Studies concerning charged nickel hydroxide electrodes. IV. Reversible potentials in LiOH, NaOH, RbOH and CsOH

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The variation of reversible potential E_R with log a_{MOH} and log a_{H_2O} has been studied for several nickel hydroxide/oxyhydroxide couples in various alkali hydroxides. Both 'activated' and 'deactivated' β-phase couples show only a small dependence of E_R with log a_{MOH} (or log a_{H_2O} where known) in LiOH, NaOH, RbOH and CsOH electrolytes. The change in MOH content on oxidation/reduction is found to be about 0.1 mol MOH per two-electron transfer and is the same as found previously in KOH. These results confirm that the bulk oxidized β-phase lattice is devoid of alkali cation although a small quantity may be adsorbed by the surface. On the other hand both 'activated' and 'deactivated' α/γ-phase couples show a marked dependence of ~ 0.45 mol MOH per two-electron transfer in LiOH, NaOH and RbOH (at concentrations > 0.5 m), also in good agreement with earlier data for KOH. On the basis of these results a general stoichiometry can be inferred for the γ-phase, namely $M_{0.32} NiO_2 \cdot 0.7H_2O$ where $M = Li^+, Na^+, K^+$ or Rb^+. Measurements imply that the Cs^+ ion or the Rb^+ ion at low concentration (< 0.5 m) do not enter the interlayer structure of the γ-phase. This behaviour is thought to be related to the low Rb–O and Cs–O bond strengths afforded by the γ-phase structure.

1. Introduction

In a recent paper [1] the reversible potentials (E_R) for various nickel hydroxide/oxyhydroxide couples have been determined in KOH and the results interpreted using the concept of coexisting phases [2, 3]. Both the β-phase and α/γ-phase systems showed a dependence of reversible potential with KOH and H_2O activity. However, the α/γ-phase couple showed the largest dependence because of the incorporation of K^+ ions and H_2O in the interlayer structure of the charged active material. A range of so-called 'activated' and 'deactivated' couples for both the α-Ni(OH)$_2$/γ-NiOOH and β-Ni(OH)$_2$/β-NiOOH systems can be identified and differences in formal potential (E_0') can be related to crystal structure [4]. It is generally found that the most ordered crystalline phases ('deactivated') have the highest E_0' values and *vice versa*.

The purpose of the present investigation was to extend the study by including measurements for the above couples in other alkali hydroxides thereby obtaining further information relating to the ease of penetration of the lattice by alkali cations and water.

2. Experimental

Reversible potentials were measured using the same techniques and electrode materials described previously [1]. All measurements were made at $25 \pm 1^\circ$ C. Electrolytes were made up using triply distilled water. Samples of LiOH and NaOH were of AnalaR grade supplied by BDH Ltd, whilst the RbOH and CsOH were obtained from Koch-Light Ltd. The solutions were pre-electrolysed between large areas of nickel sinter for several days to remove trace impurities.

3. Results

In Table 1 the results are presented for the dependence of reversible potential E_R with molal alkali concentration, m, for various nickel hydroxide/oxyhydroxide couples in LiOH, NaOH, RbOH and CsOH. Regretably no alkali or water activities could be found in the literature for RbOH and

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

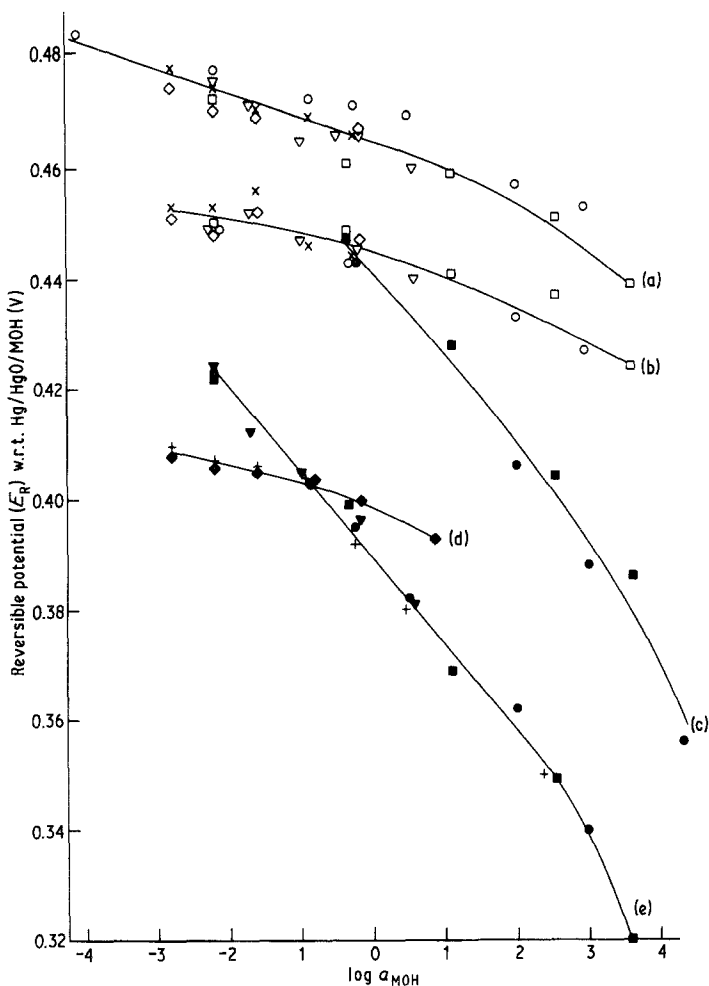| Molality (m) | Alkali | log a_{MOH} | Reference | log a_{H_2O} | Reference | Reversible potential (E_R) w.r.t. Hg/HgO/MOH (V) | | | |
| | | | | | | α-phase/γ-phase | | β-phase/β-phase | |
						'activated'	'deactivated'	'activated'	'deactivated'
0.1	LiOH	− 2.2384	[8]	− 0.0015	Estimated	0.424 ± 0.009	—	0.449 ± 0.008	0.475 ± 0.016
0.2		− 1.7053		− 0.0028		0.412 ± 0.012	—	0.452 ± 0.007	0.471 ± 0.007
0.5		− 1.0229		− 0.0072		0.405 ± 0.012	—	0.447 ± 0.009	0.465 ± 0.004
1.0		− 0.5130		− 0.0149		—	—	—	0.466 ± 0.008
1.5		− 0.2025		− 0.023		0.396 ± 0.009	—	0.445 ± 0.002	0.466 ± 0.017
4.0		+ 0.5684		− 0.07		0.381 ± 0.007	—	0.440 ± 0.006	0.460 ± 0.010
0.1	NaOH	− 2.2144	[6]	− 0.0015	[6]	0.422 ± 0.007	—	0.450 ± 0.009	0.472 ± 0.011
1.0		− 0.3402		− 0.0149		0.399 ± 0.004	0.448 ± 0.008	0.448 ± 0.007	0.461 ± 0.004
4.0		+ 1.1253		− 0.0754		0.369 ± 0.010	0.428 ± 0.002	0.441 ± 0.007	0.459 ± 0.005
8.4		+ 2.5689		− 0.2354		0.349 ± 0.009	0.404 ± 0.002	0.439 ± 0.003	0.451 ± 0.004
12.0		+ 3.6302		− 0.4282		0.520 ± 0.007	0.386 ± 0.003	0.424 ± 0.007	0.439 ± 0.006
0.05	RbOH	− 2.77	Estimated	− 0.0007	Estimated	0.410 ± 0.009	—	0.453 ± 0.009	0.478 ± 0.009
0.1		− 2.20		− 0.0015		0.407 ± 0.007	—	0.453 ± 0.009	0.474 ± 0.013
0.2		− 1.64		− 0.003		0.406 ± 0.002	—	0.456 ± 0.005	0.470 ± 0.001
0.5		− 0.87		− 0.008		0.404 ± 0.003	—	0.446 ± 0.007	0.469 ± 0.001
1.0		− 0.23		− 0.02		0.392 ± 0.003	—	0.444 ± 0.007	0.466 ± 0.002
2.2		—		—		0.380 ± 0.005	—	—	—
5.6		—		—		0.350 ± 0.004	—	—	—
0.05	CsOH	− 2.7629	[9]	− 0.0007	Estimated	0.408 ± 0.009	—	0.451 ± 0.007	0.474 ± 0.008
0.1		− 2.1916		− 0.0015		0.406 ± 0.007	—	0.449 ± 0.001	0.470 ± 0.010
0.2		− 1.6351		− 0.003		0.405 ± 0.003	—	0.452 ± 0.002	0.469 ± 0.005
0.5		− 0.8543		− 0.009		0.404 ± 0.003	—	—	—
1.1		− 0.13		− 0.03		0.400 ± 0.05	—	0.447 ± 0.005	0.467 ± 0.007
2.4		—		—		0.393 ± 0.002	—	—	—

Fig. 1. Variation of reversible potential E_R as a function of log a_{MOH} for various nickel hydroxide/oxyhydroxide couples in LiOH, NaOH, KOH, RbOH and CsOH. (a) 'Deactivated' β-Ni(OH)$_2$/β-NiOOH couples; (b) 'Activated' β-Ni(OH)$_2$/β-NiOOH couples; (c) 'Deactivated' α-Ni(OH)$_2$/γ-NiOOH couples; (d) and (e) 'Activated' α-Ni(OH)$_2$/γ-NiOOH couples; α/γ-phase couples in: ▼, LiOH; ■, NaOH; ●, KOH; +, RbOH; ◆, CsOH. β/β-phase couples in: ▽, LiOH; □, NaOH; ○, KOH; ✕, RbOH; ◇, CsOH.

water activity data were also lacking for LiOH and CsOH. This absence of suitable data necessitated estimating values for the activity coefficient of RbOH by drawing a curve mid-way between those for CsOH and KOH on the $\gamma_\pm$ versus $m^{1/2}$ plot given by Harned and Owen [5]. Water activities for LiOH, RbOH and CsOH were estimated by comparison with the water activities of NaOH and KOH at the same molality [6, 7]. In Fig. 1 reversible potentials for the various nickel hydroxide/ oxyhydroxide couples are plotted against log a_{MOH} for the various alkalis studied in this work together with the data obtained previously [1] using KOH. Generally the additional reversible potential data obtained for the various nickel hydroxide/oxyhydroxide couples in LiOH, NaOH, RbOH and CsOH fit well on the curves obtained previously with KOH. However, there are two

notable exceptions: the 'activated' α-Ni(OH)$_2$/γ-NiOOH couple in CsOH over the whole molality range and in RbOH below 0.5 m.

The dependence of E_R on alkali and water activity can be fitted to an empirical equation of the form used previously [1]:

$$E_R = E_0' - p \log a_{MOH} + q \log a_{H_2O} \qquad (1)$$

where E_0' is the formal potential and p and q are constants. Values of p and q were calculated from the experimental E_R values where possible (e.g. NaOH and KOH data) using a multiple linear regression analysis (Texas Instruments TI58 programmable calculator). In practice, however, the E_R data and/or a_{H_2O} values are insufficiently accurate to determine q in the cases of LiOH, RbOH or CsOH electrolyte by the above procedure. This problem was surmounted by first

Table 2. Calculated data for multiple linear regression analysis on results given in Table 1 and presented previously [1] for KOH fitted to Equation 1

Couple	Alkali	Formal potential E_0' (V)	$-p$	q	Coefficient of determination
'Activated' α-Ni(OH)$_2$/γ-NiOOH	LiOH	0.3921	− 0.0134	(1)	--
	NaOH	0.3925	− 0.0136	0.0507	0.994
	KOH	0.3922	− 0.0136	0.0443	0.997
	RbOH > 0.5 m	0.390 (2)	--	−	−
'Activated' α-Ni(OH)$_2$/γ-NiOOH	RbOH < 0.5 m	0.4015	− 0.0029	(1)	--
	CsOH (3)	0.4014	− 0.0023	(1)	--
'Deactivated' α-Ni(OH)$_2$/γ-NiOOH	NaOH	0.4441	− 0.0130	0.0256	0.9997
	KOH	0.4403	− 0.0139	0.0467	0.9999
'Activated' β-Ni(OH)$_2$/β-NiOOH	LiOH	0.4448	− 0.0028	(4)	--
	NaOH	0.4476	− 0.0011	0.0437	0.97
	KOH	0.4428	− 0.0029	0.0300	0.9999
	RbOH	0.4491	— 0.0021	(4)	−
	CsOH	0.4486	− 0.0009	(4)	−
'Deactivated' β-Ni(OH)$_2$/β-NiOOH	LiOH	0.4644	− 0.0040		--
	NaOH	0.4636	− 0.0031	0.0282	0.97
	KOH	0.4703	— 0.0031	0.0372	0.99
	RbOH	0.4641	— 0.0047	(4)	--
	CsOH	0.4662	− 0.0023	(4)	−

(1) E_R data insufficiently accurate to use multiple linear regression analysis, simple linear regression used instead with voltage adjustment (E_{H_2O}), where $E_{H_2O} = 0.04 \log a_{H_2O}$.
(2) $\log a_{RbOH}$ and $\log a_{H_2O}$ known with insufficient accuracy to determine p and q, so formal potential E_0' is obtained by voltage adjustment $(E_{RbOH} + E_{H_2O})$ where $E_{RbOH} = 0.0134 \log a_{RbOH}$ and $E_{H_2O} = 0.04 \log a_{H_2O}$.
(3) CsOH concentration 2.4 m not included in analysis.
(4) E_R data insufficiently accurate to use multiple linear regression analysis, simple linear regression used instead with voltage adjustment (E_{H_2O}), where $E_{H_2O} = 0.035 \log a_{H_2O}$.

applying a voltage correction to the E_R data, based on the q values obtained in the previous study [1] and using in the case of α-Ni(OH)$_2$/γ-NiOOH couples:
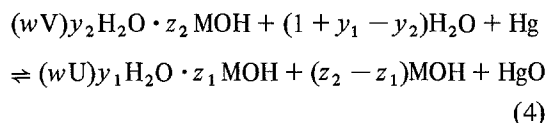
$$E_{H_2O} = 0.04 \log a_{H_2O} \qquad (2)$$

and for β-Ni(OH)$_2$/β-NiOOH couples:

$$E_{H_2O} = 0.035 \log a_{H_2O} \qquad (3)$$

followed by a simple linear regression analysis of the E_R versus $\log a_{MOH}$ data. The results of such data processing are summarized in Table 2. With the exception of the 'deactivated' α-Ni(OH)$_2$/γ-NiOOH couple the regression analysis obtained by collectively grouping all the E_R data (Table 3) is essentially the same as that obtained by considering each alkali separately (Table 2).

The overall generalized cell reaction for a Ni(OH)$_2$/NiOOH couple against a Hg/HgO/MOH reference electrode may be written thus:

$$(wV)y_2 H_2O \cdot z_2 MOH + (1 + y_1 - y_2)H_2O + Hg$$
$$\rightleftharpoons (wU)y_1 H_2O \cdot z_1 MOH + (z_2 - z_1)MOH + HgO \qquad (4)$$

where U and V (in the β-phase system) or U' and V' (in the α/γ-phase system) denote the coexisting phases as discussed previously [1–3]. The quantity w is defined as before [1] as 2/number of electrons required to oxidize 1 mol of phase U (or U') to V (or V') and depends on the compositions of the pairs of coexisting phases.

In this work the reversible potentials have only been measured in the region where the potential is independent of the state of oxidation of the nickel [1]; consequently a simplified Nernst equation can be written devoid of terms for the

Table 3. Summary of e.m.f. data obtained for 'activated' and 'deactivated' nickel hydroxide/oxyhydroxide couples

Couple	Alkali	Formal potential E'_0 (V)	Change in MOH content $(z_2 - z_1)$	Change in H_2O content $(1 + y_1 - y_2)$
'Activated' α-Ni(OH)$_2$/γ-NiOOH	LiOH NaOH KOH RbOH > 0.5 m	0.3924†	0.453	1.743
'Deactivated' α-Ni(OH)$_2$/γ-NiOOH	NaOH KOH	0.4441 0.4403	0.439 0.470	0.865 1.578
'Activated' α-Ni(OH)$_2$/γ-NiOOH	RbOH < 0.5 m CsOH	0.4015	0.088	–
'Activated' β-Ni(OH)$_2$/β-NiOOH	LiOH NaOH KOH RbOH CsOH	0.4450†	0.095	0.851
'Deactivated' β-Ni(OH)$_2$/β-NiOOH	LiOH NaOH KOH RbOH CsOH	0.4663†	0.111	1.030

† Mean value for all alkalis in the group.

solid phases, thus:

$$E_R = E'_0 + 2.303 \frac{RT}{2F} \log \frac{(a_{H_2O})^{1+y_1-y_2}}{(a_{MOH})^{z_2-z_1}} . \quad (5)$$

The quantity E'_0 is the formal potential, a_{H_2O} and a_{MOH} are the activities of H_2O and alkali respectively, and RT and F have their usual significance.

By combining Equations 1 and 5, the relative changes in MOH and H_2O content, i.e. $(z_2 - z_1)$ and $(1 + y_1 - y_2)$, on oxidation/reduction can be evaluated from the relationships:

$$p = 0.0296 (z_2 - z_1) \quad (6)$$

and

$$q = 0.0296 (1 + y_1 - y_2). \quad (7)$$

The relative changes in MOH and H_2O content found for the various couples are listed in Table 3.

4. Discussion

4.1. β-phase couples

Examination of Table 3 and Fig. 1 reveals that in the case of 'activated or 'deactivated' β-Ni(OH)$_2$/

β-NiOOH systems, within experimental error, the formal potentials for the respective couples in LiOH, NaOH, RbOH and CsOH are the same as for KOH (namely 0.445 and 0.466 V with respect to Hg/HgO/MOH for the 'activated' and 'deactivated' systems, respectively). The change in MOH content $(z_2 - z_1)$ on oxidation/reduction is small for both 'activated' and 'deactivated' β-phase couples, being about 0.1 mol per two-electron transfer. These results are consistent with previous suggestions[1], based on the known structure for β-phase materials [10, 11], that the alkali cations are unable to enter the narrow interlayer region in the bulk lattice. The small dependence found reflects adsorption of these ions by the surface only.

4.2. α/γ-phase couples

'Activated' α-Ni(OH)$_2$/γ-NiOOH couples in LiOH, NaOH, KOH and RbOH (at concentrations greater than 0.5 m) have a similar formal potential E'_0 (0.392 V with respect to Hg/HgO/MOH) which is lower than for the corresponding β-phase couples

Table 4. Ionic radii for alkali hydroxides [12]

Ion	Crystallographic radii (nm)	Solvated ion radii (nm)
Li^+	0.080	0.25
Na^+	0.095	0.217
K^+	0.133	0.175
Rb^+	0.148	0.153
Cs^+	0.169	0.147

(see Fig. 1 and Table 3). The 'activated' α/γ-phase couples show a marked but similar dependence of e.m.f. with $\log a_{MOH}$, as can be seen from Fig. 1. The change in MOH content on oxidation/reduction is found to be ~ 0.45 mol per two-electron transfer (Table 3) and is much greater than for the β-phase system. These results imply that Li^+, Na^+, K^+ and Rb^+ ions are able to enter the interlayer region of the γ-phase structure which is expanded by at least 0.34 nm compared to the β-phase lattice [11]. The crystallographic and hydrated alkali cation sizes [12] are given in Table 4 for ease of comparison.

Limited data (Fig. 1 and Table 3) for the 'deactivated' α-Ni(OH)$_2$/γ-NiOOH couples in NaOH and KOH suggest that, although the E_0' is higher (~ 0.44 V with respect to Hg/HgO/MOH), the dependence of E_R with $\log a_{MOH}$ is similar to that found for the 'activated' α/γ-phase couples.

The behaviour of 'activated' α-Ni(OH)$_2$/γ-NiOOH couples in dilute RbOH (< 0.5 m) and CsOH over the whole concentration range is interesting in as much as only a small dependence of e.m.f. is observed with $\log a_{MOH}$ (Fig. 1). The change in MOH content $(z_2 - z_1)$ on oxidation/reduction is found to be 0.088 mol per two-electron transfer and is of a similar magnitude to that found for the β-phase materials. These observations indicate that the Cs^+ ion does not enter the γ-phase lattice whilst Rb^+ is able to enter but only at concentrations above 0.5 m.

4.3. General stoichiometry for the γ-phase

Bode *et al.* [13] found that γ-phases could be made incorporating Na^+, K^+ and probably H_3O^+ in the interlayer structure but not Rb^+ and Cs^+. The Li^+ ion was claimed to be incorporated in a special way. The results obtained in this investi-

gation confirm the findings of Bode *et al.* [13] in that Na^+ and K^+ are present in the γ-phase. Because both Rb^+ (at concentrations > 0.5 m) and Li^+ can be incorporated, showing the same dependence as found for Na^+ and K^+, it is highly likely that the γ-phase has one general stoichiometry. Our results agree with those of Bode *et al.* [13] in that Rb^+ at low concentration (< 0.5 m) and Cs^+ are not taken into the γ-phase interlayer regions; water and perhaps H_3O^+ being the only components present in the interlayers. It should be noted with respect to the rubidium data that Bode *et al.* [13] only considered formation of the γ-phase in dilute (~ 0.1 m) RbOH.

The results of this and the previous investigation [1] suggest that the e.m.f.–alkali activity data are consistent with a general formulation for the coexisting phase V' of $Mo_{0.32}NiO_2 \cdot 0.7H_2O$ where $M = Li^+$, Na^+, K^+ and Rb^+, a formula established previously by Bartl *et al.* [14] and Volynskii and Chernykh [15] for the γ-phase. Although estimates of water changes on oxidation/reduction $(1 + y_1 - y_2)$ are given in Table 3, the overall accuracy of the e.m.f. data is not considered sufficiently great to establish water contents with any certainty in the γ-phase. Consequently a detailed analysis of the data has not been pursued.

4.4. Anomaly of α/γ-phase couples in RbOH and CsOH

Steric hindrance is unlikely to be entirely responsible for the lack of incorporation of Cs^+ in the γ-phase structure. Although the Cs^+ ion is relatively large (0.388 nm diameter) water molecules having a similar diameter (0.34 nm) are already present in the interlayers. Certainly considerations of steric hindrance for the Rb^+ ion (0.296 nm diameter) cannot explain why the Rb^+ ion enters at high concentration but not at low concentration. The lack of a γ-phase containing Cs^+ is probably related to the expected low Cs–O bond strength. Gulyamov *et al.* [16] and also Volynskii and Chernykh [15] have found that the tendency of the alkali cation M to be incorporated in the γ-phase is related to the M–O bond strength which decreases in the order $Li^+ > Na^+ > K^+$. It would seem likely that both the Rb–O and Cs–O bond energies afforded by the γ-phase environment are

small. The observation of the entry of Rb^+ only at high concentration suggests that there is indeed a close balance between the energy gained by inserting Rb^+ in the γ-phase lattice and the hydration energy of Rb^+ in the bulk electrolyte.

5. Conclusion

Generally the results obtained in this investigation for nickel hydroxide/oxyhydroxide couples in the various alkali hydroxides show close similarities to those found previously in KOH. The relatively well-defined formal potentials obtained in a wide variety of alkali types, for the same $Ni(OH)_2$ starting material, adds credence to the application of the technique of Conway and co-workers for the measurement of quasi-reversible potentials. Because of the effect of order/disorder in the layer lattices (i.e. the presence of so-called 'deactivated' and 'activated' types), absolute E_0 values can never be attained. Nevertheless, formal potentials E_0' can be measured which are sufficiently reproducible for the various 'activated' and 'deactivated' couples to give considerable insight into the operation of the nickel hydroxide/oxyhydroxide electrode system.

On the basis of the well-defined alkali dependence of the e.m.f. (i.e. 0.1 or 0.45 mol per two-electron transfer) it is possible to distinguish clearly between couples based on the β- or α/γ-crystal systems operating in LiOH, KOH or RbOH (at concentrations above 0.5 m). The oxidized β-phase (β-NiOOH) is shown to be devoid of alkali cation in the bulk lattice although a small quantity is adsorbed by the surface. A general stoichiometry for the γ-phase of $M_{0.32}NiO_2 \cdot 0.7H_2O$ can be inferred, where $M = Li^+, Na^+, K^+$ or Rb^+.

Measurements imply that the Cs^+ ion does not enter the γ-phase interlayer structure. The same observation is also found for the Rb^+ ion at low concentration (< 0.5 m). These results point to the importance of the balance between the M–O bond strength afforded by the γ-phase lattice and the hydration of the alkali cation in the bulk electrolyte.

Acknowledgement

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