

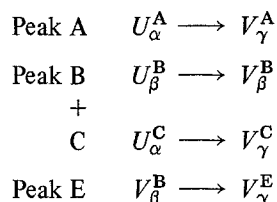
Studies concerning charged nickel hydroxide electrodes. VII. Influence of alkali concentration on anodic peak positions

R. BARNARD, C. F. RANDELL

Berec Group Limited, Group Technical Centre, St. Ann's Road, London N15 3TJ, UK

Received 24 May 1982

After repetitive potential cycling employing a high positive potential limit (> 700 mV wrt Hg/HgO/KOH) three anodic and one cathodic peak can be observed using a β -Ni(OH)₂ starting material. Anodic peaks found at 425, 470 and 555 mV in 5 mol dm⁻³ KOH shift to less positive potentials as the alkali concentration is increased appearing at 365, 410 and 455 mV respectively in 12.5 mol dm⁻³ KOH. Four anodic processes involving various pairs of coexisting phases within both the β and α -/ γ -phase system can be identified as summarized below in order of increasing positive potential:



Observed shifts in anodic and cathodic peak potentials are consistent with the known influence of alkali and water activity on the reversible potentials for the above processes.

1. Introduction

Previous studies have reported [1, 2] the cyclic voltammetric behaviour of the nickel hydroxide/oxyhydroxide electrode system in 7 mol dm⁻³ KOH only. In this investigation the influence of alkali concentration in the range 5–12.5 mol dm⁻³ on the potential of the anodic peaks is discussed in detail. An attempt has been made to relate shifts in peak potential with the changes in alkali and water activities expected for the oxidation reactions on the basis of reversible potential measurements [3, 4].

2. Experimental procedure

2.1. Techniques

The linear sweep voltammetry/coulometry technique coupled with simultaneous measurement of

oxygen volumes has been described in detail elsewhere [1].

2.2. Electrode materials and pre-treatment

The sintered plate electrodes were of the types A and B designated previously [1] containing β -Ni(OH)₂ · 0.25H₂O. Sample B was 'aged' more than sample A. Electrodes of types A and B contained 0.0467 and 0.0903 g of Ni(OH)₂ respectively in a sample size of 1 cm × 1 cm.

Electrodes were charged galvanostatically at the C/2 rate for 12 hours to produce a γ -phase having a nickel oxidation state ~ 3.5 [2]. These electrodes were then discharged using a linear potential scan at 20 or 10 mV min⁻¹. Discharged electrodes containing residual γ -phase had an oxidation state of ~ 2.65 .

Potentials are referred to Hg/HgO/KOH at $22 \pm 1^{\circ}$ C, the KOH concentration in the reference

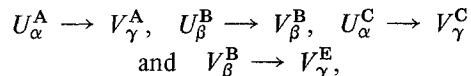
electrode being the same as that in the working compartment (5, 7, 10 or 12.5 mol dm⁻³ KOH).

3. Results and discussion

Figures 1a and 1b compare *I-E* curves obtained at a sweep rate of 2 mV min⁻¹ in 5 mol dm⁻³ KOH for samples of the pre-treated active material derived from β-Ni(OH)₂ samples A and B. Three anodic peaks can be identified at 425, 470 and 555 mV. The broken lines give suggested peak deconvolutions after correction for the oxygen evolution current component. The most significant difference between Figs. 1a and 1b lies in the better resolution of peak A at 425 mV when using

sample A. This observation was made previously [2] using 7 mol dm⁻³ KOH and the same nickel hydroxide starting materials.

In a previous study [2] the processes associated with each region of the oxidation envelope were identified and it was found that two overlapping reactions B and C could be involved near 470 mV. Employing the coexisting phase notation developed in earlier studies [1-4] peaks A, B+C and E are ascribed to the processes;



where the coexisting phases have the following compositions:

$$V_{\beta}^B = [0.9\text{NiOOH} \cdot 0.1\text{Ni}(\text{OH})_2] \cdot 0.21\text{H}_2\text{O} \cdot 0.033\text{KOH}$$

$$U_{\beta}^B = [0.25\text{NiOOH} \cdot 0.75\text{Ni}(\text{OH})_2] \cdot 0.25\text{H}_2\text{O}$$

$$V_{\gamma}^A, V_{\gamma}^C, V_{\gamma}^E = [0.833\text{NiO}_2 \cdot 0.166\text{Ni}(\text{OH})_2] \cdot 0.35\text{H}_2\text{O} \cdot 0.33\text{KOH}$$

$$U_{\alpha}^A, U_{\alpha}^C = [0.125\text{NiO}_2 \cdot 0.875\text{Ni}(\text{OH})_2] \cdot 0.67\text{H}_2\text{O}$$

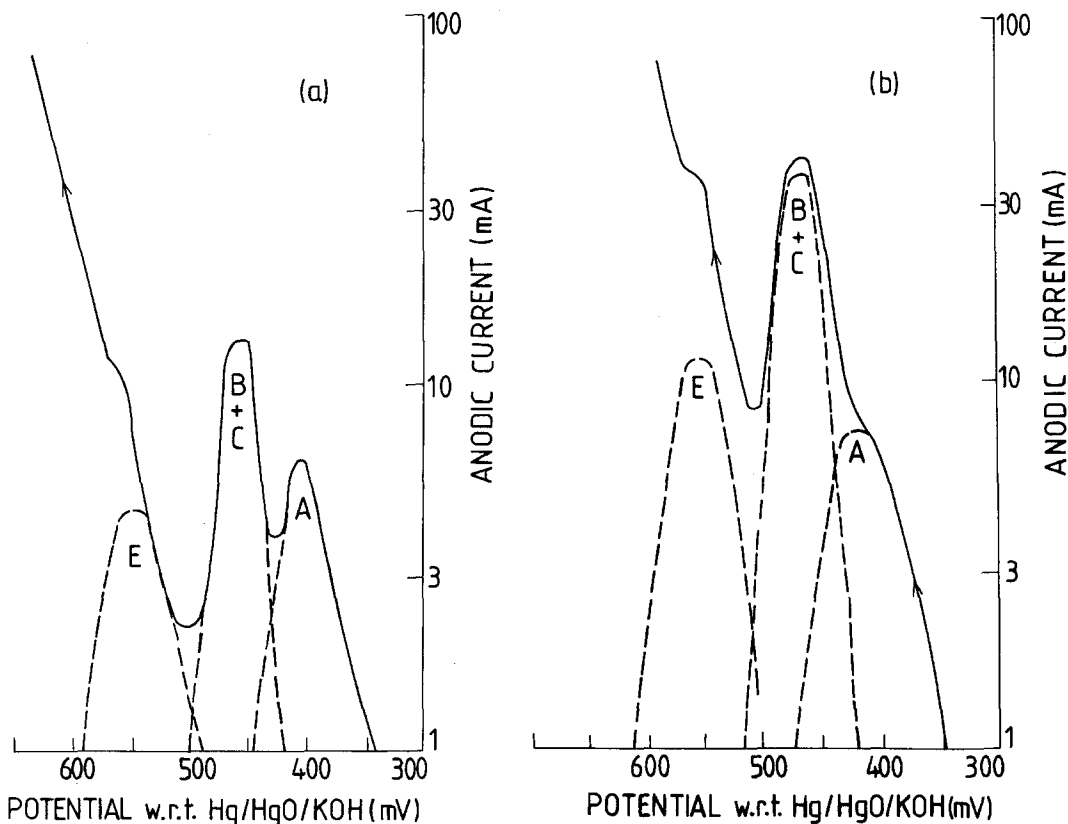


Fig. 1. Comparison of anodic linear sweeps made on different pre-treated nickel hydroxide starting materials in 5 mol dm⁻³ KOH at a sweep rate of 2 mV min⁻¹. (a) Sample A, (b) Sample B; - - - - -, peak deconvolutions after correction for oxygen evolution.

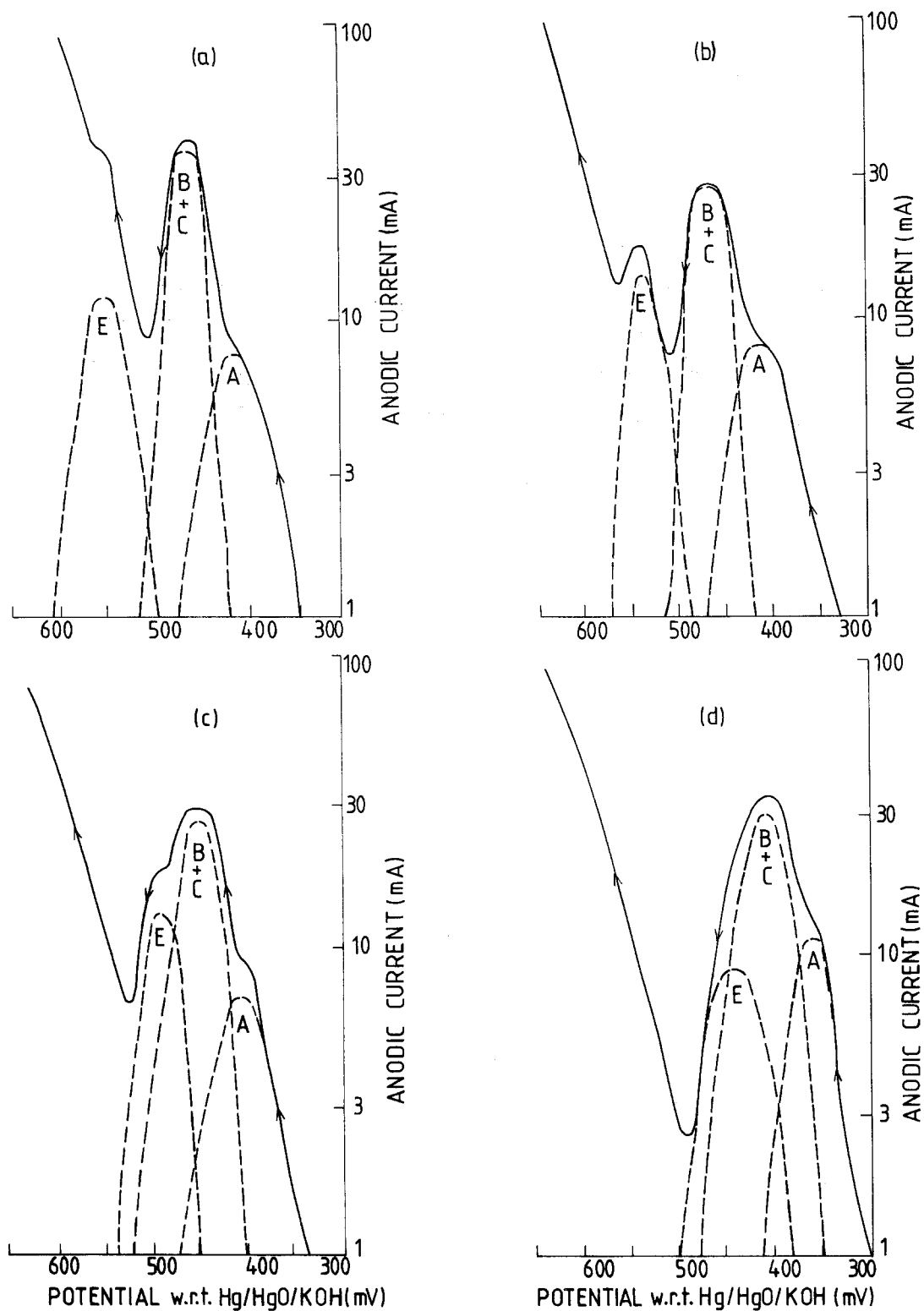


Fig. 2. Influence of alkali concentration on anodic peaks in various alkali concentrations. Pre-treated sample B; sweep rate 2 mV min^{-1} (a) 5 mol dm^{-3} KOH, (b) 7 mol dm^{-3} KOH, (c) 10 mol dm^{-3} KOH and (d) 12.5 mol dm^{-3} KOH. ---, peak deconvolutions after correction for oxygen evolution.

Peak A involves conversion of an α -phase directly to a γ -phase requiring oxidation of Ni^{2+} species to Ni^{4+} . Although, $\alpha\text{-Ni}(\text{OH})_2$ is completely absent in both type A and B starting materials, it is regenerated [2] during the pre-treatment stage (see Experimental Section 2.2) via discharge of a γ -phase. Peak B+C embraces overlapping processes involving separate single and double electron transfer paths. The phase U_α^C related to $\alpha\text{-Ni}(\text{OH})_2$ can be regarded as being formed by aging of phase U_α^A . The most positive peak E involves oxidation of the V_β^B intermediate containing Ni^{3+} to V_γ^E containing Ni^{4+} . This process also necessitates expansion of the interlayer region to allow admission of alkali cations and water. Because of the involvement of alkali cations and water in the oxidation reactions where γ -phases are formed, a dependence of the anodic peak potential with alkali and water activity would be anticipated. Such dependences should be related to the reversible potentials for the oxidation/reduction reactions irrespective of additional kinetic factors causing potential shifts.

Figures 2a-d illustrate the influence of changes in KOH concentration in the range 5-12.5 mol dm^{-3} on the positions of the voltammetric anodic peaks for the pre-treated $\beta\text{-Ni}(\text{OH})_2$ sample B. As in the previous diagrams, the broken lines show the deconvoluted peaks after removal of the oxygen current component. In all cases, the oxidation envelope can be regarded as made up of three peaks. Generally as the alkali concentration is increased the peaks appear at progressively less positive potentials. The peak E shows the largest shift in potential with variation in alkali concentration. As may be seen from Figs. 2c and 2d at

KOH concentrations of 10 and 12.5 mol dm^{-3} the oxidation reactions tend to converge and reach completion before the oxygen evolution reaction becomes significant (at > 500 mV).

Table 1 summarizes the voltammetric peak potentials and areas (charges) for various KOH concentrations. Data are included for both the anodic and cathodic processes. Coulometric measurements showed that all the charge removed on the first conditioning discharge cycle was returned on the oxidation cycles shown in Figs. 1a, b and 2a-d, that is only oxygen evolution takes place beyond peak E. From Table 1 considering electrodes derived from $\beta\text{-Ni}(\text{OH})_2$ sample B it is found that the ratio of peak areas A : B+C : E is largely independent of electrolyte concentration and amounts to an average value of 1 : 2.6 : 1.1. This suggests that the overall oxidation mechanism (i.e., the contribution of one and two electron transfers to the overall process) has not changed as a result of the change in alkali concentration. The peak area ratio A : B+C : E appears to be set largely by the nickel hydroxide starting material. The sample A for example shows a different peak area ratio of 1 : 1.6 : 1.

The final oxidation product at the positive sweep limit is, in all cases the γ -phase (V_γ^E) consequently, a predominantly single cathodic process is observed as illustrated before [1, 2]. The reduction potential of the γ -phase is, however, dependent on alkali concentration and this additional feature is indicated in Table 1. Experiments in which the positive going sweep has been interrupted at various points have only been performed in the present study in 7 mol dm^{-3} KOH and these

Table 1. Summary of voltammetric peak potentials and areas in various KOH concentrations for samples A and B

<i>Ni(OH)₂</i> <i>sample</i> <i>type</i>	<i>Anodic peaks</i>						<i>Cathodic peak</i>		<i>KOH</i> <i>concentration</i> (mol dm^{-3})
	<i>Peak A</i>		<i>Peak (B+C)</i>		<i>Peak E</i>		<i>Potential</i> (mV)	<i>Charge</i> (C)	
	<i>Potential</i> (mV)	<i>Charge</i> (C)	<i>Potential</i> (mV)	<i>Charge</i> (C)	<i>Potential</i> (mV)	<i>Charge</i> (C)			
A*	425	9	470	14	555	9	220	31	5
B	425	18	470	51	555	21	220	91	5
B	410	19	470	39	535	21	175	80	7
B	395	17	450	46	490	19	160	82	10
B	365	19	410	53	455	21	125	92	12.5

* Note lower active material weight in sample A (See Section 2.2).

results have been discussed fully previously [1, 2].

Reversible potentials have been measured [3, 4] for both the U_β/V_β and U_α/V_γ couples for a range of alkali concentrations and alkali type. If it is assumed that the changes in peak potential E_p occur mainly from changes in reversible potential with alkali and water activity then the peak potential for a process involving a $U_\beta \rightarrow V_\beta$ couple would be expected to follow the relationship:

$$E_p = K_1 - 0.0030 \log a_{\text{KOH}} + 0.033 \log a_{\text{H}_2\text{O}} \quad (1)$$

For the $U_\alpha \rightarrow V_\gamma$ couple the alternative expression:

$$E_p = K_2 - 0.0139 \log a_{\text{KOH}} + 0.043 \log a_{\text{H}_2\text{O}} \quad (2)$$

would be expected to be followed. In both Equations 1 and 2, the constant potential terms K_1 and K_2 involve a contribution from E'_0 and a concentration polarization term.

The anodic peak A involves oxidation of an α -phase to the γ -phase as already discussed; thus Equation 2 would be expected to be obeyed. The middle peak B+C, however, could involve both $U_\beta^B \rightarrow V_\beta^B$ and $U_\alpha^C \rightarrow V_\gamma^C$ oxidation processes and thus it is not clear whether Equations 1 or 2 will be followed.

The most positive peak E involves the process $V_\beta^B \rightarrow V_\gamma^E$ and is only observed on the positive going branch of the voltammogram. The reverse reaction has not been identified and it is thus difficult to measure the reversible potential directly for the process. If it is assumed that the phases V_β^B and V_γ^E have nickel oxidation states of

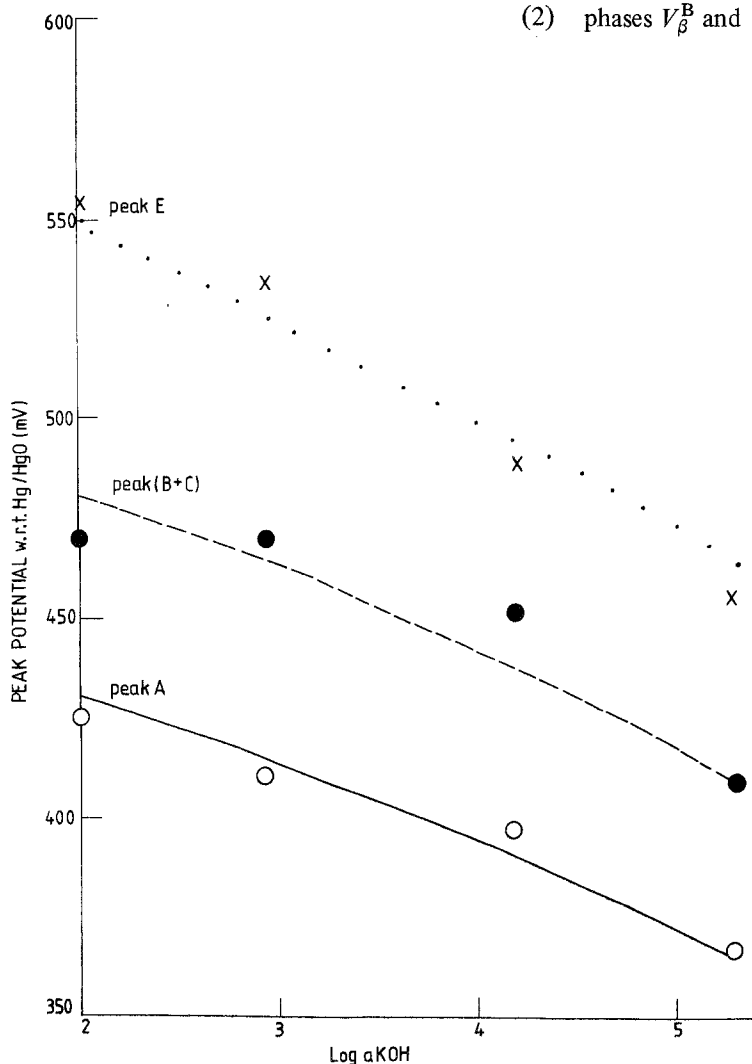
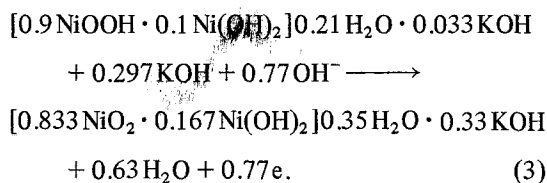


Fig. 3. Variation of anodic peak potential with $\log a_{\text{KOH}}$. \circ , experimental points for peak A; \bullet , experimental points for peak (B+C); \times , experimental points for peak E. —, theoretical line using Equation 2; ---, theoretical line using Equation 2; . . . , theoretical line using Equation 4.

2.9 and 3.67 respectively, then the process relating to peak E can be described by the reaction:



Accordingly an alkali and water dependence for the anodic peak E can be deduced from Equation 3 as follows:

$$E_p = K_3 - 0.0228 \log a_{\text{KOH}} + 0.0188 \log a_{\text{H}_2\text{O}} \quad (4)$$

Figure 3 shows a plot of peak potential for the peaks A, B+C and E as a function of $\log a_{\text{KOH}}$ found experimentally together with the theoretical lines based on Equation 2 for peaks A and B+C and Equation 4 for peak E. Examination of Fig. 3 indicates that the fits between the theoretical expressions and the experimental points are reasonably good for peaks A and E but less satisfactory for peak B+C. This discrepancy is most probably due to the involvement of two processes and the requirement of an expression intermediate between 1 and 2. The dependence of peak B+C on alkali concentration is experimentally greater than

would be expected for process B only namely $U_\beta^B \rightarrow V_\beta^B$.

Figure 4 shows the variation of cathodic peak potential as a function of $\log a_{\text{KOH}}$ together with the theoretical line based on Equation 2. Again the fit is reasonable confirming the involvement of alkali and water in the oxidation/reduction reactions associated with the γ -phase.

The process relating to anodic peak E, as indicated by Equation 3, necessitates the uptake of the full amount of potassium ion into the inter-layer region needed in the formation of the γ -phase. This takes place over a narrow oxidation interval and is responsible for the marked dependence of peak E on alkali concentration. These observations confirm that conversion of the oxidized β -phase V_β^B (or β -NiOOH) to the γ -phase takes place more readily in high alkali concentrations. Furthermore, because the oxidation reactions in high alkali concentrations can reach completion (nickel oxidation state > 3.5) before significant oxygen evolution takes place sintered plate electrodes have higher charge efficiencies under these circumstances.

Acknowledgements

The authors wish to thank Dr. F. L. Tye for

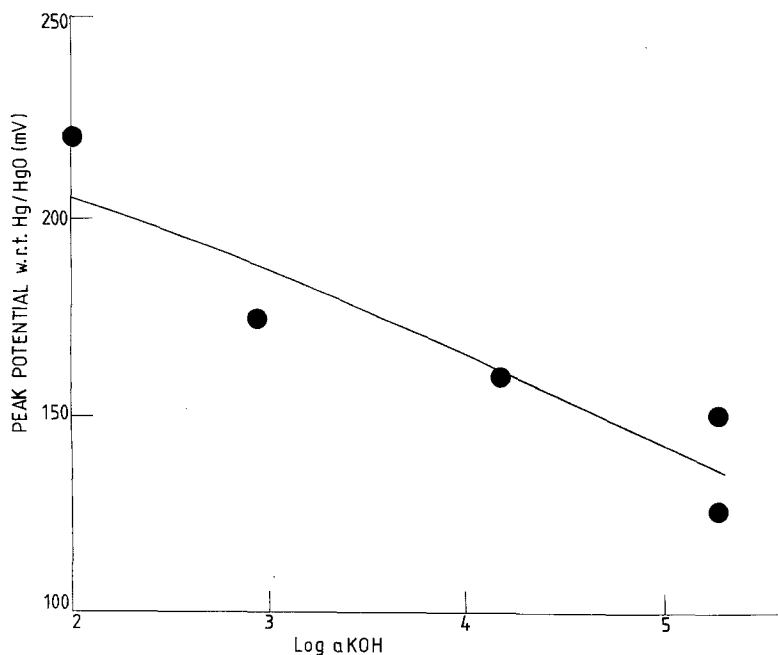


Fig. 4. Variation of cathodic peak potential with $\log a_{\text{KOH}}$. •, experimental points; —, theoretical line using Equation 2.

helpful discussions and the directors of Berc Group Limited for permission to publish this work.

References

- [1] R. Barnard and C. F. Randell, Paper presented at 'Electrochemical Energy Storage 1981', *J. Power Sources*, in press.
- [2] R. Barnard and C. F. Randell, *J. Appl. Electrochem.* to be published.
- [3] R. Barnard, C. F. Randell and F. L. Tye, *ibid.* **10** (1980) 109.
- [4] *Idem, ibid.* **11** (1981) 517.