-existing phase as discussed previously. Clearly if the least oxidized phase was considered to have an oxidation state of 2·0 then using the analytically determined composition of the γ-phase this would lead to the requirement of a 0·395 mole change of KOH for a 2e transfer which clearly does not agree with the measured e.m.f. data (0·47 moles KOH per 2e transfer).

As can be seen from Fig. 6 the e.m.f. data of MacArthur [23] fall between the results obtained in this work for the 'activated' and 'de-activated' α-$Ni(OH)_2/\gamma$-phase couples. MacArthur deduced a KOH dependence of 0·494 moles for a 2e transfer in reasonable agreement with this work.

It is clear from the known crystal structure of β-NiOOH [19, 26] that the interlayer spacing is to too small to accomodate K^+ ions or water molecules. Thus any K^+ ions or H_2O molecules present in phase V, i.e. [0·75 NiOOH · 0·25 $Ni(OH)_2$] 0·22 H_2O · 0·025 KOH must be confined to the surface only. On the other hand in the γ-phase the interlayers are expanded by at least 0·34 nm which is more than sufficient [26] to allow incorporation of H_2O molecules (radius, 0·17 nm) or K^+ ions (radius, 0·133 nm).

3.7. *Significance of the E_0 values*

This study has drawn attention to the difficulty in establishing E_0 values for the nickel hydroxide/oxyhydroxide system. Considerable care must be taken to define whether the couple under study is derived from the α- or β-crystal structure. In addition, the values of E_0' can also vary between measurements using $Ni(OH)_2$ samples belonging essentially to the same crystal classification. It should be noted in this context, that aging of 'active' α-Ni(OH)$_2$ in aqueous KOH does not lead immediately to conversion to β-Ni(OH)$_2$ but to an intermediate 'de-activated' α-Ni(OH)$_2$ phase. Eventually an 'activated' β-phase is formed and this may later age to give a 'de-activated' β-phase.

Fig. 6 demonstrates that by measuring E_R values over a range of alkali concentrations it is possible to distinguish between nickel hydroxide/oxyhydroxide systems having a small or large interlayer spacing. At least the quantity of KOH and H_2O taken into the interlayer regions appears to be a relatively well-defined quantity in the γ-phase material. Although, only one curve for each type of 'activated' and 'de-activated' phase are shown in Fig. 6 it is highly likely that a more extensive range of parent Ni(OH)$_2$ lattices can be obtained. It is possible for both α-Ni(OH)$_2$ and β-Ni(OH)$_2$ phases to give rise to couples having an identical E_0' value the only distinction between the two cases being the dependence of E_R with alkali concentration. The general trend appears to be that the most 'aged' β-Ni(OH)$_2$ phases give rise to couples having the highest E_0' values whilst the most 'activated' α-Ni(OH)$_2$ phases give the lowest E_0' value. It is undoubtedly this overlap between the α- and β-systems which has given rise to so much confusion in the literature and to the well-known but little understood hysteresis effect [1].

The difference in E_0' between couples derived from Ni(OH)$_2$ belonging essentially to the same crystallographic type is probably related to the intrinsic order/disorder created in the lattice at the time of preparation, i.e. entropy differences. Both α- and β-Ni(OH)$_2$ belong to a system of layer lattices [26] and it is an inherent feature of such systems that slippage between the layers can give rise to a sequence of stacking faults. This is particularly prone to occur in the α-Ni(OH)$_2$ class of materials as evidenced by the reduced intensity and broadening or even total absence of X-ray diffraction lines. Turbostratic layer structures can be envisaged analogous to those in bitumens and graphites [26]. It could be postulated for the least oxidized phases that the more ordered structures give rise to the highest E_0' values, conversely the lowest E_0' values relate to disordered structures. This trend would be reversed if the more oxidized phases are considered, i.e. ordering in the oxidized phase would give rise to a fall in E_0'.

Whilst the hydration state of the Ni(OH)$_2$ is important with regard to the electrochemical process this value does not appear to be significantly different between the 'activated' and 'de-activated' species although there is a definite difference in hydration between the α- and β-classes. Rademacher *et al.* [46] have similarly observed differences in the electrochemical behaviour between various β-phase materials and concluded that it is difficult to reconcile this entirely with water content.

An alternative source for the shift in E_0' values might be related to asymmetry in the compositions of the co-existing phases, i.e. excess free energy of mixing. However, as will be shown in the next paper [38] vary large differences, in composition of the respective pairs of co-existing phases, between the 'activated' and 'de-activated' systems would be required to account for the experimental differences ($\sim$ 20 mV) in the E_0' values observed. Excess energy differences are typically of the order of 0·4 kJ mole^{-1} whereas the observed change is about an order of magnitude higher. This argument is unacceptable since both the 'activated' and 'de-activated' types of system show heterogeneous regions over the same range (see Fig. 3).

According to IUPAC [47] the formal potential E_0' for the Ni(OH)$_2$/NiOOH couple is 0·42 V w.r.t. Hg/HgO/1 M KOH citing as the data source Conway and Gileadi [17]. In this study the corresponding values of E_0' for 'activated' and 'de-activated' β-phase couples are in the range 0·443–0·470 V w.r.t. Hg/HgO/1 M KOH. This compares with values of 0·392–0·440 V w.r.t. Hg/HgO/1 M KOH for 'activated' and 'de-activated' α-Ni(OH)$_2$/γ-phase couples. MacArthur [23] gives a value of E_0' of 0·411 V w.r.t. Hg/HgO/1 M KOH for the α-Ni(OH)$_2$/γ-phase couple.

This study has been restricted to an evaluation of the 'aging' of the least oxidized phase. However, previous investigations have revealed the possibility of the oxidized phase 'de-activating' with time and increased temperature. For example, sintered plate β-Ni(OH)$_2$/β-NiOOH electrodes show a lowering in operating potential of about 50 mV after 'aging' at 75° C for several weeks [48]. The measurement of reversible potentials where the oxidized phase has been aged are currently under investigation.

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