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Behaviour of nitrate impurity in nickel-cadmium cells

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The oxidation-reduction behaviour of NO_3^-, NO_2^-, $N_2O_2^{2-}$, NH_2OH and NH_3 at a platinum electrode in alkaline solution has been investigated using cyclic voltammetry. The results have been compared with the corresponding behaviour of these species at charged, porous cadmium and nickel hydroxide electrodes in order to understand the likely behaviour of NO_3^- impurities in nickel-cadmium cells. The reactions are shown to be irreversible processes and strongly dependent on the nature of the electrode surfaces. The reactions which are likely to be involved in a charged cell can be represented by the overall scheme:

$$NO_3^- \underset{\text{slow}}{\overset{\text{fast}}{\rightleftharpoons}} NO_2^- \underset{\text{fast}}{\overset{\text{slow}}{\rightleftharpoons}} NH_3 \xrightarrow{\text{slow}} N_2$$

It is suggested that the self-discharge of cells containing NO_3^- is limited by slow kinetic effects rather than by diffusion as previously supposed.

1. Introduction

Manufacturers of nickel-cadmium cells are well aware that nitrate impurity, which is difficult to avoid in the electrode impregnation process, leads to adverse charge retention characteristics. The self-discharge mechanism commonly invoked is the 'nitrate–nitrite shuttle' [1]; however, this lacks direct experimental verification.

Frequently the oxidation and reduction [2] of anions are highly irreversible and the potentials at which they occur depend strongly on both the chemical nature and heterogeneity of the electrode surface. Preferential discharge of O_2 and H_2 from aqueous media are additional complications. Electrode potentials derived indirectly from thermodynamic data [3] are, in most cases, inapplicable and it is necessary to consider the rate constants.

The reduction [4] of NO_3^- in alkaline solution is complicated by the large number of possible products, namely, NO_2^-, $N_2O_2^{2-}$, NH_2OH, NH_3, N_2O, and N_2. It is not difficult to envisage the overall self-discharge process involving several oxidation-reduction loops.

Although, the kinetics of the HNO_3/HNO_2 electrode have been thoroughly investigated [5], little is known of the oxidation/reduction behaviour of NO_2^-/NO_3^- in alkaline solution. In the former case the rate determining step is considered to be the slow heterogeneous chemical decomposition of HNO_2 to NO^+. Oxidation of NO_2^- at a platinum electrode in neutral solution is considered by Japanese workers [6] to be due to slow charge transfer reactions yielding NO^+ and NO_2^+. The reaction order is less than unity indicating the presence of adsorption. Chemisorbed oxygen films on the electrode are reported to inhibit the oxidation reaction. Guidelli *et al.* [7] on the other hand, studying the oxidation of NO_2^- in weakly acidic media, consider that the charge transfer reaction is fast and involves the formation of NO_2 which undergoes homogeneous disproportionation to NO_2^- and NO_3^-. In order to avoid complications arising from the discharge of water the oxidation of NO_2^- has been investigated in non-aqueous solvents such as dimethyl sulphoxide [8]. The rate-determining step is thought to involve NO_2^- discharge via an adsorbed intermediate at the electrode surface. The reduction of NO_2^+ in concentrated sulphuric acid has been shown [9] to involve a fast charge transfer reaction yielding NO_2.

Moshtev and Khristova [10] studying the reduction of NO_3^- in Na_2SO_4 at an iron electrode have shown the reaction to be nearly first-order with some adsorption of NO_3^-. A slow 2-electron transfer step is considered to be rate-controlling. The voltammetric behaviour of NH_2OH in neutral and weakly acidic media has been investigated using rotating disc [11] and ring-disc [12] techniques. The oxidation of NH_2OH is thought [11] to occur by a complicated multi-stage process involving adsorption and desorption of reactants and products. The electrochemistry of $N_2O_2^{2-}$ has been little explored. The oxidation of NH_3 at a platinum electrode in alkaline solution has been investigated by a number of workers [13, 14]. Although, there is general agreement that the reaction proceeds with 100% faradaic efficiency yielding N_2, the steps in the discharge mechanism are difficult to establish unequivocally.

2. Experimental

2.1. *Voltammetric measurements*

Steady-state and cyclic voltammetric measurements were made using a Chemical Electronics potentiostat (TR40/3A), motorized linear sweep unit, function generator (RB1), Bryans X–Y plotter (21004) and Solartron oscilloscope (CD 1740) fitted with a Polaroid camera. Potentials were measured by means of a digital voltmeter (Bradley 173B) and are referred to Hg/HgO/30% KOH except where otherwise stated.

The H-shaped cell was of a conventional design employing a Pt counter electrode separated from the working compartment by means of a frit. The electrolyte was purged with nitrogen before use.

2.2. *Electrodes*

Porous cadmium and nickel hydroxide electrodes were obtained by impregnation of nickel sinters with $Cd(OH)_2$ and $Ni(OH)_2$ respectively. Because of the difficulties in defining the surface area of these porous electrodes all electrical and kinetic parameters are related to the dimensions of the electrode sample.

Cadmium hydroxide test electrodes of dimensions 1 cm × 1 cm cut from the same master plaque (thickness, 0·065 cm) contained 0·096 g of Cd $(OH)_2$. Their nominal capacities were 35 mA h. Before use the electrodes were 'formed' by charging in 30% KOH for at least 24 h at the 3*C*/2 rate (i.e. 50 mA for a 1 cm × 1 cm electrode). This allowed the electrode to remain on overcharge for several hours thereby destroying any adsorbed NO_3^- introduced during manufacture.

Nickel hydroxide test electrodes of dimensions 1 cm × 1 cm × 0·065 cm containing 0·087 g of $Ni(OH)_2$ had nominal capacities of 17 mA h. The electrodes were given at least one constant current charge-discharge cycle in a large free volume of 30% KOH containing 20 g/l of LiOH [15] before finally recharging at the *C*/8 rate (i.e. 2·5 mA in the case of a 1 cm × 1 cm electrode).

The electrodes finally employed in this study were analytically free from NO_3^-.

The Pt disc electrode (0·318 cm²) was sheathed in a tightly fitting P.T.F.E. tube and abraded (P600 SiC) before use.

2.3. *Reagents and solutions*

A.R. grade reagents were used where available in triply-distilled water. The supporting electrolyte used in most cases was 30% w/w KOH. A 0·2 M solution of hydroxylamine was prepared by mixing stoichiometric quantities of barium hydroxide and hydroxylammonium sulphate. The filtered solution was stored in a polyethylene bottle at −5°C. Sodium hyponitrite $Na_2N_2O_2$ was prepared by the method of Scott [16], and its identity confirmed by I.R. spectroscopy [17]. No organic impurities could be detected but a trace of CO_3^{2-} was present.

2.4. *Analytical*

Nitrate/nitrite mixtures were determined as NH_3 after reduction using ferrous hydroxide with and without a silver catalyst [18]. Nitrite is reduced quantitatively with ferrous hydroxide alone whilst nitrite is not reduced unless the silver is present.

Hyponitrite was identified [4] as yellow $Ag_2N_2O_2$ or as green $Cu_2(OH)_2N_2O_2$, whilst the alkaline cupric oxide test [4] was used for NH_2OH.

All measurements were made at room temperature (22 ± 2°C) except where otherwise stated.

3. Results

3.1. *Reduction of* NO_3^-, NO_2^- *and* $N_2O_2^{2-}$ *at porous cadmium electrodes*

Analysis revealed that on open circuit (−0·900 to −0·956 V) charged cadmium electrodes reduced NO_3^- predominantly to NO_2^- in 30% KOH. Samples of electrode (2 cm × 2 cm) in 25 ml aliquots approximately halved the initial NO_3^- concentration after 5 h. The fraction of NO_2^- produced was found to be independent of the initial NO_3^- concentrations* in the range 0·01 M to 0·1 M, i.e. first-order behaviour. A typical set of analytical results is presented in Table 1.

Table 1. Analytical data for the reduction of NO_3^- *at charged cadmium electrodes (2 cm × 2 cm) after 5 h*

Initial NO_3^- *concentration* ($\times 10^3$ M)	*Final* NO_3^- *concentration* ($\times 10^3$ M)	*Final* NO_2^- *concentration* ($\times 10^3$ M)
9·2	4·3	4·9
46·9	22·3	24·6
89·6	40·0	49·6

Ammonia was only detectable after several days. Nitrite solutions reduced under identical conditions produced approximately 10% NH_3 after 6 days and showed similar first-order behaviour. Other products such as $N_2O_2^{2-}$ and NH_2OH were undetectable.

By using the expression for a first-order process [19], i.e.

$$t = \frac{2{\cdot}303}{k}\cdot\mathrm{Log}_{10}\left(\frac{a}{a-x}\right) \qquad (1)$$

where k is the rate constant (s^{-1}), a is the number of moles of reactant initially present in unit volume and x the number of moles in unit volume that have reacted after time t, empirical rate constants for the reduction of NO_3^- to NO_2^- and NO_2^- to NH_3 at the rest-potential of cadmium were found to be about 4×10^{-5} and 2×10^{-7} s^{-1} respectively. It must be emphasized that these rate constants are heterogeneous, apply only to the above experimental conditions and are not absolute; however, they do provide a useful basis for comparison. Sufficient natural convection was present in the test solutions so that uniform mixing and hence reproducible analytical results could be obtained without additional stirring.

Analysis showed that 25 ml aliquots of 30% KOH containing 0·01 M $Na_2N_2O_2$ were unaffected by 2 cm × 2 cm samples of porous cadmium after 9 days. No NH_3 or NH_2OH could be detected. The $N_2O_2^{2-}$ ion is therefore more stable towards reduction than NO_2^- under the same conditions.

Fig. 1 compares steady-state log current-

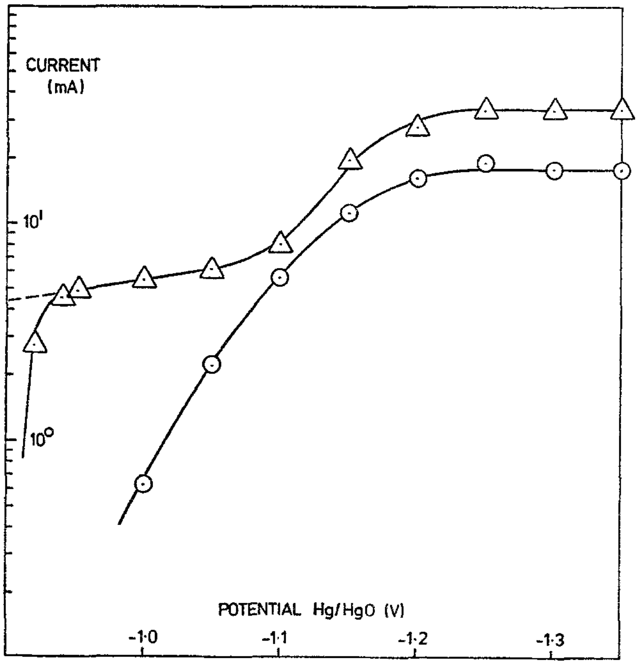

Fig. 1. Comparison of log. current-potential curves for the reduction of NO_3^- and NO_2^- in 30% KOH at a porous cadmium electrode (1 cm × 1 cm). Steady-state 5 min per point.
△, 0·1 M KNO_3; ○, 0·1 M KNO_2.

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* Concentrations of electroactive species in experiments of this type were such, that the electrodes were never discharged to more than 20–30% of their total capacity.

potential curves (hydrogen background currents subtracted) for the reduction of NO_3^- and NO_2^- at a porous cadmium electrode (1 cm × 1 cm) in 30% KOH. The curve for NO_3^- shows two well-defined diffusion controlled plateaux whilst the curve for NO_2^- shows only one. In the light of the analytical evidence it is reasonable to assign the first near −0·95 V to

$$NO_3^- + H_2O + 2e \rightarrow NO_2^- + 2OH^- \quad (2)$$

and the second near −1.25 V to

$$NO_2^- + 5H_2O + 6e \rightarrow NH_3 + 7OH^- \quad (3)$$

Analysis of samples of electrolyte containing initially nitrite after 2 h reduction periods at −1·0, −1·1, −1·2 and −1·3 V in separate experiments showed that only NH_3 was formed. No NH_2OH or $N_2O_2^{2-}$ could be detected. As expected for diffusion-controlled processes the plateau currents were directly proportional to the NO_3^-/NO_2^- concentrations.

3.2. *Voltammetric behaviour of* NO_3^- *and* NO_2^-

Fig. 2a shows a typical oscillographic voltammogram for platinum in pure 30% KOH. The characteristic peaks due to chemisorbed hydrogen and oxygen observed here are typical of those reported by other workers [20]. Addition of NO_3^- produced surprisingly little change; the hydrogen and oxygen peaks were almost unaffected (Fig. 2b). Any reduction taking place at higher cathodic potentials (> −1·0 V) was masked by the hydrogen evolution reaction.

The sequence of voltammograms from Fig. 2c to 2e shows the effects of NO_2^- generated *in situ* by reduction of the previous NO_3^- solution using a charged porous cadmium electrode (5 cm × 3 cm) immersed in the platinum electrode working compartment. The voltammogram after 5 min immersion (Fig. 2c) shows considerable changes in the hydrogen and oxygen peaks. A new peak at 0·82 V adjacent to the original hydrogen adsorption peak at −0·75 V develops on the cathodic sweep. This grows rapidly with time and is fully developed after about 40 min as shown in Fig. 2e. If the latter is compared with a voltammogram for platinum in 30% KOH containing pure KNO_2 (Fig. 2f) then the close similarities are apparent. Thus the changes observed are not due to dissolved cadmium or other impurities.

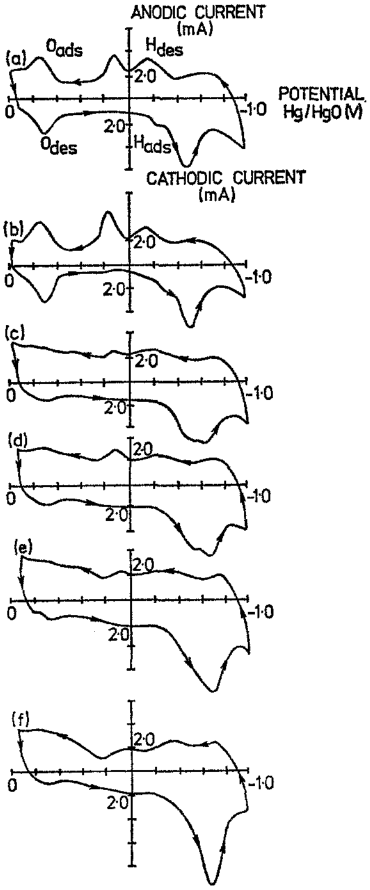

Fig. 2. Effects of NO_2^- generated by *in situ* reduction of NO_3^- at a porous cadmium electrode, on the voltammetric behaviour of platinum in 30% KOH. Sweep rate, 10 V s^{-1}.

(a) Background, pure 30% KOH.
(b) 30% KOH containing 0·1 M KNO_3.
(c) As (b) but reduced by cadmium electrode for 5 min.
(d) As (b) but reduced by cadmium electrode for 15 min.
(e) As (b) but reduced by cadmium electrode for 40 min.
(f) 30% KOH containing 0·1 M KNO_2.

The fast sweep rate (10 V s^{-1}) chosen for this investigation gave a continuous trace which allowed instantaneous comparisons to be made. At slow sweep rates (2 V min^{-1}) the voltammograms showed a number of changes as can be seen from Fig. 3. Characteristic cathodic peaks occur at −0·78 V on both cathodic and anodic sweeps, i.e. a net cathodic current is observed in both sweep directions.

The peak at −0·78 V on the anodic sweep disappears at sweep rates above 1 V s^{-1}.

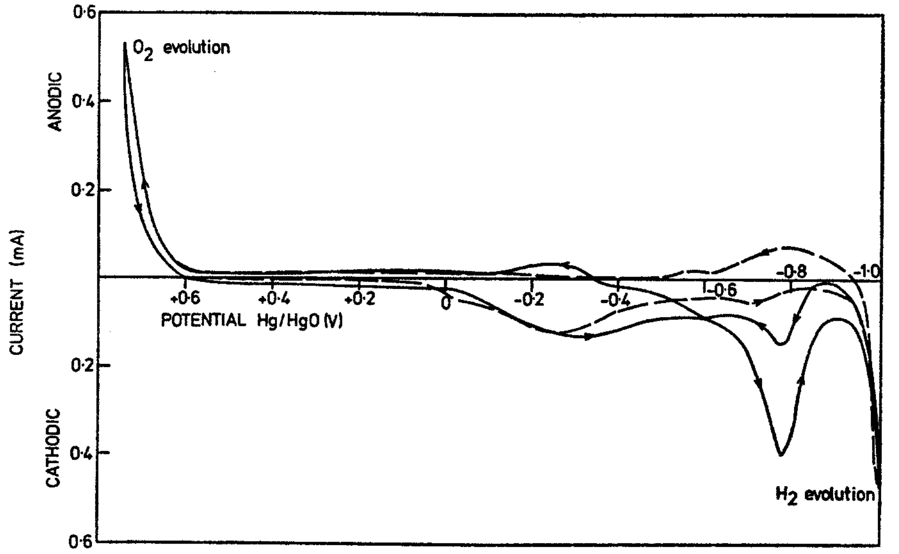

Fig. 3. Effect of 0·1 M KNO_2 on the voltammetric behaviour of platinum in 30% KOH. Sweep rate 2 V min^{-1}. ------ Background, pure 30% KOH.

3.3. *Voltammetric behaviour of NH_2OH*

Fig. 4a and 4b show voltammograms for platinum in equal volumes of 30% KOH and 0·2 M NH_2OH at 0°C for sweep rates of 1 V min^{-1} and 10 V s^{-1} respectively. At the slowest sweep rate the cathodic and anodic curves are almost coincident and produce a sharp cathodic peak at −0·76 V cf. NO_2^- at −0·78 V. The anodic and cathodic curves separate with sweep rate in a manner similar to that observed for NO_2^-. The currents rose to high values at potentials more anodic than −0·1 V because of rapid oxidation of NH_2OH.

A temperature of 0°C was chosen to minimize the decomposition of aqueous hydroxylamine which is catalysed by strong base [4] thus

$$3NH_2OH \rightarrow N_2 + NH_3 + 3H_2O \qquad (4)$$

$$4NH_2OH \rightarrow N_2O + 2NH_3 + 3H_2O \qquad (5)$$

3.4. *Voltammetric behaviour of $N_2O_2^{2-}$*

Hyponitrite showed little sign of reduction at a platinum electrode between the potentials of 0 and −1·0 V as can be seen from Fig. 4c. As in the case of NO_3^-, the chemisorbed hydrogen and oxygen peaks are little affected. Fig. 4d shows the effect of holding the platinum electrode at +1·0 V for 30 s prior to starting the sweep. A shoulder develops on the hydrogen adsorption peak which is most probably due to NO_2^- formed by oxidation of $N_2O_2^{2-}$ at far anodic potentials.

3.5. *Oxidation of NO_2^- at a platinum electrode*

Inspection of Fig. 3 shows that there is little evidence for the oxidation of NO_2^- at the platinum electrode in 30% KOH. The region near oxygen evolution (0 to +0·8 V) is identical to the background. The slight hump near −0·26 V is most probably due to oxidation of small quantities of NH_3 (see Section 3·8) produced during reduction of NO_2^- at more cathodic potentials.

In contrast, NO_2^- is readily oxidized in neutral solution as shown in Fig. 5 for platinum in M Na_2SO_4 containing 0·1 M KNO_2. A diffusion-controlled peak is observed at *ca.* +0·85 V versus the S.C.E. The peak is similar to that reported by Japanese workers [6] for NO_2^- in neutral phosphate buffers.

3.6. *Oxidation of NO_2^- at charged nickel hydroxide electrodes*

The oxidation of NO_2^- by charged nickel hydroxide electrodes on open circuit (+0·525 V) was found to be a slow and rather variable pro-

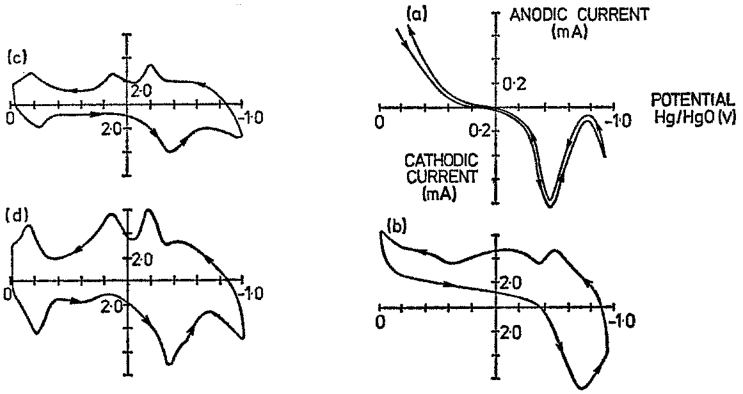

Fig. 4. Voltammetric behaviour of NH_2OH and $N_2O_2^{2-}$ at a platinum electrode.
(a) Electrolyte, equal volumes of 0·2 M NH_2OH and 30% KOH at 0°C, sweep rate, 1 V min^{-1}.
(b) As (a) except sweep rate 10 V s^{-1}.
(c) Electrolyte, 30% KOH containing 0·01 M $Na_2N_2O_2$, sweep rate 10 V s^{-1}.
(d) As (c) but electrode held at +1·0 V for 30 s prior to the sweep.

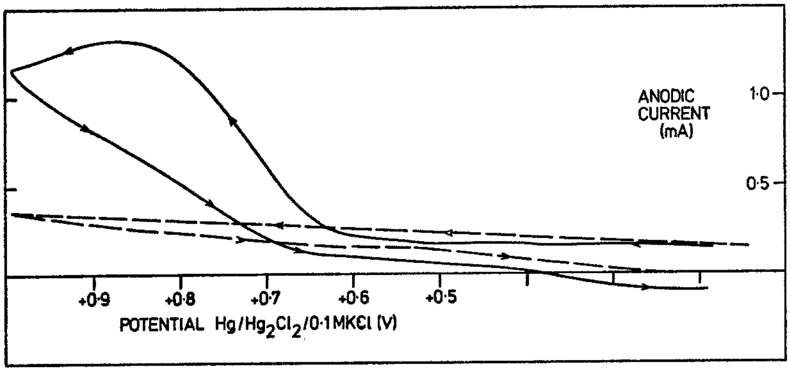

Fig. 5. Oxidation of 0·1 M KNO_2 in M Na_2SO_4 at a platinum electrode. Sweep rate, 1 V min^{-1}. – – – – – – Background, M Na_2SO_4.

cess depending to a large extent on the electrode batch. Thus with (2 cm × 2 cm) samples of electrode in 25 ml aliquots of 30% KOH containing NO_2^- usually not more than about 10% NO_3^- was produced after 7 days. Some electrodes caused no detectable oxidation even after 6 weeks. In cases where measurable oxidation took place the fraction of NO_3^- produced was independent of the initial NO_2^- concentration in the range 0·01 M to 0·1 M. Using data showing a 10% level of oxidation after 7 days gives an effective rate constant of about 2×10^{-7} s^{-1} assuming first-order behaviour.

The rate of oxidation was found to increase at higher anodic potentials as indicated in Table 2. These potentiostatic data were obtained using a pre-charged electrode (1 cm × 1 cm). Samples (25 ml) of electrolyte in the vicinity of the electrode were analysed after 2 h periods.

Nitrite had little effect on the voltammetric behaviour of nickel hydroxide electrodes as can be seen from Fig. 6. The peak at 0·48 V on the anodic sweep attributed [12] to the formation of β-NiOOH and its corresponding discharge peak* at +0·25 V show little change. Slight changes in the peak heights occur with cycling in

*According to MacArthur [12] the discharge peak may correspond to the γ-phase formed by overcharge of the β-phase. Although, we have not performed active-oxygen measurements, the electrodes used in the analytical studies were not overcharged and should contain only the β-phase.

the absence of NO_2^- and those observed here are due to this effect. Changes in the electrode surface and the large oxygen evolution currents in the potential region +0·5 to +1·0 V obscured the relatively small NO_2^- oxidation currents even at high NO_2^- concentrations (1 M).

Table 2. Potentiostatic oxidation of NO_2^- at a charged nickel hydroxide electrode (1 cm × 1 cm)

Potential w.r.t. Hg/HgO (*V*)	*Final NO_2^- concentration* (M)	*Final NO_3^- concentration* (M)
+0·525	0·104	0·000
+0·600	0·103	0·001
+0·700	0·101	0·003
+0·800	0·093	0·011

3.7. *Oxidation of NH_3 at charged nickel hydroxide electrodes*

Analysis revealed that on open circuit charged nickel hydroxide electrodes oxidized NH_3 rapidly and mainly to NO_2^- in 30% KOH. This was concluded from about fifty such oxidation experiments. In all cases NO_3^- was undetectable over the 1–2 day duration of the experiments. A typical set of analytical results is given in Table 3.

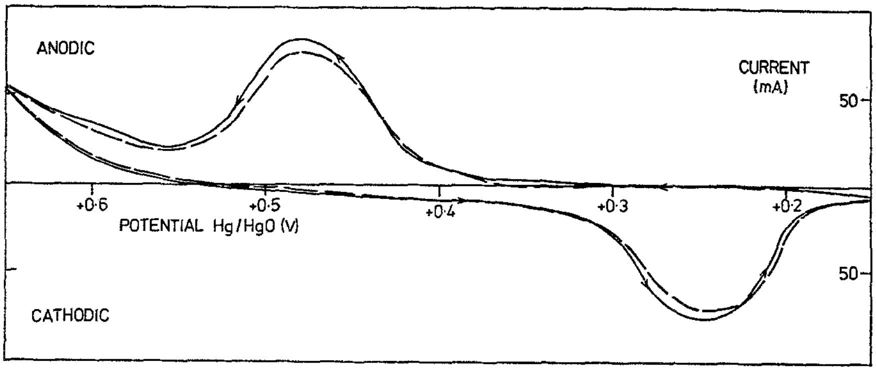

Fig. 6. Effect of 0·1 M KNO_2 on the voltammetric behaviour of a nickel hydroxide electrode (1 cm × 1 cm) in 30% KOH containing 20 g l^{-1} LiOH.
Sweep rate 5 mV min^{-1}. Curves after 5-cycles in each case.
----- Background, 'lithiated' 30% KOH.

The sum of the NO_2^- and NH_3 concentrations is not exactly equal to the initial NH_3 concentration. This discrepancy is due mainly to losses of NH_3 from test solutions and to a smaller extent to the formation of N_2. The latter was inferred from the slightly increased gas evolution rates observed. Oxygen was also evolved because of the slow oxidation of water by Ni (III).

Table 3. Oxidation of NH_3 by charged nickel hydroxide electrodes (2 cm × 2 cm)

Time (*h*)	*NH_3 concentration* (× 10^3 M)	*NO_2^- concentration* (× 10^3 M)
0	11·8	0·0
2	9·7	1·8
5	7·7	3·6
7	6·7	4·5
16	4·5	6·3
24	2·6	7·8
31	1·8	8·6

Reasonable care was taken to minimize loss of NH_3 by using tightly sealed vessels, storing samples at −5°C and performing the analyses as soon as possible after the oxidation experiments.

The oxidation of about 0·01 M NH_3 in 30% KOH at charged nickel hydroxide electrodes at their rest-potential was found to exhibit first-order behaviour (Equation 1) as exemplified by the plot of t versus Log_{10} $(a/a\text{-}x)$ given in Fig. 7. The data were obtained using (2 cm × 2 cm) samples of electrode in 25 ml aliquots of electrolyte at 25°C. From the slope of the line $(2{\cdot}303/k)$

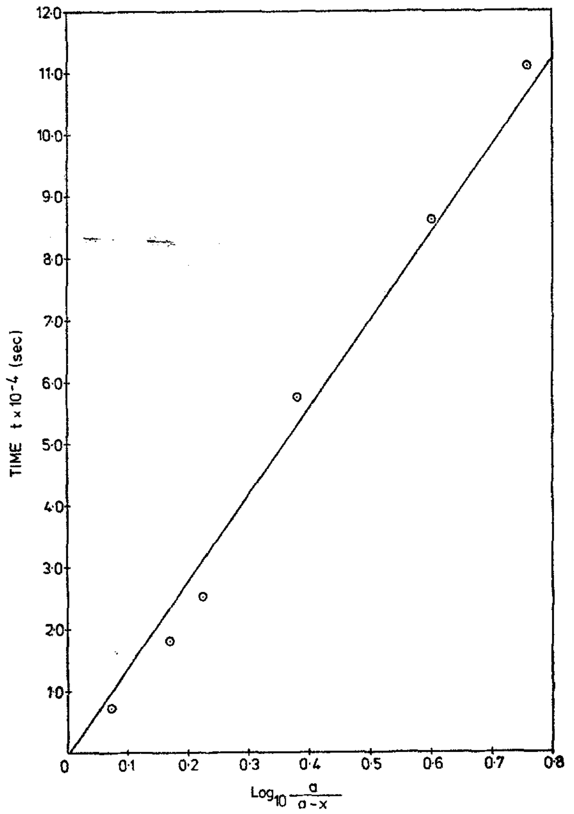

Fig. 7. First-order rate plot for the oxidation of NH_3 in 30% KOH at charged nickel hydroxide electrodes.

the pseudo-first order heterogeneous rate constant was found to be $1{\cdot}64\times10^{-5}$ s^{-1} giving a half-life, $t_{\frac{1}{2}}$ of 11·6 h. A duplicate determination gave values of k and $t_{\frac{1}{2}}$ of $1{\cdot}95\times10^{5-}$ s^{-1} and 10 h respectively.

Fig. 8 compares linear potential sweeps for charged nickel hydroxide electrodes in 30% KOH with and without *ca.* 0·7 M NH_3. It can be seen that NH_3 causes a large cathodic shift in the rest-potential from +0·525 to 0·350 V and considerably increases the anodic current.

3.8. *Oxidation of NH_3 at a platinum electrode*

Fig. 9 shows a cyclic voltammogram for platinum in 30% KOH containing NH_3. It can be seen that there is a large anodic peak at −0·26 V in the region of oxygen adsorption on platinum. This peak is considered [13, 14] to be due to oxidation of NH_3 to N_2 according to the overall equation

$$NH_3+3OH^- \rightarrow \tfrac{1}{2}N_2+3H_2O+3e \qquad (6)$$

The fact that NO_2^- is not produced is supported by the absence of the characteristic cathodic nitrite peaks at −0·78 V. There is, however, a slight increase in the size of the hydrogen

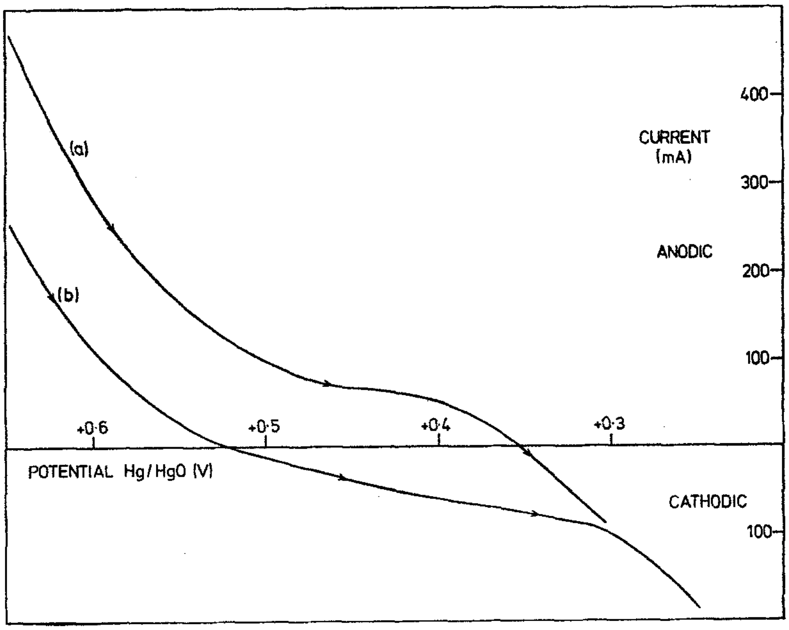

Fig. 8. Comparison of linear potential sweeps for charged nickel hydroxide electrodes (1 cm×1 cm) in 30% KOH with and without NH_3.
Sweep rate, 50 mV min^{-1}.
(a) 30% KOH containing *ca.* 0·7 M NH_3.
(b) Pure 30% KOH.

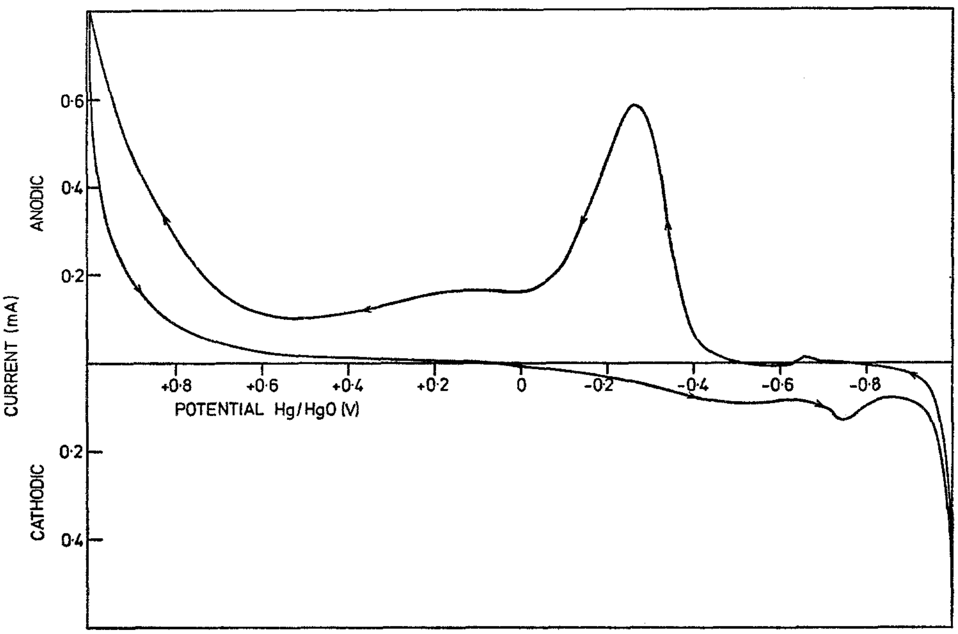

Fig. 9. Effect of NH_3 on the voltammetric behaviour of platinum in 30% KOH. Sweep rate, 2 V min^{-1}.

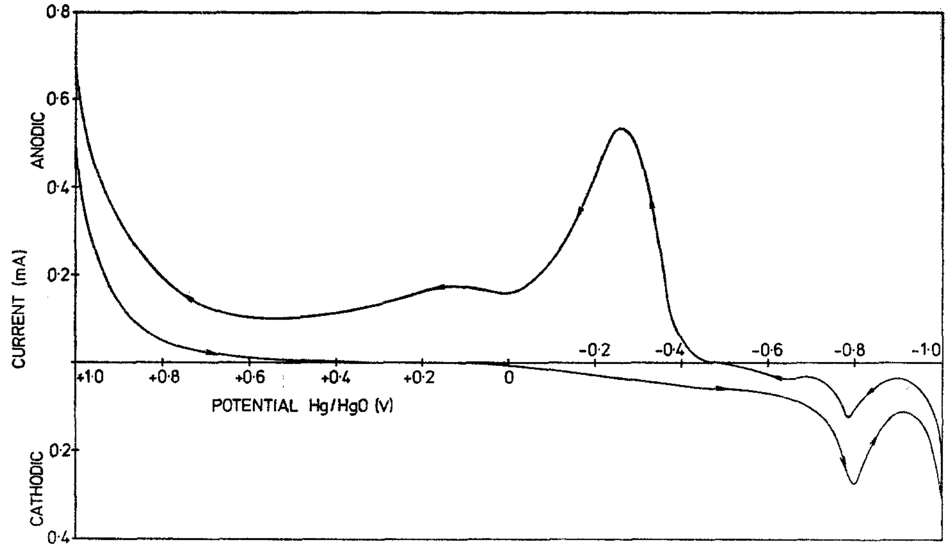

Fig. 10. Effect of a mixture of 0·1 M NH_3 and 0·1 M KNO_2 on the voltammetric behaviour of platinum in 30% KOH.
Sweep rate, 2 V min^{-1}.

adsorption peak at −0·75 V as noted by other workers.

Fig. 10 shows a voltammogram for a known mixture of NH_3 and NO_2^- in 30% KOH. The characteristic peaks due to NO_2^- are clearly visible at −0·8 V.

In agreement with other workers [11, 14] platinum electrodes were found to be deactivated after prolonged cycling in NH_3 solutions. This has been attributed to a nitride [14]. Abrasion was found to restore reactivity.

4. Discussion

The behaviour of the cadmium electrode in NO_3^- solutions can be explained on the basis of the familiar mixed-potential system [5]. At the rest-potential the anodic current component is generated as a result of

$$Cd+2OH^- \rightarrow Cd(OH)_2+2e \qquad (7)$$

whilst the main cathodic current components are derived from reactions (2), (3), and (8).*

$$2H_2O+2e \rightarrow H_2+2OH^- \qquad (8)$$

Studying reaction 2 necessitates working at potentials close to the cadmium rest-potential if further reduction (Equation 3) is to be avoided (see Fig. 1). Preliminary investigations [21] using a cadmium rotating disc electrode have shown that surface films form on the electrode at potentials less cathodic than −1·15 V making detailed kinetic investigations difficult.

The fact that NO_3^- is rapidly reduced at a cadmium but not at a platinum electrode illustrates the high degree of irreversibility of its reduction in alkaline solution. The peculiarities of anion reduction are believed to be in part a result of the repulsion of anions at the negatively charged electrode surface. The polarographic reduction of NO_3^- and NO_2^- on mercury has long been known to be anomalous [2]. Some means of linking the anion to the electrode surface appears to be a pre-requisite of the reduction process. In aqueous solution the adsorbed layer of water molecules in the inner double layer is an added complication preventing close approach of the anions. On metals having a low hydrogen overpotential, discharge of hydrogen occurs preferentially. Cadmium, presumably because of its high oxygen affinity and high hydrogen overpotential, provides a suitable surface.

It is apparent from the voltammograms that both NO_2^- and NH_2OH give sharp cathodic peaks at very similar potentials (−0·78 V and −0·76 V respectively) in the hydrogen adsorption region on platinum.

Furthermore it was found that the peak currents varied little with concentration in the range 0·01 M to 0·1 M. At a concentration of 0·1 M the currents are about two orders of magnitude too small on the basis of the Delahay equation for irreversible processes [6]. The peak currents are therefore limited by adsorption rather than by diffusion processes. This suggests that the reactant is reduced in a chemical step with the adsorbed hydrogen atoms on the platinum surface rather than by a direct electrochemical process.

The unusual shapes of the voltammograms at slow sweep rates for NO_2^- (Fig. 3) and NH_2OH (Figs. 4a and 4b) where similar cathodic peaks are observed in both sweep directions are thought to be caused by competitive adsorption between hydrogen and the reactant and/or product.

It is highly likely that NO_2^- and NH_2OH are strongly adsorbed at the platinum surface which has a high nitrogen affinity [14]. Unlike the planar NO_3^- ion which bonds exclusively through oxygen, the NO_2^- ion, having a bent structure ($O\hat{N}O$, 116–132°), can bond equally well through either nitrogen or oxygen [22]. Their reduction product, i.e. NH_3, can also be strongly adsorbed.

A possible explanation for the voltammograms may be as follows. In the potential region near −0·7 V where the cathodic peak starts to form, simultaneous adsorption of reactant and hydrogen takes place together with the chemical reduction step. At the peak the coverage of hydrogen, θ_H tends to unity whilst the coverage of reactant, θ_R tends to zero. As the potential is increased, because the reactant can no longer adsorb, reduction ceases and the hydrogen evolution reaction takes control. On reversal of the sweep the hydrogen atoms start to desorb allowing the reactant to readsorb and react with the remaining hydrogen atoms. The peak thus reappears at the same potential on the anodic sweep and shows a net cathodic current.

Disappearance of this cathodic peak on the anodic sweep at fast sweep rates and the predominance of hydrogen desorption peaks (see Figs. 2a–2f and Figs. 4a and 4b) suggest that slow desorption of the product may also be involved.

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* This reaction is negligible in the case of a pure Cd surface but the presence of Ni in the sintered electrode results in a lowered hydrogen overvoltage. The rate of this reaction is, however, small by comparison with that of NO_3^- reduction below −1·15 V w.r.t. Hg/HgO.

As in the case of NO_3^-, $N_2O_2^{2-}$ shows little interaction with the adsorbed hydrogen on platinum. The stability of the $N_2O_2^{2-}$ ion towards reduction also on cadmium, is in general agreement with the fact that hyponitrous acid is a powerful reducing agent [4] and is not reduced for example by sodium amalgam or by tin and sulphuric acid. Hyponitrite is most probably formed by condensation between NH_2OH and NO_2^- thus

$$NH_2OH + NO_2^- + OH^- \rightarrow N_2O_2^{2-} + 2H_2O \quad (9)$$

It is best regarded as a side reaction in the reduction of NO_2^- to NH_3. Unlike the free acid, the hyponitrite ion is stable [23] indefinitely in strongly alkaline solution. Hyponitrite was not detected in this investigation during reduction of NO_2^- at cadmium electrodes. Its formation is in general favoured by a higher NO_2^- concentration but even under optimum conditions the yields are always small.

Hydroxylamine is likely to be an intermediate in the reduction of NO_2^- to NH_3 in spite of the fact it could not be detected in this investigation, i.e.

$$NO_2^- + 4H_2O + 4e \rightarrow NH_2OH + 5OH^- \quad (10)$$

$$NH_2OH + H_2O + 2e \rightarrow NH_3 + 2OH^- \quad (11)$$

Some homogeneous decomposition of NH_2OH may also occur particularly at elevated temperature to yield NH_3, N_2 and N_2O (reactions 4 and 5).

This study confirms that NO_2^- can be readily oxidized in neutral solution at a platinum electrode in agreement with the Japanese workers [6]. However, no oxidation could be detected in strongly alkaline solution. As discussed in the Introduction, oxidation of NO_2^- in neutral and weakly acidic media is thought to involve species such as NO^+, NO_2^+ and NO_2 [6, 7]. Production of these species is favoured by a low rather than a high pH [22]. Thus a decrease in oxidation rate could be expected in alkaline solution. The oxidation reaction may also be inhibited by the competing oxygen evolution reaction which is favoured by a high OH^- concentration [12].

The oxidation of NH_3 mainly to NO_2^- rather than to N_2 at the rest-potential of charged nickel hydroxide electrodes was unexpected in view of the fact that in the case of platinum, N_2 is considered [24] to be the only product. However, it is reported in the early literature [4] that catalysts such as Cu (III) promote the formation of NO_2^- and NO_3^- during anodic oxidation of NH_3 at platinum electrodes in alkaline solution. This suggests that two separate reaction schemes need to be considered.

According to Gerischer and Mauerer [14] the oxidation of NH_3 at a platinum electrode involves the formation of NH_x ($x = 1, 2$) radicals by reaction between coadsorbed NH_3 and OH radicals. These NH_x radicals combine to form N_2H_y ($y = 4, 2$) or N_2H_3 radicals which are easily oxidized to form N_2.

Studies concerning the oxidation of NH_3 on platinum by oxygen at high temperature to yield NO have shown [25] that NH_2OH is likely to be the initial reaction product. Similarly where transition metal oxide catalysts are used as the oxygen carrier, it has been postulated [26] that the reaction first involves adsorption of NH_3 on the metal oxide surface with subsequent formation of NH_2OH thus

$$NH_{3\,ads} + \bar{O} \xrightarrow{M_xO_y} NH_2OH \quad (12)$$

It seems reasonable to suppose that the anodic oxidation of NH_3 at the nickel oxyhydroxide electrode proceeds by a similar surface reaction. Hydroxylamine is very readily oxidised to NO_2^- in alkaline solution.

The oxidation-reduction reactions which are likely to be involved in a complete nickel-cadmium cell can be represented by the following scheme:

$$NO_3^- \underset{\text{slow}\, k_{-1}}{\overset{\text{fast}\, k_1}{\rightleftharpoons}} NO_2^- \underset{\text{fast}\, k_{-2}}{\overset{\text{slow}\, k_2}{\rightleftharpoons}} NH_3 \xrightarrow{\text{slow}\, k_3} N_2 \quad (13)$$

The simple nitrate-nitrite shuttle mechanism previously proposed [1] assumed that the reactions were reversible and that the self-discharge rate was limited only by diffusion through the separator. This investigation shows that the converse is true and that other reactions need to be considered. The overall self-discharge rate is dependent essentially on the slow kinetic parameters k_{-1} and k_2 which are of a similar order of magnitude.

As $k_1 \gg k_{-1}$ and $k_2 \ll k_{-2} \gg k_3$ it is obvious that once the steady-state has been established the predominant species in the cell should be NO_2^-. Analyses have shown that NO_2^- represented nearly 90% of the total nitrogen present in charged cells.

The shuttle-breaking step indicated in the above scheme is the formation of N_2 by oxidation of NH_3. Its formation could not be confirmed easily because of the small quantities involved. Partial confirmation has been found from work on complete cells. Aged nickel-cadmium cells known to contain NO_3^- showed a build-up of internal gas pressure above that normally expected. Chromatographic analysis revealed a considerable enrichment of N_2 in the gas sample.

If NH_2OH is formed transiently it is possible that some homogeneous decomposition to N_2 and N_2O could occur giving an alternative but less likely shuttle-breaking route.

An important consequence of the kinetic limitations is that the observed self-discharge rates would be considerably smaller than previously supposed [1]. This is in agreement with work carried out in these laboratories.

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