

# Electroreduction of nitrate ions in concentrated sodium hydroxide solutions at lead, zinc, nickel and phthalocyanine-modified electrodes

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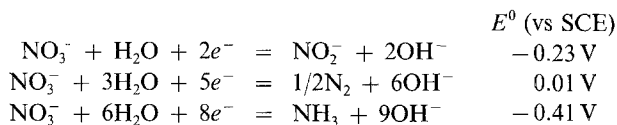
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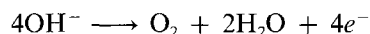
The electrochemical reduction of nitrate in strongly alkaline solution has been studied using nickel, lead, zinc and iron cathodes. Intermediate formation of nitrite ion and ammonia product was observed for all electrode materials. Coating a nickel sponge electrode with phthalocyanine renders it less active toward nitrate reduction, while iron electrodes appear to be activated. Electrolysis between a lead cathode and a nickel anode is an efficient means of removing nitrate from strongly alkaline solutions.

## 1. Introduction

In strongly alkaline media, nitrate ions can be reduced electrochemically to mixtures of ammonia, nitrogen gas and other products [1, 2]. Inspection of  $E^0$  values calculated from data given by Plieth [3] reveals that the thermodynamic potentials for the electrode reactions are relatively positive.



Coupled to the generation of oxygen at the anode,



these cathodic half-reactions are the basis for a patent describing the removal of nitrate from sodium hydroxide solutions by electrolysis between nickel electrodes [4].

In previous work [2] we studied the reduction of nitrate and nitrite ions in NaOH/Na<sub>2</sub>CO<sub>3</sub> solutions using nickel, platinum and platinized nickel electrodes. Voltammetric and coulometric experiments showed that, while the electrode reactions were mechanistically complex, reduction to dinitrogen gas and ammonia took place at high current efficiency. In the present work we have extended our studies to other metal cathodes. Electrode pretreatment and solution conditions were chosen to correspond to those that might be encountered in practical applications, for example the clean-up of radioactive waste solutions.

## 2. Experimental details

### 2.1. Electrode materials and chemicals

Certified A.C.S. grade reagent NaOH, Na<sub>2</sub>CO<sub>3</sub>, NaNO<sub>2</sub> and NaNO<sub>3</sub> (Fisher), the latter two dried at 120°C, were used to prepare the solutions. All solutions were 3.0 M in NaOH and 0.25 M in Na<sub>2</sub>CO<sub>3</sub> unless noted otherwise. Electrolyses were carried out in an undivided cell using a Ni-200 anode and a solution volume of approximately 40 ml. The solution was stirred with a magnetic stirrer.

The zinc and lead working electrodes were made from Zn plate (99.9995%, Aldrich) and Pb plate (99.9995%, Aldrich) and had dimensions of 2 × 3 cm<sup>2</sup>. The sintered nickel sponge electrode material, which was obtained from Eagle Picher (Electronics Division, Colorado Springs, CO), consisted of Inco 287 nickel powder on a nickel 200 wire mesh. Contact to the working electrode (1.5 × 2.5 cm<sup>2</sup>) was made with a tungsten wire.

The iron-phthalocyanine electrodes were prepared following the procedure of Wohrle *et al.* [5]. Iron foil (2 mm thick) was pretreated by polishing first with sand paper and then lapping compound (25–0.3 μm), etching with Kroll's acid and cleaning with copious amounts of distilled water. The dried electrodes were then suspended in a reaction vessel containing 10 mg of 1,2,4,5-tetracyanobenzene which was evacuated and sealed. After reaction at 573–673 K for 24 h, dark blue phthalocyanine surfaces were obtained in accord with the literature [5]. Nickel sponge/phthalocyanine electrodes were prepared in the same manner.

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## 2.2. Instrumentation

Constant potential electrolyses were performed with either a BAS-100 Electrochemical Analyzer or a P.A.R. Model 173 potentiostat equipped with a Model 179 digital coulometer. Constant current electrolyses were performed with the Model 173 potentiostat/galvanostat.

Ion chromatography was performed using a Dionex anion exchange column (AS4A) and a carbonate buffer (pH 10, 0.2498 g  $\text{NaHCO}_3$ , 0.8570 g  $\text{Na}_2\text{CO}_3/4\text{l}$ ) mobile phase, flow rates:  $2.00 \text{ ml min}^{-1}$  for nitrate and  $1.00 \text{ ml min}^{-1}$  for nitrate/nitrite mixtures. Optical detection at 202 nm (L.D.C. SpectroMonitor II, Model 1202) provided adequate sensitvity for the relatively high concentrations of ions in the electrolysis solutions.

## 3. Results and discussion

### 3.1. Ion chromatography of electrolysis solutions

All the electrolyses were followed by ion chromatographic analysis for nitrate and nitrite ions. Figure 1 shows typical results for electrolyses of approximately  $0.04 \text{ M NaNO}_3$  in  $3 \text{ M NaOH}/0.25 \text{ M Na}_2\text{CO}_3$  at a lead cathode at room temperature for a fixed period of time. Each chromatogram in Fig. 1 was obtained on a separate solution that had undergone electrolysis at increasingly negative potentials. This procedure permits an estimate of the effective potential for the irreversible nitrate reduction in spite of the poorly defined voltammetric waves that were observed at lead

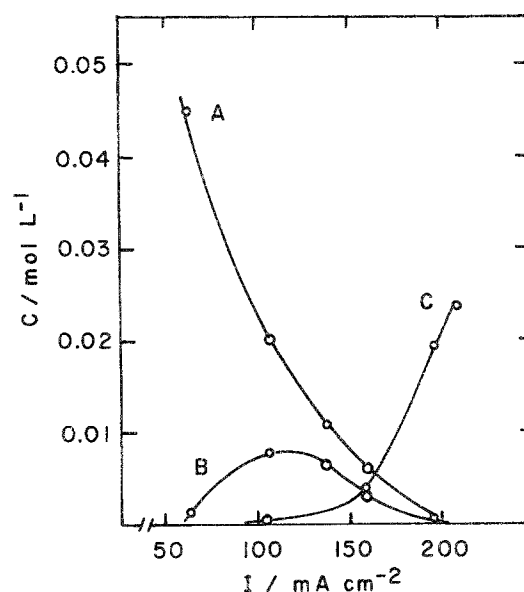


Fig. 2. Variation of nitrate (A), nitrite (B) and ammonia (C) concentration during constant current electrolysis between a lead cathode and a nickel anode; see Fig. 1 for solution composition.

(or nickel) disk electrodes. Under the conditions of Fig. 1, efficient reduction of nitrate was observed at potentials more negative than approximately  $-2.0 \text{ V}$  vs SCE.

Partial reduction of nitrate under these conditions using either constant potential or constant current produces a significant amount of nitrite ion as an intermediate. The nitrite ion was also detected by ion chromatography using UV detection. Figure 2 shows the concentration changes of nitrate, nitrite and ammonia as a function of current density for a series

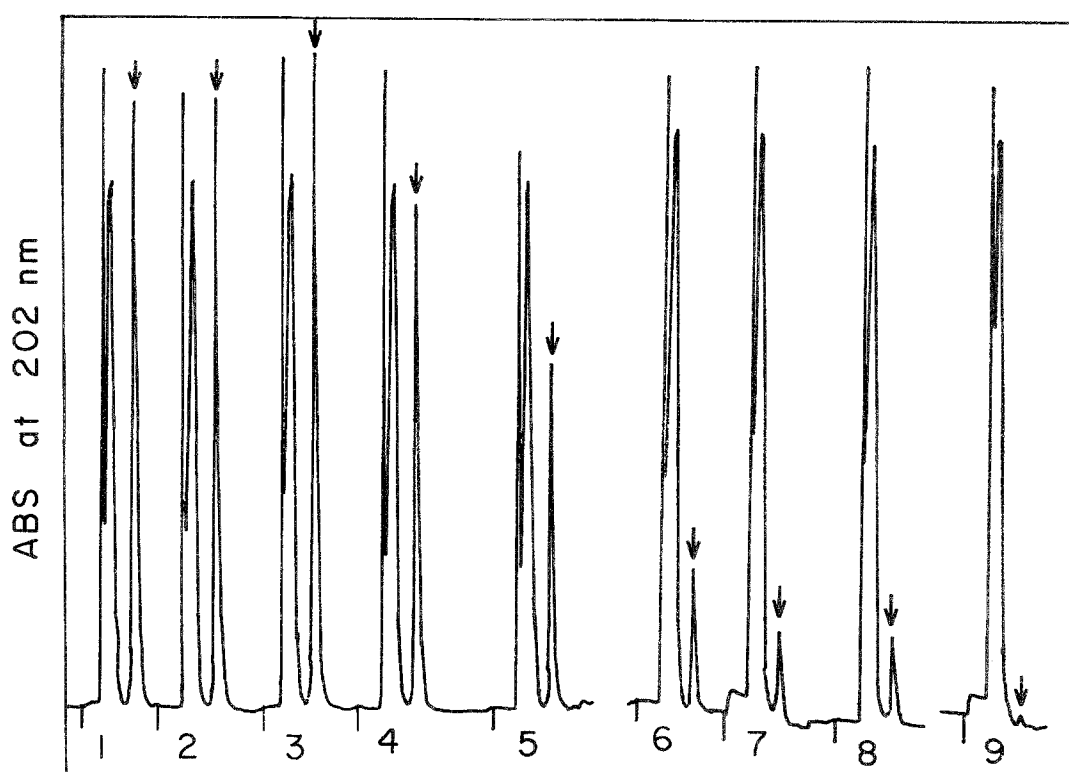


Fig. 1. Ion chromatography of  $0.047 \text{ M NaNO}_3$ ,  $3.0 \text{ M NaOH}$ ,  $0.25 \text{ M Na}_2\text{CO}_3$  electrolysis solutions; 1-9: applied potential =  $-1.5 \text{ V}$ ,  $-1.6 \text{ V}$ , open circuit (initial solution),  $-1.7 \text{ V}$ ,  $-1.8 \text{ V}$ ,  $-1.9 \text{ V}$ ,  $-2.0 \text{ V}$ ,  $-2.1 \text{ V}$ ,  $-2.2 \text{ V}$ , respectively, vs SCE for a 60-min electrolysis between a lead cathode and a nickel anode; see Experimental details for chromatographic conditions; the arrows mark the nitrate peaks.

Table 1. Constant potential electrolysis of  $\text{NaNO}_3$  in 3 M NaOH, 0.25 M  $\text{Na}_2\text{CO}_3$  at room temperature

Electrode material	Initial <sup>a</sup> concentration	Controlled <sup>b</sup> potential	% Reduced <sup>c</sup>	% Yield of $\text{NH}_3$	Current <sup>d</sup> efficiency (%)
Zinc	4 mg ml <sup>-1</sup>	-1.5	96	93	94
Lead	4 mg ml <sup>-1</sup>	-2.0	92	11	70
	1 mg ml <sup>-1</sup>	-2.1	83	77	30
	2 mg ml <sup>-1</sup>	-2.1	90	69	33
Iron	4 mg ml <sup>-1</sup>	-1.5	81	98	<sup>e</sup>
Iron/PC	4 mg ml <sup>-1</sup>	-1.5	75	71	77
Porous nickel	4 mg ml <sup>-1</sup>	-1.5	56	29	70

<sup>a</sup> Volume: approximately 40 ml.

<sup>b</sup> V vs SCE.

<sup>c</sup> Based on amount of nitrate reduced.

<sup>d</sup> Per cent efficiency calculated assuming electrolysis products are nitrite, nitrogen and ammonia.

<sup>e</sup> Extensive corrosion observed.

of 60-min constant current electrolyses at different current densities. Product distribution profiles similar to Fig. 2 were observed for electrolyses with each electrode material. Dinitrogen gas, which was detected by mass spectrometry but not quantitated, and hydroxylamine are the other products assumed to be formed in these electrolyses in order to account for a mass balance on nitrogen. Since it seems unlikely that nitrogen gas and ammonia lie on the same reaction pathway, at least a dual pathway mechanism is indicated for the nitrate reduction process. Alternatively, the formation of  $\text{N}_2$  can be explained by oxidation of  $\text{NH}_3$  at the nickel anode in the undivided cell used for the electrolyses.

The mechanism of the nitrate reduction is clearly complex. It can be noted that at the more negative potentials the 'background' currents at the electrodes under study are large. Since high current efficiencies are obtained based on the measured amounts of nitrite ion, ammonia and dinitrogen (the latter obtained by difference), adsorbed hydrogen or hydride intermediates are probably involved in the electrode process.

### 3.2. Constant potential electrolyses

The results of constant potential electrolyses using different cathode materials are surveyed in Table 1. Both zinc and lead cathodes were effective in reducing the nitrate concentration by more than 90% after 60 min electrolysis time. Reduction of nitrate to mixtures of  $\text{NO}_2^-$ ,  $\text{NH}_2\text{OH}$  and  $\text{NH}_3$  in *N,N*-dimethylformamide/ $\text{H}_2\text{O}$  and ethanol/ $\text{H}_2\text{O}$  solutions at zinc cathodes has been observed previously [6]. Small weight losses were observed for the experiments using zinc cathodes indicating the existence of a parallel nonelectrochemical route for the reduction process. The weight losses were of the order of 10 mol % of the initial amount of nitrate added to the cell. More extensive weight losses were observed for the attempted electrolyses with iron cathodes. Modifying the iron electrode with a phthalocyanine film in the manner of Wohrle *et al.* [5] stabilized the iron cathode with respect to dissolution, but did not increase the per cent nitrate reduced.

Inspection of the current-time curves for the electrolyses indicated that the process proceeded in at least two stages. A representative example is shown in Fig. 3 for an electrolysis at a lead cathode. Typically the electrolysis current increased during the first 10–20 min before decreasing in the expected exponential fashion. In Fig. 3 the circles represent the total cell current minus the steady background current obtained at completion of the electrolysis and the solid line is calculated for exponential decay of the current. The inset shows the chromatograms before and after electrolysis. These electrolyses were conducted without a cell divider in low resistance solutions and solution heating effects were minimal at these concentration

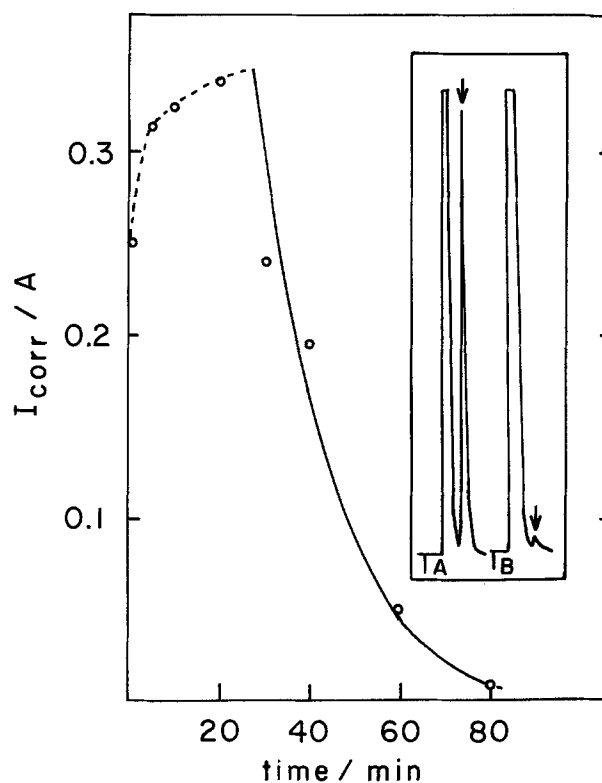


Fig. 3. Variation of corrected electrolysis current ( $I_{\text{corr}} = I - I_{\text{bckg}}$ ) with time during electrolysis of 0.047 M  $\text{NaNO}_3$  at  $-2.0$  V using a lead cathode. Inset shows ion chromatograms of solution (A) before and (B) after electrolysis; the arrows mark the nitrate peak.

levels. The potentiostat was not voltage or current limited under these conditions. Activation of the electrode surface, perhaps by reduction of an oxide layer, or catalysis by an intermediate are possible explanations for this behaviour which deserves further study.

Cyclic voltammograms of the electrolysis solutions were not particularly informative. In the presence of nitrate ion the cathodic currents in the negative region prior to solvent discharge were increased for zinc and lead electrodes at slow sweep rates ( $< \text{approximately } 50 \text{ mV s}^{-1}$ ). For example, the CV at lead exhibits a broad irreversible wave in the region of  $-2.0 \text{ V}$  vs SCE which is proportional to nitrate concentration up to approximately  $0.2 \text{ M NaNO}_3$ . The cyclic voltammograms at lead also displayed a couple at  $-0.8 \text{ V}$  vs SCE that can be identified with the  $\text{PbO/Pb}$  process [7]. Cycling the electrode potential through this latter process increased the currents for nitrate reduction upon a subsequent potential sweep to the more negative region. The current increase is presumably due to the reforming of the electrode surface that takes place at  $-0.8 \text{ V}$ .

### 3.3. Constant current electrolyses

The electrolyses were also performed under constant current conditions with results completely consistent with the data in Table 1. Mixtures of  $\text{NH}_3$  and  $\text{N}_2$  are produced with the yield of  $\text{NH}_3$  increasing as the current density increases. The largest yields of ammonia were obtained using zinc and lead cathodes as for the constant potential electrolyses. Lower current efficiencies were realized, however, indicating more extensive coevolution of hydrogen gas.

The effect of electrode material on the reduction of the nitrate concentration is shown in Figs 4 and 5. The most rapid reduction of the nitrate levels was found for the chemically active electrode materials. The effect of phthalocyanine modification shown in Fig. 5 is

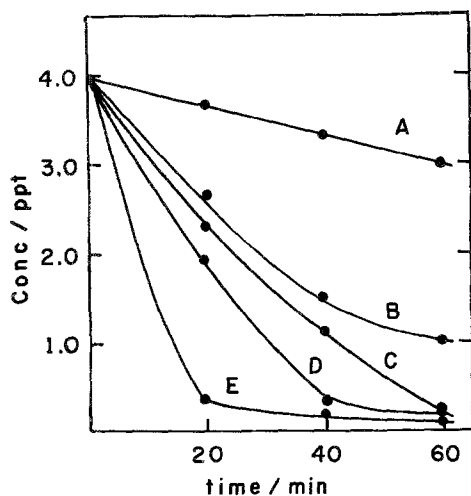


Fig. 4. Effect of electrode material on the reduction of nitrate during constant current electrolysis at  $173 \text{ mA cm}^{-2}$  in  $3.0 \text{ M NaOH}$ ,  $0.25 \text{ M Na}_2\text{CO}_3$ ; working electrode: (A) Ni, (B) porous nickel, (C) iron, (D) lead, (E) zinc; concentration units: ppt sodium nitrate.

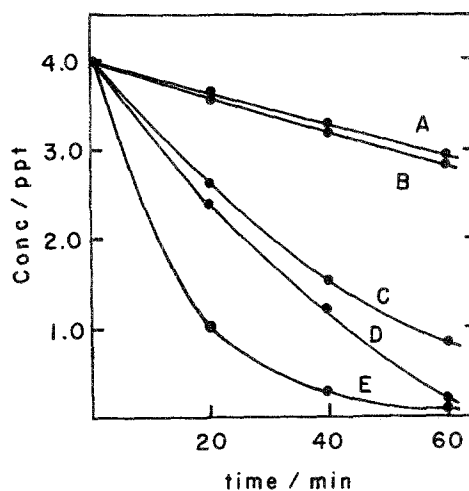


Fig. 5. Effect of phthalocyanine (PC) modification on the reduction of nitrate in  $3.0 \text{ M NaOH}$ ,  $0.25 \text{ M Na}_2\text{CO}_3$ ; constant current electrolysis at  $173 \text{ mA cm}^{-2}$ ; working electrode: (A) nickel, (B) porous nickel/PC, (C) porous nickel, (D) iron, (E) iron/PC.

interesting. Coating a porous nickel electrode with phthalocyanine renders it less active toward nitrate reduction, while the iron electrode appears to be activated. The activity of the  $\text{Fe(Pc)}$  electrode is consistent with the work of Zagal *et al.* [8], who found that iron-tetrasulphonated phthalocyanine had the greatest catalytic activity among metal-phthalocyanine complexes and gave stable voltammetric behavior in  $1 \text{ M NaOH}$ . Metal phthalocyanine complexes have long been known to be effective catalytic materials in the gas and solution phases [9]. It should also be noted that significant weight losses were again observed for iron cathodes when they were not coated with the phthalocyanine layer.

### 4. Conclusions

These results further substantiate prior reports that nitrate can be electrochemically reduced to gaseous mixtures of nitrogen and ammonia in alkaline media. While the electrode reaction can proceed with moderately high current efficiencies, the mechanism is complex and details remain obscure.

The patent of Mindler and Tuwiner [4] advocates the use of nickel electrodes for the electrolytic destruction of nitrate in alkaline media. The present results suggest that the use of a zinc or lead cathode and a nickel anode for this purpose will improve the efficiency of the overall cell process.

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