

Electrochemical Reduction of Nitrate and Nitrite in Concentrated Sodium Hydroxide at Platinum and Nickel Electrodes

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SODIUM HYDROXIDE AT PLATINIUM AND NICKEL ELECTRODES**

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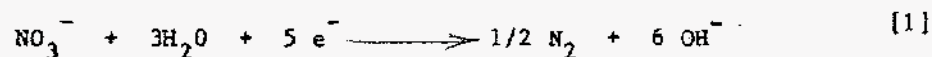
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The present work was undertaken in order to learn more about the electrochemical reduction of nitrate in alkaline solutions. Conditions which maximize the current efficiency for the production of dinitrogen and/or ammonia gases



could have far-reaching significance regarding the treatment of radioactive waste solutions. This has been realized for some time and one patent(1) and several reports in the closed literature(2,3) give conditions for the above processes in two-electrode cells under essentially constant current conditions. Reduction of nitrate to harmless gases would permit recycling of caustic

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electrolysis solutions for the neutralization of nitric acid waste solutions. In this fashion the volume of radioactive waste solution requiring disposal would be reduced.

The reduction of nitrate and nitrite ions at platinized platinum electrodes in 1M NaOH has been studied by Horanyi and Rizmayer(4). These authors found pronounced maxima in the polarization curves and presented coulometric data supporting complete reduction to ammonia at high overpotentials. At less negative potentials reduction to dinitrogen (N_2) was indicated.

In the present study the overall electrode reaction for the reduction of nitrate in alkaline medium has been established under conditions approaching those encountered in actual radioactive waste solutions. Previous applied studies(1-3) have not considered the possible effects of the presence of oxygen on the reduction of nitrate. Oxygen gas generated at the anode in these cells is transported to the cathode where it can be reduced and possibly decrease the current efficiency for the cell reaction. Accordingly, in the studies reported below the cathode compartment was isolated from anode by a membrane separator. Furthermore, oxygen was added to the gas stream in the cathode compartment in order to determine its effect on the course of the electrolysis.

Experimental

Electrodes and Materials.--For voltammetric studies two platinum electrodes with geometric areas of 0.21 cm^2 and 0.5 cm^2 were used. They were polished with 0.3 micron lapping compound, washed in 1:1 nitric acid, and rinsed thoroughly with distilled

water before use. A nickel disk electrode with an area of ca. 0.2 cm², which was made from a nickel-200 rod (Huntington Alloys) encased in Teflon, was polished, treated with 1:1 HCl, and washed with distilled water as above. Large area nickel-200 plate and platinum gauze electrodes were used for the coulometric experiments. Nickel plate electrodes (3 cm x 2 cm x 0.12 cm) were platinized by simple immersion in a 3% PtCl₄/0.025% Pb(acetate)₂ solution for ca. 5 min. These electrodes were used extensively for the coulometric experiments describe below. A S.C.E. reference electrode was employed.

Certified A.C.S. grade reagent NaOH, Na₂CO₃, NaNO₂, and NaNO₃ (Fisher), the latter two dried at 120°C, were used to prepare the solutions. The manufacturer specified that the nitrite content in the NaNO₃ was less than 0.001%. High purity nitrogen and oxygen were used to purge the solutions. Metering valves (MC Scientific), flow rates 0.05 to 0.5 mL/min and 0.2 to 2.0 mL/min, were used to provide the gas mixtures.

Instrumentation.--Cyclic voltammetry was carried out with a BAS CV-27 voltammeter and a BAS 100 Electrochemical Analyzer. The controlled potential coulometry was done using a P.A.R. Model 173/179 potentiostat-coulometer. Most of the electrolyses were performed in a two-compartment cell with a 0.007-inch-thick Nafion-117 (Aldrich) membrane separator (area = 1.75 cm²). Temperature control (±2°C) was achieved using a Sargent thermonitor, model ST S-82052. Mass spectra of the gases produced at the

cathodes were obtained by direct injection into the EI ionization chamber of a Hewlett-Packard model 5934A mass spectrometer.

Ion chromatography was performed using a Dionex anion exchange column (AS4A) and a carbonate buffer (pH 10, 0.2498g NaHCO₃, 0.8570 g Na₂CO₃/4 L) mobile phase, flow rates: 2.00 mL/min for nitrate and 1.00 mL/min for nitrate/nitrite mixtures. Optical detection at 202 nm provided adequate sensitivity for the relatively high concentrations of ions in the electrolysis solutions.

RESULTS

Bulk Electrolyses.—Constant potential coulometry was performed at platinum, nickel, and platinized nickel electrodes on NaNO₂, NaNO₃, Na₂CO₃, NaOH solutions under a variety of conditions. Results are given in Table 1. The concentration of nitrite and nitrate during the course of the electrolyses was determined by chromatographic analysis as described in the experimental section. Most of the electrolyses were carried out with a divided cell using a Nafion membrane to separate the anodic and cathodic cell compartments.

Figure 1 shows a typical experiment in which a nitrite intermediate chromatographic peak appears during the course of an electrolysis. Coulometric current efficiencies based on the five-electron reduction to dinitrogen (N₂) were quite high, ranging up to ca. 90% in some experiments. At short times (less than 20% electrolysis) close to 100% current efficiencies were obtained. In most of the electrolyses a nitrite intermediate peak was evident,

although further reduction was always observed. No other peaks appeared in the ion chromatograms.

Qualitative identification of N_2 as the major electrolysis product was achieved by mass spectroscopy. In these experiments the cathode was inserted in an inverted collection tube in quiet solution. The gas produced at the cathode was collected by displacement of the aqueous NaOH solution, transferred to an evacuated sampling vessel via a drying tube, and injected directly into the ionization chamber of a mass spectrometer. The signal at $m/e = 28$, attributed to N_2^+ dominated the mass spectra. Weak signals attributed to water were also seen, and in one experiment a trace of ammonia was present. No peak at $m/e = 44$ for N_2O was observed, although this species has been observed by others(2).

The amount of gas evolved at the cathode in these experiments was small, less than 5 mL, and the electrolyses proceeded slowly. For the coulometric experiments of Table 1, in which the solutions were stirred and the cathode compartment was flushed continuously with nitrogen or a nitrogen/oxygen gas mixture, reduction of nitrate was much more rapid.

Increasing amounts of ammonia were observed upon an increase in the cathodic current density in bulk electrolysis experiments carried out at constant current. At current densities less than or equal to 0.107 amps/cm^2 , nitrogen is the major electrolysis product. At 0.466 amps/cm^2 , ammonia was found to be the major electrolysis product. Also, the amount of ammonia was observed to increase during the course of the electrolyses.

Current efficiencies in Table 1 were calculated assuming that the products of the electrolyses were nitrite ion, a two-electron process, and dinitrogen, a five-electron process, using Eq.[3]

$$Q_T = 5F(A_0 - A_t) - 3FB_t \quad [3]$$

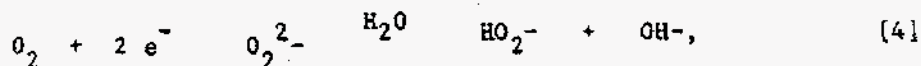
to calculate the theoretical amount of charge for the nitrate reduction. In this equation A_0 is the initial amount of nitrate in moles and A_t and B_t are the molar amounts of nitrate and nitrite, respectively, present at the end of the electrolysis. The quantities were determined by ion chromatography. It can be noted from the data in Table 1 that observation of a nitrite intermediate was favored when platinum electrodes were employed. The Ni(Pt) electrodes, on the other hand, gave greater current densities based on geometrical electrode area and more efficient reduction to nitrogen gas.

Several preliminary electrolyses at constant current were performed in the presence of ruthenium added to the solution in the form of the disodium salt of hydroxynitrosyltetranitroruthenium(II) $\text{Na}_2[\text{RuNO}(\text{NO}_2)_4\text{OH}]$. Higher conversion rates of nitrate and nitrite into ammonia were observed in these experiments. Over the course of the electrolysis elemental ruthenium deposited on the nickel cathode. Since nitro and nitrosyl ruthenium complexes are known to undergo facile electrochemical reduction to ammine complexes(5), the ruthenium complex and/or the ruthenium deposit on the cathode may in part be providing for a more facile mechanism for the reduction to ammonia.

Role of Oxygen.--Since previous studies were not concerned with the removal of dissolved oxygen gas in the electrolysis cells, several experiments were performed in which oxygen was mixed with the nitrogen gas which flushed the cathode compartment. It can be noted that not only was oxygen not removed from the cells in previous studies(1-3), but that the solutions were saturated with the oxygen formed at the anodes. Since the reduction potential of oxygen is considerably less than that of the cathode during the reduction of nitrate, reduction of oxygen is likely to be involved in the cell process.

Results are shown in Figure 2. Increasing the % oxygen content has two effects. The current efficiencies decrease presumably due to the concurrent reduction of oxygen, and the rate of nitrate reduction, as measured by the % nitrate reduced in one hour of electrolysis, increases. The increase is significant, from ca. 45% for pure nitrogen to 90% for 5% oxygen in the gas stream.

Several experiments were performed to see if hydrogen peroxide (e.g. HO_2^-) generated by the two-electron reduction of oxygen,



could be responsible for the increased rate of nitrate reduction. However, addition of aliquots of 30% H_2O_2 solution to $\text{NaOH}/\text{NaNO}_3$ or $\text{NaOH}/\text{NaNO}_2$ mixtures at 80°C did not result in the decrease of the ion chromatographic peaks for nitrate or nitrite. These results suggest an electrocatalytic role for the superoxide anion, O_2^- , in the reduction process.

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Cyclic Voltammetry.--In spite of the high efficiency electrolyses of nitrate and nitrite solutions that have been performed, only nonideal cyclic voltammograms were obtained under similar experimental conditions. Careful attention to electrode pretreatment procedures were necessary in order to obtain reproducible behavior. The cyclic voltammetric results only permit the qualitative conclusion that surface phenomena, e.g., adsorption processes and reduction of oxide films, play important roles in the electrode reaction for the reduction of nitrate/nitrite in NaOH media. Nonetheless, the voltammetric data are presented here since they provide a framework for electrolysis experiments discussed above and a rationale for the selection of the experimental conditions for the bulk electrolyses.

1. Reduction of Nitrite. Figure 3 shows a cyclic voltammogram obtained at a Pt electrode in ca. 10^{-2} M NaNO_2 , 1M NaOH at room temperature in unstirred solution. On the forward, negative-going sweep a nearly symmetrical nitrite reduction peak appears at -0.84 V vs. S.C.E. On the reverse sweep, the cathodic current increases, roughly retracing the forward current, and exhibits a cathodic peak with a pronounced shoulder. This highly unusual voltammetric pattern was reproducible and was observed for both nitrate and nitrite solution at platinum electrodes. The peak current on the negative-going sweep was proportional to $v^{0.7}$ over the sweep rate (v) range, 0.01 to 2 V/sec. This behavior is indicative of a complex, nondiffusion controlled electrode process. Importantly,

there is a wave at ca. -0.3 V which is believed to be due to reduction of a platinum oxide film (see below).

The peak current was markedly dependent on temperature, increasing by a factor of seven over the temperature range 20° to 95° C. The plot of $\ln i_p$ vs $1/T$ was nonlinear, which is further indication that a simple diffusion controlled process was not operative. Figure 4 shows the concentration dependence of the nitrite peak current. Again a nonlinear response is obtained with i_p becoming independent of concentration as the concentration increases. The nitrite reduction current was not a strong function of the NaOH concentration as is seen in Figure 4 where the circles and triangles are for $1M$ NaOH and $6.1M$ NaOH (20%), respectively. Most of the electrolyses reported below were performed in $3M$ NaOH with added Na_2CO_3 .

Interestingly, the nitrite peak current was found to be dependent on the potential selected to poise the electrode prior to initiation of the negative-going potential sweep, the "activation potential", and the length of time the electrode was maintained at this potential. This behavior is shown in Figures 5 and 6. The effect is quite dramatic as is seen in Figure 5. Potentiostatting the electrode at 0.5 V vs. S.C.E. for ca. 60 sec produces an increase in the cathodic reduction peak for nitrite of almost a factor of 10. The peak current is also enhanced by simple immersion of the platinum electrode in the $NaNO_2$ solution at open circuit (Figure 5), but longer times are required to enhance the current to the same level.

The above observations, while not fully understood, are believed to be related both to adsorption of nitrite on the electrode surface and to reduction of surface oxide films formed at the positive potentials. The latter is indicated by cyclic voltammograms of platinum disk electrodes in 3M NaOH solution in the absence of nitrite or nitrate. Potential excursions past 0.4 V vs S.C.E. result in the appearance of overlapping reduction waves in the -0.3 to -0.6 V region on the negative-going potential sweep that are dependent on the NaOH concentration. This behavior is shown in Figure 7. Oxidation of the electrode at +0.5 V vs. S.C.E. produced a single reduction wave at -0.43 V that increases as a function of the time the electrode is held at the "activation potential," see Figure 7. When the potential is extended to +0.6 V to +8.0 V, a second reduction wave appears at -0.6 V. It can be speculated that reduction of adsorbed oxygen or a thin oxide layer in the -0.4 to -0.6 V region produces an active surface for the subsequent reduction of NO_2^- at -0.86 V.

2. Reduction of Nitrate. At room temperature and concentration less than ca. 0.01M, cyclic voltammograms of nitrate at polished platinum electrodes showed very little indication of electroactivity due to a diffusion controlled process. At elevated temperature, however, a small reduction wave was evident in the cyclic voltammograms that had peak potentials and wave characteristics on the forward and reverse potential sweeps quite similar to the above description of the nitrate voltammetry. These peak

currents, which increased with NaNO_3 concentration, are attributed to reduction of a nitrite intermediate or a common intermediate in the nitrate and nitrite reductions. The possibility of a nitrite impurity in the NaNO_3 at a sufficient level to give this behavior is discounted by the absence of a nitrite peak in the ion chromatograms of the initial nitrate solutions.

At more negative potentials and high concentrations of nitrate a broad voltammetric wave due to nitrate reduction was observed; see Figure 8. The peak currents were dependent on the initial potential in a fashion similar to the nitrite voltammetry, but the effect was less dramatic. Also the currents were dependent on the NaOH concentration, increasing with % NaOH up to 12% NaOH (ca. 3.4M) at which point the currents became independent of % NaOH. At 20% NaOH the currents did not vary with the carbonate content over the range 0 to 3M Na_2CO_3 .

Small amounts of chromate were found to decrease markedly the voltammetric current ascribed to the reduction of nitrate. During constant current electrolysis with nickel electrodes, the rate of nitrate reduction is decreased upon addition of chromate. A mole ratio of chromium to nitrate of 3.1×10^{-4} is sufficient to inhibit the reduction of nitrate. It is believed that chromate is reoxidizing nitrite or lower oxidation state intermediates with the chromate being reduced to a Cr(III) species. Presumably, the Cr(III) species is reoxidized to chromate at the anode establishing a catalytic cycle. Further studies of this phenomenon with different electrode materials are in progress.

At nickel electrodes cyclic voltammograms of nitrate solutions in NaOH displayed no well defined peak currents, even at elevated temperatures. However, currents in the region of the cathodic discharge process were dependent on the nitrate concentration. A typical voltammogram of a 0.1M NaNO₃ solution in 3M NaOH, 0.25M NaCO₃ solution at 80°C is shown in Figure 9. In view of the bulk electrolysis results described above and the concentration dependence of the voltammetric behavior, the hysteresis evident on the reverse sweep in Figure 9 is related to the reduction of nitrate. The current difference at -1.2 V between the current on the positive-going sweep and the current on the negative-going sweep was found to be strongly dependent on the nitrate concentration and the temperature as is shown in Figure 10.

The above results with platinum and nickel electrodes suggested the use of platinized nickel working electrodes. Much larger reduction currents and some definition of a voltammetric wave are evident in the voltammograms of nitrate of Ni(Pt) electrodes. At slow sweep rates (30 mV/sec) a peak current ($E_p = -1.0$) was evident in the voltammograms that had features similar to the nitrite peak voltammograms described above. Assignment of this wave to the reduction of nitrate or a nitrite intermediate in the nitrate reduction is supported by the electrolysis results presented above.

A significant result of the voltammetric study is that nitrite is easier to reduce than nitrate. This is consistent with the observation of nitrite as an intermediate in the bulk electrolyses.

DISCUSSION

The overall electrode reaction for the reduction of nitrate and nitrite under a variety of conditions in alkaline electrolyte solutions has been determined in this study. Previous work, which indicated that nitrate and nitrite in alkaline solution can be reduced at high current efficiencies to gaseous products, has been confirmed. This study has confirmed previous work that nitrate and nitrite in alkaline solutions can be reduced at high current efficiencies to gaseous nitrogen products. At platinized nickel cathodes using controlled potential electrolysis techniques, in contrast to previous studies, only small or zero amounts of ammonia were detected. This is presumably related to the significantly lower current densities used in the present study relative to the constant current electrolyses of others(1-3). This should be an advantage in certain applications since reduction to nitrogen requires five equivalents of electricity while reduction to ammonia requires eight equivalents. Furthermore, problems due to the generation of possible explosive mixtures of oxygen and ammonia would be avoided. It can be noted that nitrogen was the major nitrogen-containing product in all of the electrolyses reported by Alter et al.(2).

In the present study the largest voltammetric current densities were observed with the Ni(Pt) electrodes, ca. 0.05A/cm² of geometrical area. These levels are approximately an order of magnitude less than those employed by Alter et al. who used Armco iron and cold rolled steel cathodes. They are also less than the current densities employed in the patent of Mindler and Tuwiner(1) where nickel electrodes were used. In the constant potential electrolyses, the current densities decrease with time and are much less than the above values at the completion of the electrolysis.

In summary, controlled potential electrolysis of alkaline sodium nitrate solution at 80°C using platinized nickel electrodes produces gaseous nitrogen at high current efficiency. Voltammetric studies indicate that the electrode reaction involves surface phenomena and is not mass transfer controlled. Preliminary evidence suggests an electrocatalytic role for oxygen via the generation of the superoxide anion. While the nature of this role is not understood, it is clear that reduction of small amounts of oxygen at the cathode is not deleterious to the performance of the cell.

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TABLE 1

Constant Potential Electrolysis of Alkaline Nitrate/Nitrite Solution in 3M NaOH, 0.25M Na₂CO₃ at 80°C,
Vol = 80 ml.

No.	Electrode Material	E _{appl} (V vs. S.C.E.)	Atmosphere	Amount of NaNO ₃ Reduced (mg)	Charge Required (coul)	Current Efficiency (%)	% Decr in 1 hr	Product
1	Ni	0.5 V - 1.35 V	N ₂	99	562	62	-	N ₂
2	Pt	0.5 V - 1.15 V	N ₂	36.3	293	70	-	NO ₂ → N ₂
3	Pt	-1.2 V	N ₂	99.4	702	80	-	NO ₂ → N ₂
4	Pt	-1.2 V	Air	112	1196	53	48	N ₂ >> NO ₂ ⁻
5	Ni(Pt)	-1.2 V	N ₂	44	296	86	48	N ₂ > NO ₂ ⁻
6	Ni(Pt)	-1.2 V	N ₂ (99%) O ₂ (1%)	71	547	74	71	N ₂ = NO ₂ ⁻
7	Ni(Pt)	-1.2 V	N ₂ (95%) O ₂ (5%)	90	803	63	90	N ₂
8	Ni(Pt)	-1.2 V	N ₂ (91%) O ₂ (9%)	90	1620	31	88	N ₂
9	Ni(Pt)	-1.2 V	N ₂ (83%) O ₂ (17%)	84	1751	27	84	N ₂
10	Ni(Pt)	-1.2 V	Air	91	988	53	54	N ₂
11	Ni(Pt)	-1.1 V	Air	99	711	79	92	N ₂
12	Ni(Pt)	-1.0 V	Air	107	740	82	67	N ₂
13	Ni(Pt)	-0.9 V	Air	28	168	94	17	N ₂
14	Ni(Pt)	-1.1 V	N ₂ (70%) O ₂ (30%)	100	718	79	87	N ₂
15	Ni(Pt)	-1.0 V	N ₂ (70%) O ₂ (30%)	69	541	73	52	N ₂
16	Ni(Pt)	-0.9 V	N ₂ (70%) O ₂ (30%)	53	266	79	20	N ₂
17	Ni(Pt)	-1.1 V (54°C)	N ₂ (70%) O ₂ (30%)	53	432	78	88	N ₂
18	Ni(Pt)	-1.1 V (25°C)	N ₂ (70%) O ₂ (30%)	36	314	64	14	N ₂
19	Ni	-1.3 V	N ₂ (70%)	14	578	13	5	N ₂ > NO ₂ ⁻
20	Ni(Pt)	-1.2 V	N ₂	144 ^b	540	88	94	N ₂
21	Ni(Pt)	-1.1 V	Air	100 ^b	491	85	97	N ₂

a) Electrolysis at 0.5V for 20 sec, followed by electrolysis at -1.35V for 100 sec.

b) Weight of NaNO₂

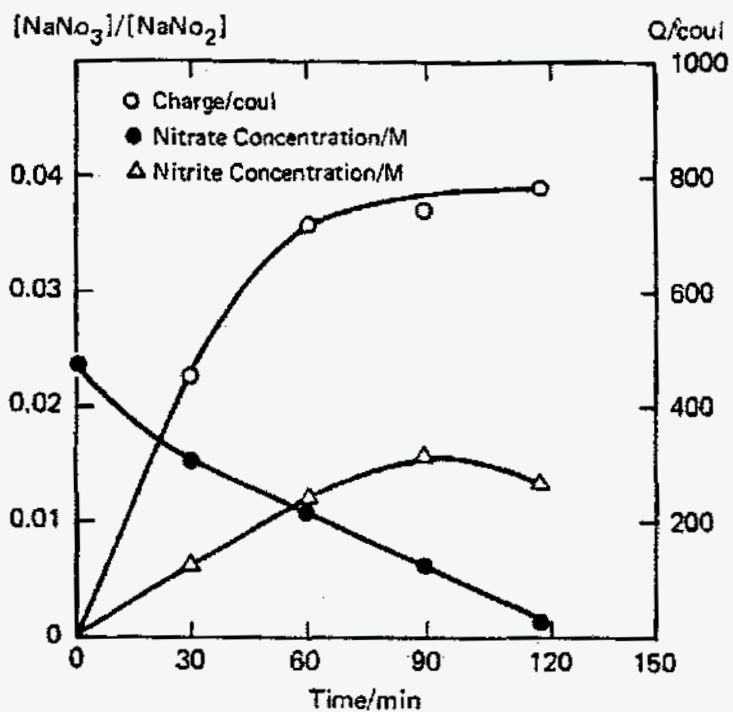


FIGURE 1. Variation of Nitrate and Nitrite Concentrations during Electrolysis of NaNO_3 in 3M NaOH , 0.25M NaCO_3 at a Ni(Pt) Electrode; -1.2 V vs S.C.E. ; 80°C

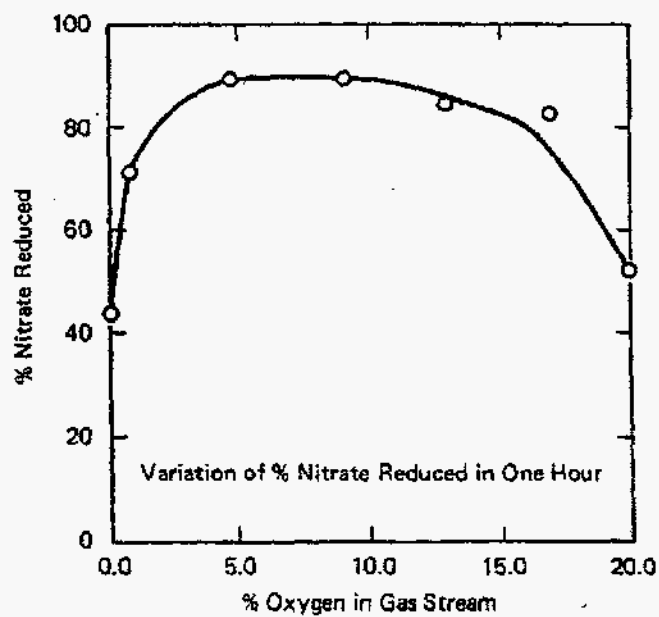
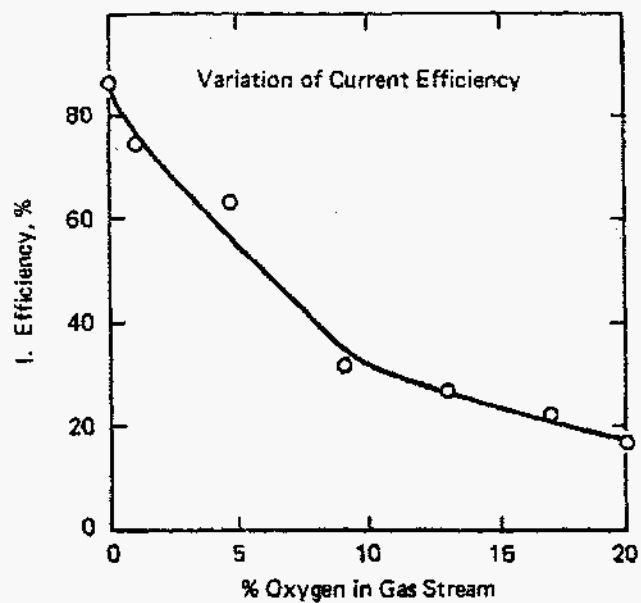


FIGURE 2. Effect of Oxygen on Cathodic Electrolysis of Nitrate Solutions at 80°C, in 3M NaOH, 0.25M Na₂CO₃ at a Ni(Pt) Electrode

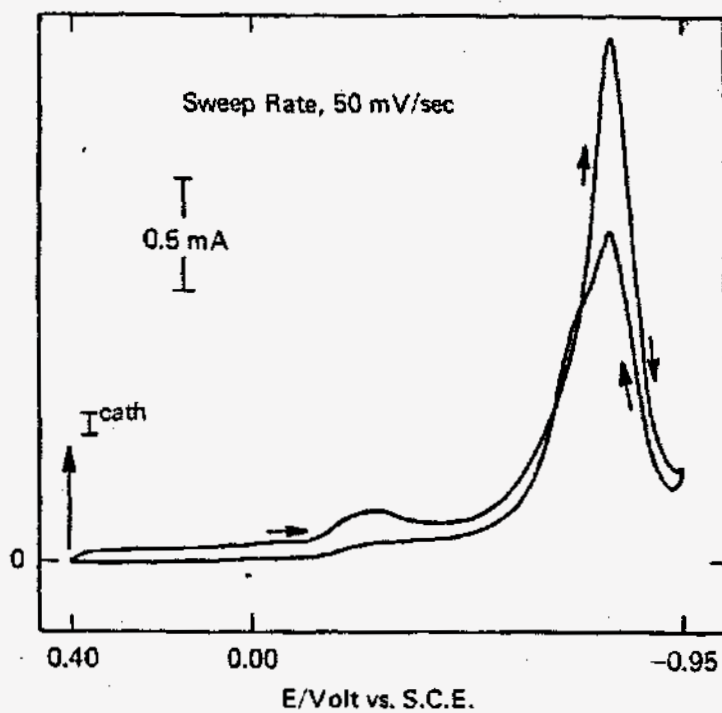


FIGURE 3. Cyclic Voltammogram for the Reduction of 0.015M Nitrite at 23°C in 1M NaOH; Platinum Electrode

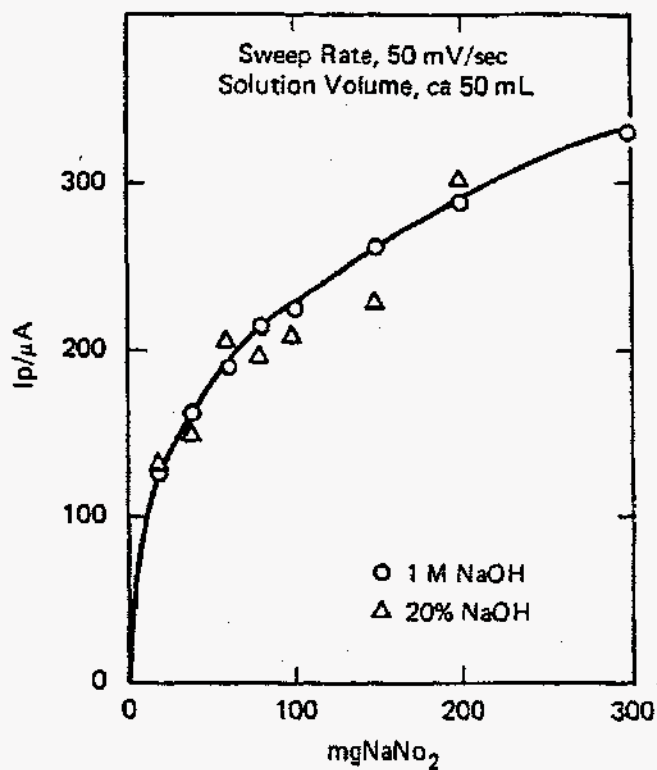


FIGURE 4. Variation of the Peak Current for the Reduction of Nitrite in 1M NaOH and in 20% NaOH; Platinum Electrode

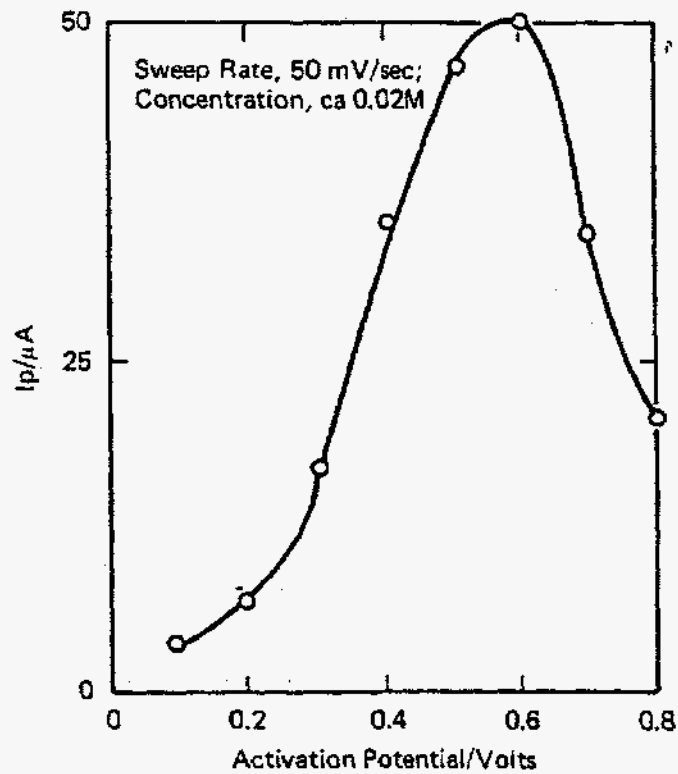


FIGURE 5. Variation of the Nitrite Voltammetric Peak Current in 1M NaOH with Initial Potential ("activation potential")

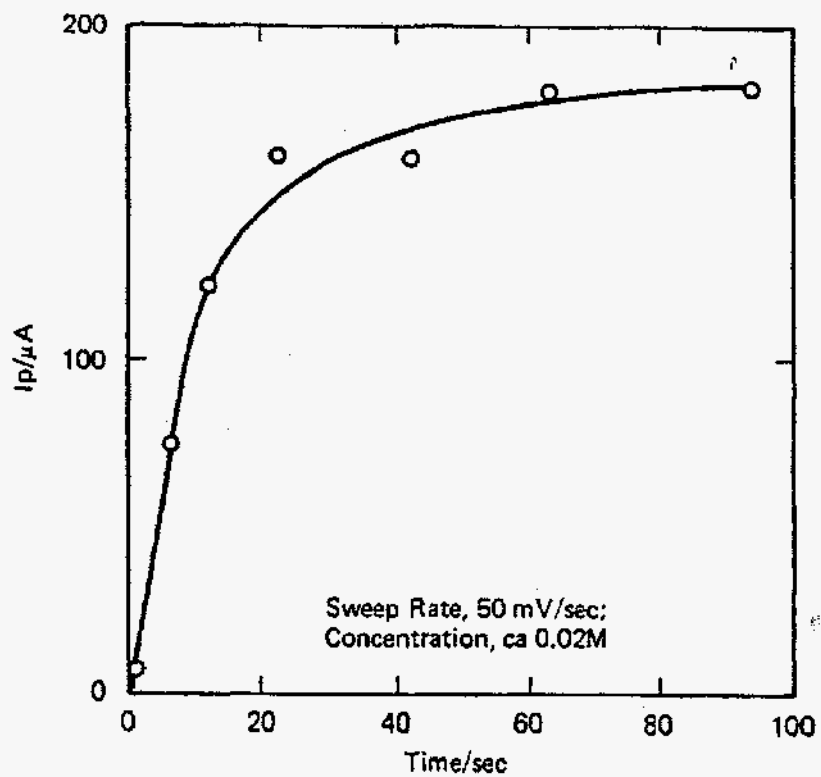
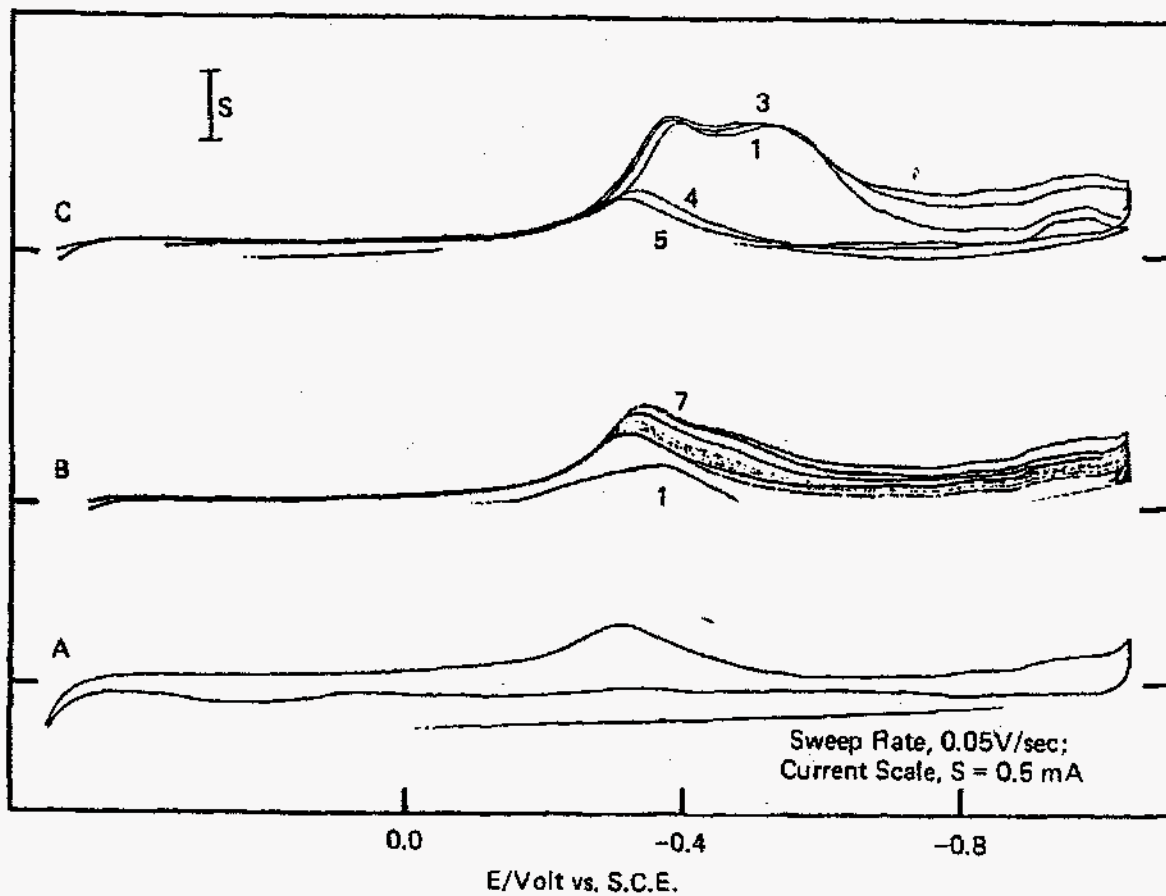


FIGURE 6. Variation of the Nitrite Voltammetric Peak Current in 1M NaOH with "Activation Potential" Pulse Time



- A Steady-State Cyclic Voltammogram
- B Linear-Sweep Voltammograms with "Activation" at +0.5V vs. S.C.E.
for (1-7) 5, 10, 20, 30, 40, 50, 60 sec
- C Linear-Sweep Voltammograms with Initial Potential = +0.8, +0.7, +0.6,
+0.5, +0.4V vs. S.C.E. for Curves 1-5

FIGURE 7. Voltammograms of 3M NaOH, 0.25M Na₂CO₃ at Platinum (0.21 cm²); Temperature, 80°C

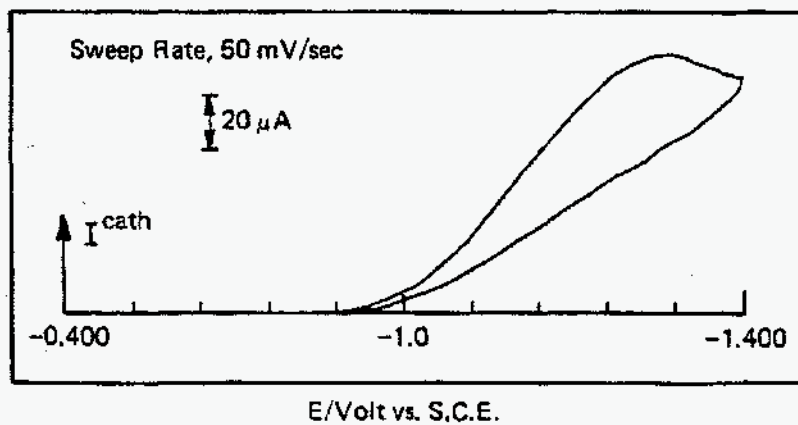


FIGURE 8. Cyclic Voltammogram of 0.59M NaNO_3 in 3M NaOH , 0.25M Na_2CO_3 at 80°C

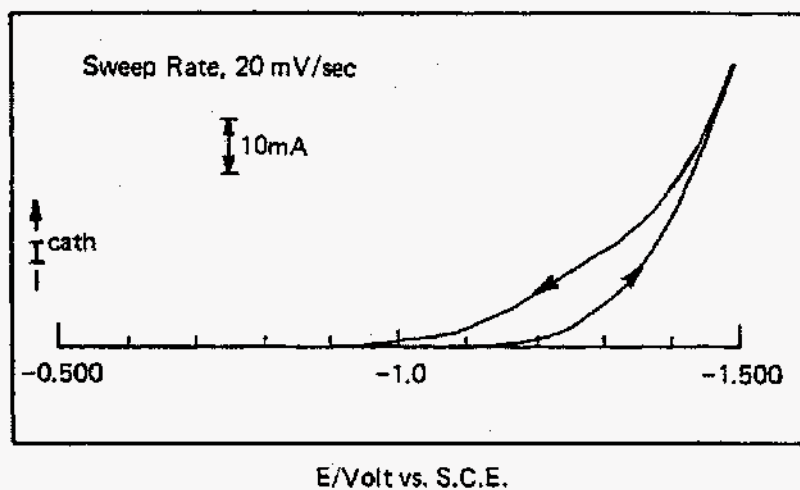


FIGURE 9. Cyclic Voltammogram of 0.39M NaNO₃ in 3M NaOH, 0.25M Na₂CO₃ at 80°C; Nickel Electrode

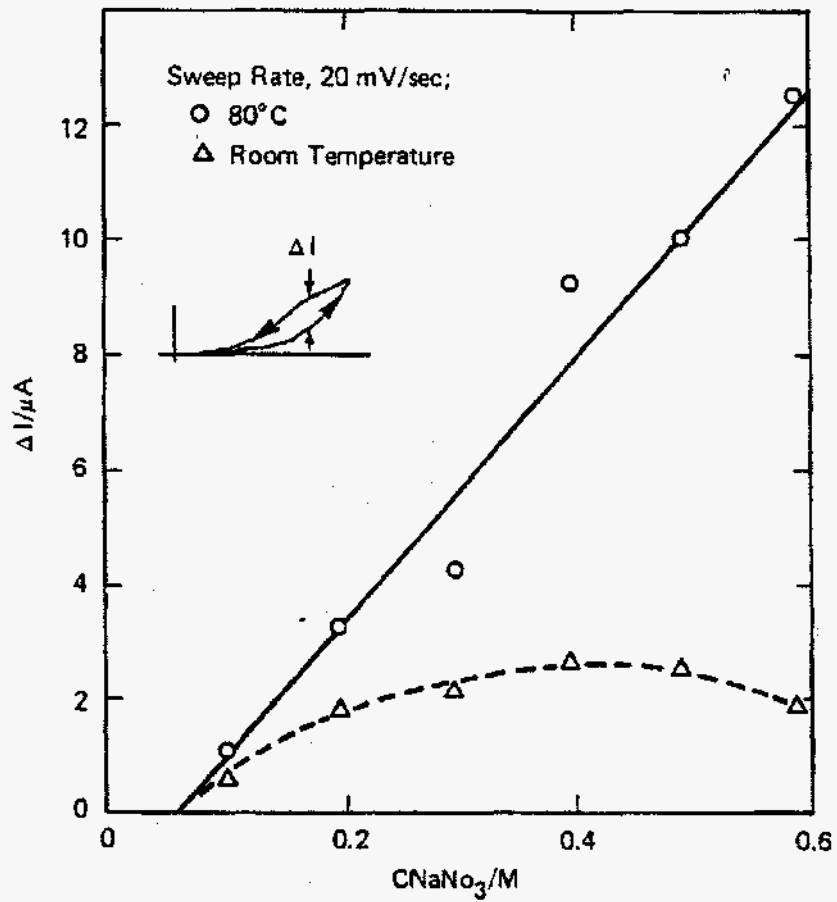


FIGURE 10. Variation of I at Nickel Electrode with Concentration of NaNO_3 in NaOH at 80°C