The electrochemical reduction of nitrate in acidic nitrate solutions

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Cathodic regeneration of nitrous acid by electrochemical reduction of nitrates could yield a catholyte which is useful in the processing of manganiferous ores. The purpose of the present investigations was to study the cathodic reaction in an electrolytic cell with an acidic nitrate electrolyte. Electrochemical reduction of nitrate has been investigated in the ranges 0.45–2.70 M H^+, 0.0–0.1 M HNO_2, 0.5–2.0 M NO_3^- and 20–80 °C at several cathode materials. Potentiodynamic scanning experiments with a platinized titanium cathode showed limiting current densities of 0–300 A m^{-2} at cathode potentials of $+950$–$+700$ mV vs SHE. At cathode potentials less than $+700$ mV vs SHE, cathodic reduction of nitrous acid to nitric oxide took place. A linear relation between the nitrous acid concentration and the limiting current density was found in this experimental range. Nitrous acid can be produced by cathodic reduction of nitric acid in a membrane cell. However, the maximum concentration of nitrous acid that can be produced is limited by two reactions; decay of nitrous acid to nitric acid and nitric oxide and cathodic reduction of nitrous acid to nitric oxide.

Keywords: *nitrates, electrochemical reduction, nitrous acid*
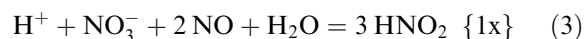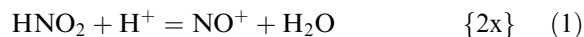
1. Introduction

In industrial practice, electrolytic manganese dioxide is produced in cells from a manganese sulfate electrolyte containing 25–65 g dm^{-3} Mn^{2+} and 0.5–1.0 M H_2SO_4, at 50–150 A m^{-2} at an electrolyte temperature of 90–100 °C. Anodic current efficiencies of 75–95% are obtained, the main competing reaction being oxygen formation [1]. The cathodic reaction in these industrial cells is hydrogen formation. Anodic production of electrolytic manganese dioxide is also possible from a manganese nitrate electrolyte, yielding a γ-MnO_2 deposit of similar composition as produced from a sulfate electrolyte at a current efficiency of approximately 80% [2]. The characteristics of the cathodic reaction in such an electrolyte are, however, not known. Thus, the purpose of the present investigations was to study the cathodic reaction in an acidic nitrate electrolyte. The experimental work was aimed at investigating the cathodic reaction as a function of the electrolyte composition, temperature and cathode material in a parallel-plate membrane cell. By measurement of the limiting current densities and observation of the production characteristics, the feasibility of cathodic nitrous acid production was assessed.

Cathodic regeneration of nitrous acid by electrochemical reduction of nitric acid would yield a valuable catholyte, since a mixture of nitrous acid (HNO_2) and nitric acid (HNO_3) is a very effective lixiviant for manganiferous ores [2]. Moreover, the cell voltage in a nitrate electrolyte, as opposed to the cell voltage in a sulfate electrolyte, would be lower due to the theoretically higher potential of the cathodic redox couple HNO_3/HNO_2 ($E_o = 0.934$ V [3]), which could replace the H^+/H_2 redox couple.

1.1. Reduction mechanism

Investigations into the mechanism for the cathodic reduction of nitric acid by Schmid and coworkers [4, 5] were summarized in the following reaction scheme:

$$HNO_2 + H^+ = NO^+ + H_2O \qquad \{2x\} \quad (1)$$

$$NO^+ + e^- = NO \qquad \{2x\} \quad (2)$$

$$H^+ + NO_3^- + 2\,NO + H_2O = 3\,HNO_2 \quad \{1x\} \quad (3)$$

$$\overline{NO_3^- + 3\,H^+ + 2\,e^- = HNO_2 + H_2O} \qquad (4)$$

The charge transfer step in this reaction scheme is Reaction 2 which is followed by the autocatalytic Abel Reaction, Reaction 3. To investigate Reactions 1 and 2 separately, it was necessary to remove the nitrate ions in order to exclude the complicated autocatalytic reaction (Reaction 3). The protons, usually supplied by the nitric acid, were therefore supplied by sulfuric acid. The experimentally ob-

tained current–voltage curve of a sulfuric acid electrolyte with additions of both nitrates and nitrous acid could not be constructed by the addition of the reduction curve of a sulfuric acid–nitrate test solution to the reduction curve of a sulfuric acid–nitrous acid test solution, since a larger current was observed in the potential range of the first reduction step of nitrous acid. It was concluded that the first reduction step of nitrous acid coincides with the reduction of nitrate in acidic solutions.

Nitrous acid is an amphoteric electrolyte. In alkaline environment, it is almost completely present as nitrous ion, NO_2^-. In a highly acidic environment, it is predominantly present as the nitrosyl ion, NO^+. In the intermediate acid range, it is mostly present as the non-dissociated HNO_2, accompanied by small fractions of NO_2^-, NO^+, NO_2 and NO. The latter two are the products of the homolytic decay of HNO_2. This homolytic decay of nitrous acid is described by

$$2\,HNO_2 - H_2O = N_2O_3 = NO + NO_2 \qquad (5)$$
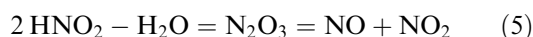
Two possible charge transfer reactions for the reduction of nitric acid were proposed:

$$NO^+ + e^- = NO \qquad (2)$$
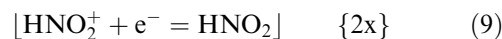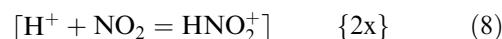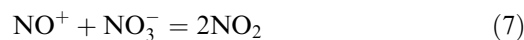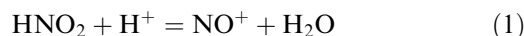$$NO_2 + e^- = NO_2^- \qquad (6)$$
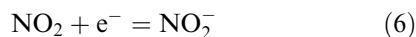
When Reaction 2 is taken as the dominating charge transfer step at a certain experimental condition, the occurrence of limiting currents under moderately acidic conditions can be ascribed to the slow production of the electron acceptor NO^+, as produced by Reaction 1. When Reaction 6 is taken as the dominating charge transfer step at certain experimental conditions, the occurrence of limiting currents can be ascribed to the low concentration of the electron acceptor NO_2. Schmid et al. [4] ascribed the production of this NO_2 to the homolytic decay of nitrous acid, according to Reaction 5. In moderately acidic conditions, the concentration of HNO_2 will be relatively low due to decay. Therefore, Schmid et al. concluded that the concentration of NO_2, as produced by Reaction 5, would also be low. It was concluded that Reaction 6 could not be the dominating charge transfer step.

Schmid's hypothesis was contrary to earlier work by Vetter and coworkers [6–8] who identified the main charge transfer step as Reaction 6, instead of Reaction 2. In distinction to the NO^+/NO system with small amounts of NO_3^-, in the HNO_3/HNO_2 system the dominating species is the nitrogen dioxide formed by

$$NO^+ + NO_3^- = 2\,NO_2 \qquad (7)$$

This reaction is a source of the charge-transferring NO_2, together with Reaction 5. The overall reaction scheme proposed by Vetter and coworkers for the reduction of nitric acid therefore differs from the one presented by Schmid due to a difference in experimental conditions [6, 9]:

$$HNO_2 + H^+ = NO^+ + H_2O \qquad (1)$$
$$NO^+ + NO_3^- = 2NO_2 \qquad (7)$$
$$\lceil H^+ + NO_2 = HNO_2^+ \rceil \qquad \{2x\} \qquad (8)$$
$$\lfloor HNO_2^+ + e^- = HNO_2 \rfloor \qquad \{2x\} \qquad (9)$$
$$\overline{NO_3^- + 3\,H^+ + 2\,e^- = HNO_2 + H_2O} \qquad (4)$$

Both reaction schemes, as proposed by Vetter and as proposed by Schmid, have Reaction 1 as the first step in the reduction mechanism of nitrate in common. The formation of the nitrosyl ion is a prerequisite for the reduction of nitric acid and the reduction rate can expected to be strongly dependent on the concentrations of H^+ and HNO_2.

1.2. Cathode material

Some of the reactions presented above can be characterized as homogeneous in the liquid phase (e.g., Reaction 3), while other can be characterized as catalysed on the electrode surface (e.g., Reactions 2 and 6, 7). The ability of various cathode materials to catalyze these reactions has been investigated by several authors under widely differing conditions.

Iridium and gold cathodes yielded reduction curves similar to platinum cathodes under acidic test conditions that were aimed at revealing the charge transfer mechanism [10]. Recent investigations show a higher activity for a Pt : Ir alloy cathode than for the pure metals [11]. Gold–palladium cathodes reduce nitrates at positive cathode potentials [12]. Within the potential range $+20$–$+450$ mV vs SHE, it was found that the layer of Au : Pd on a Pt sheet produced a constant electrochemical reduction current. However, the reduction currents were smaller than $40\,A\,m^{-2}$, and problems with the stability and reproducibility of the cathode were encountered. Graphite cathodes were tested for the reduction of nitric acid in order to produce NO from acidic nuclear waste solutions to minimize the storage volume [13]. The initial amount of HNO_2 needed for the reduction of NO_3^- was thought to be formed by oxidation of the carbon cathode according to

$$2\,HNO_3 + C = CO_2 + 2\,HNO_2 \qquad (10)$$
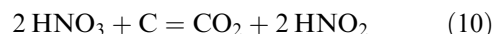
The amount of gaseous carbon oxides evolved by this reaction was less than equivalent to the amount of nitric acid reduced.

1.3. Electrolyte composition

The effect of the electrolyte composition on cathodic reduction of nitrate ion has been reported by several authors. Early references reported an impossibility to reduce nitric acid at concentrations smaller than 3 M HNO_3 [14, 15]. Vetter [7] identified the pronounced effect of the presence of nitrous acid on the reduction of nitric acid in experiments at several nitric and nitrous acid concentrations. Schmid et al. [4, 10] mainly measured the influence of nitrous ion and proton

concentration on limiting cathodic currents while excluding nitrate ions. Petrii [16] observed a linear dependency of the current density on the nitrate ion concentration in sulfuric acid solutions and studied the cathodic reduction of nitrate in the presence of several cations and adatoms. Horányi [17] observed that the polarization behaviour in nitrate reduction differed in differing supporting electrolytes. Although the effect was significant at low nitric acid concentrations, the differences disappeared at higher nitric acid concentrations. No references were found on the measurements in mixtures of nitric and nitrous acid at nitric acid concentrations smaller than 3 M HNO_3 by variation of the nitrate, nitrous acid and proton concentrations separately.

2. Experimental details

2.1. Equipment

A glass 'H'-electrolytic cell in a thermostatic water bath was applied in a batch configuration. Two 30 mm × 30 mm parallel-plate electrodes were mounted in the cell, a Nafion® 350 cation exchange membrane served as separator. Anolyte and catholyte volumes measured 500 ml. The power supply was a PC3 card installed into a PC which was controlled by CMS100 software (Gamry Instruments Inc., USA). The cathode potential versus an Ag/AgCl (1 M Cl^-) reference electrode equipped with a saturated KNO_3 bridge placed in a Luggin capillary within 1 mm distance of the platinized titanium cathode, and the current were monitored by computer. The platinum coating on the titanium sheet was obtained by cathodic deposition from an acidic H_2PtCl_6 electrolyte. The electrode to be coated was immersed for 40 min in an electrolyte of 40 mmol dm^{-3} H_2PtCl_6 and 1.2 M HCl at a current of 380 mA.

Electrolytes were obtained by dilution of 65% nitric acid. Independent levels of HNO_2, H^+ and NO_3^- were obtained by the addition of $NaNO_2$, H_2SO_4 and KNO_3, respectively. All reagents were of Baker chemical grade.

2.2. Procedure

Several cathode materials were tested. Potentiodynamic scans were recorded with platinum, titanium, graphite and platinum coated titanium cathodes. The potential of the cathode was decreased at a rate of 2 mV s^{-1}. The cathode potential versus the reference electrode and the current were registered every second. The potential was corrected for the Ag/AgCl reference potential (0.19649 V at 60 °C [18]). Hydrogen formation was observed at −0.1 V for this electrode configuration. The scanning range was from the open circuit potential to 0.0 V.

The electrolyte composition was varied in a series of experiments while using a platinized titanium cathode and a smooth platinum sheet as anode. The H^+ concentration was measured in solution samples

that were withdrawn by pipette. The sample was titrated with 1.00 M NaOH using a combined glass–Ag/AgCl electrode. An inaccuracy range of ±0.05 M H^+ was tolerated. The concentrations of NO_3^- and NO_2^- were not monitored in this series of experiments. This was motivated by the fact that the experiments only lasted over a short period of time. Decay of HNO_2 and consumption of NO_3^- were therefore ignored.

Long-term production experiments under galvanostatic conditions were conducted in a manganese nitrate electrolyte, using the same electrode configuration as in the preceding experiments. The temperature and current density were set to allow for the anodic electrowinning of manganese dioxide. Analysis for HNO_2 in the catholyte samples was performed by two separate methods: HPLC anion analysis in a potassium hydrogen phthalate solution by a Chromopack Ionospher 5A column in combination with a refractive index detector; and an analytical leach with excess β-MnO_2 powder which yielded AAS detectable Mn^{2+} concentrations proportionally to the HNO_2 concentration in the sample.

3. Experimental results and discussion

3.1. Cathode material

Several cathode materials were tested to identify a relatively low-cost, chemically stable cathode material for the cathodic reduction of nitrate media. The limiting current density in the potential range +900– +600 mV vs SHE, as compared to the limiting current density of a smooth platinum cathode, was the main criterium for material selection. Titanium was rendered passive at positive cathode potentials. Graphite showed a relative high limiting current density, but was attacked by the nitrous/nitric acid electrolyte. Platinizing of the electrode surface yielded the highest current densities. For the experiments that were performed to test the influence of the electrolyte composition, a platinized titanium cathode was therefore applied. A single platinized titanium electrode was used, in order to avoid any interference of the reproducibility of the cathode surface on the experiments. The reproducibility of the experimental electrode itself was satisfactory.

3.2. Electrolyte composition

3.2.1. Experimental results. To run the potentiodynamic scans as a function of H^+ concentration, Fig. 1, a base electrolyte was acidified stepwise by the addition of H_2SO_4. The base electrolyte contained 0.45 M H^+ + 1.0 M NO_3^- + 0.01 M HNO_2, the charge balance being Na^+ and K^+. The NO_3^- and HNO_2 concentrations were adjusted for dilution by the addition of neutral KNO_3 and $NaNO_2$ solutions.

To run the potentiodynamic scans as a function of HNO_2 concentration, Fig. 2, specific amounts of neutral $NaNO_2$ solutions were injected in a base electrolyte of 1.0 M HNO_3. The H^+ and NO_3^- con-
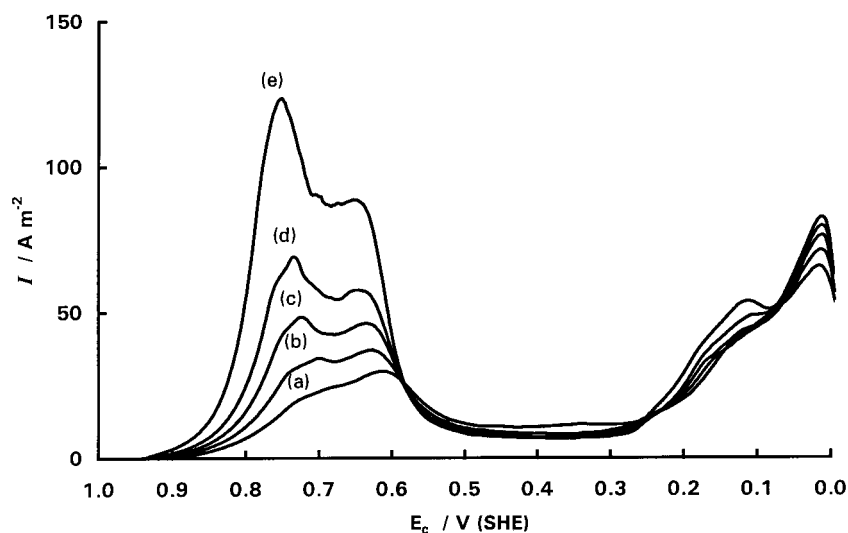
Fig. 1. Potentiodynamic scans with platinized titanium cathode at several H^+ concentrations, $60\,°C$. Scan rate $2\,mV\,s^{-1}$. Electrolyte composition $1.0\,M\ NO_3^- + 0.01\,M\ HNO_2$. Key: (a) 0.45, (b) 0.90, (c) 1.40, (d) 1.85 and (e) $2.70\,M\ H^+$.

centrations were adjusted for dilution by the addition of H_2SO_4 and KNO_3 solutions.

To run the potentiodynamic scans as a function of the NO_3^- concentration, Fig. 3, three separate electrolytes were used. H^+ and HNO_2 concentrations were obtained by the addition of H_2SO_4 and $NaNO_2$ solutions.

3.2.2. Discussion. The potentiodynamic scans that were run to determine the main electrolyte parameters all show a similar behaviour. The open circuit potential of the overall reaction

$$NO_3^- + 3\,H^+ + 2\,e^- = HNO_2 + H_2O \qquad (4)$$
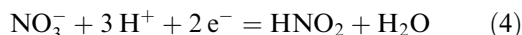
is the starting point for the cathodic scan. At increasing overpotentials, the current increases rapidly towards the maximum value for the reduction of nitric to nitrous acid. A second current peak can be observed at a potential which is approximately 0.1 to 0.2 V lower than the first peak. This peak represents the reduction of nitrous acid to NO ($E_o = 0.983\,V$ [3]), according to

$$HNO_2 + H^+ + e^- = NO + H_2O \qquad (11)$$

This is confirmed by the observation that a colourless gas starts to evolve from the cathode. At lower potentials, inhibition of the cathode reaction is observed by a sharp reduction in the current density. Other current peaks occur at lower potentials of the cathode before development of hydrogen gas takes place.

In Figs 4, 5 and 6, relationships between the limiting current density and the electrolyte parameters are constructed. The height of the first current peak in the potentiodynamic scans is considered to be the limiting current density for the reduction of nitric acid to nitrous acid. This peak height as a function of the varied electrolyte parameter is represented by the solid lines in Fig. 4 to 6. The height of the second current peak in the potentiodynamic scans is considered to be the limiting current density for the reduction of nitrous acid to nitric oxide. This
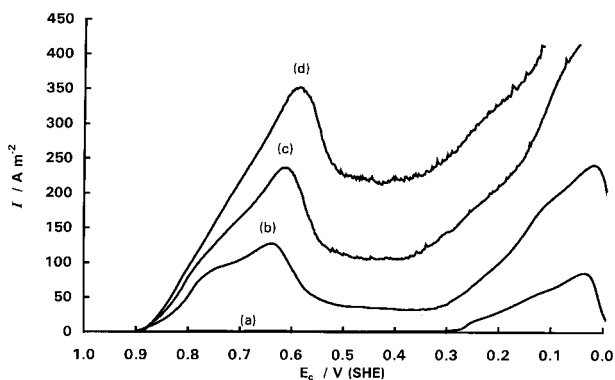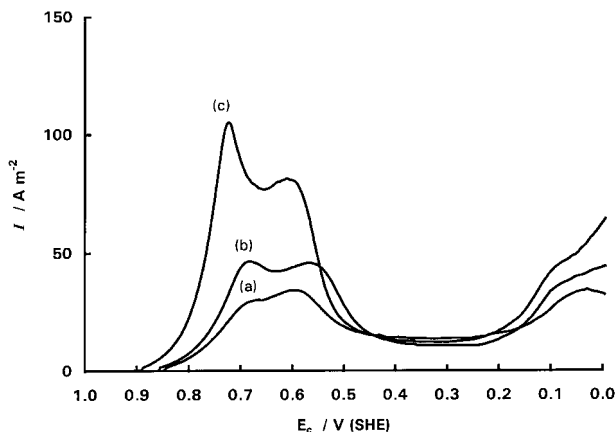

Fig. 2. Potentiodynamic scans with platinized titanium cathode at several HNO_2 concentrations, $60\,°C$. Scan rate $2\,mV\,s^{-1}$. Electrolytic composition $1.0\,M\ H^+ + 1.0\,M\ NO_3^-$. Key: (a) 0.000, (b) 0.026, (c) 0.051, and (d) $0.077\,M\ HNO_2$.

Fig. 3. Potentiodynamic scans with platinized titanium cathode at several NO_3^- concentrations, $60\,°C$. Scan rate $2\,mV\,s^{-1}$. Electrolytic composition $1.0\,M\ H^+ + 0.01\,M\ HNO_2$. Key: (a) 0.5, (b) 1.0 and (c) $1.5\,M\ NO_3^-$.
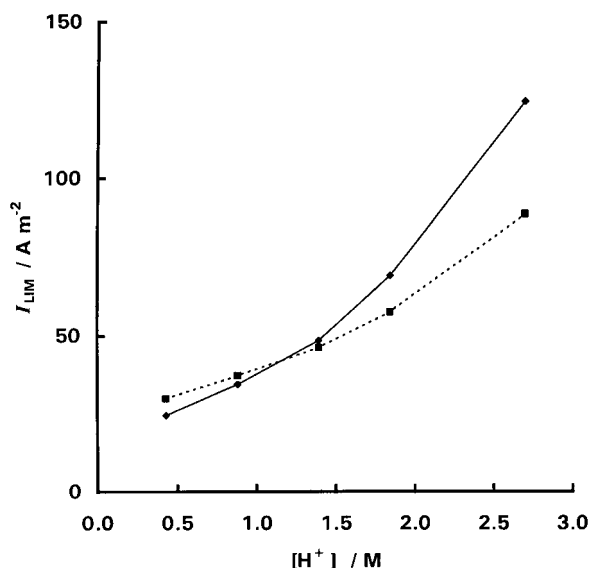
Fig. 4. Limiting current density as a function of H^+ concentration at 60 °C. Platinized titanium cathode. Electrolyte composition $1.0 \text{ M } NO_3^- + 0.01 \text{ M } HNO_2$.

Fig. 6. Limiting current density as a function of NO_3^- concentration at 60 °C. Platinized titanium cathode. Electrolyte composition $1.0 \text{ M } H^+ + 0.01 \text{ M } HNO_2$.

peak height as a function of the electrolyte parameter varied is represented by the dotted lines in Fig. 4 to 6.

Figure 4 shows the limiting current density as a function of H^+ concentration. Both the reduction of nitric and nitrous acid are strongly favored by an increase in H^+ concentration. The reduction mechanism of nitric acid is initiated by the formation of NO^+, Reaction 1. This initial formation of NO^+ is reported to be strongly dependent on H^+ concentration. This is confirmed by the experimental observations.

Figure 5 shows the limiting current densities as a function of HNO_2 concentration. A linear relationship is obtained. Both the reduction of nitric and nitrous acid are proportionally favoured by an in-
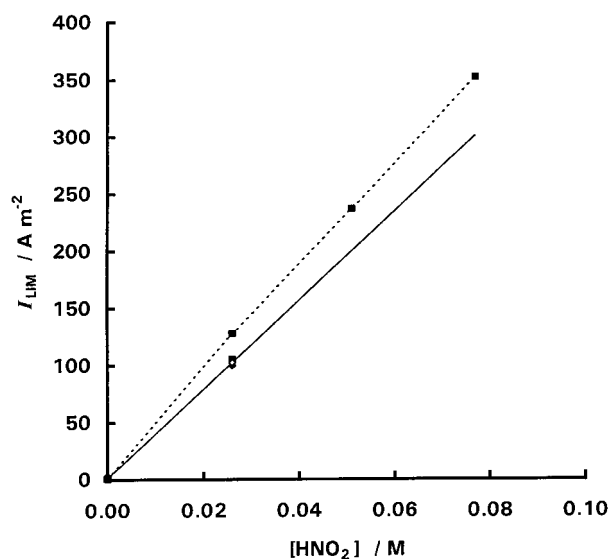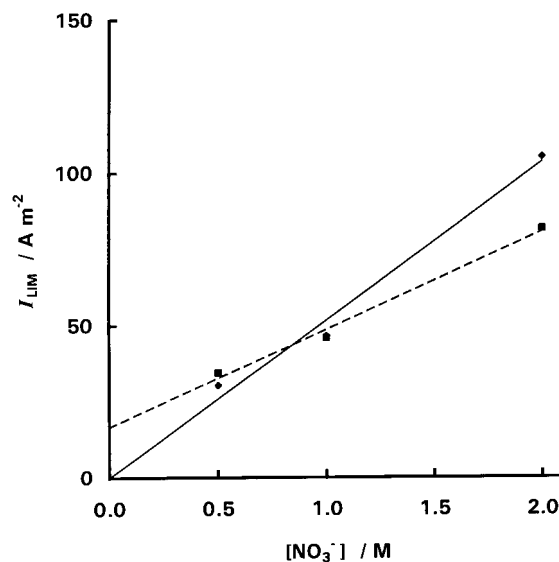
crease in HNO_2 concentration. The intercept of the solid line with the origin proves that it is impossible to reduce nitrate in acidic nitrate solution, at a high potential on a platinized titanium cathode, without the presence of nitrous acid.

Figure 6 shows the limiting current densities as a function of NO_3^- concentration. The intercept with the origin of the extrapolated solid line is in concordance with its definition, the reduction of NO_3^- to HNO_2. Interpretation of the dotted line in Fig. 6 leads to the conclusion that for reduction of nitrous acid to nitric oxide, no NO_3^- is needed.

It was observed during the experimental work that both the reduction of nitric and nitrous acid were strongly favoured by an increasing temperature due to improved reaction kinetics.

3.3. Nitrous acid production

As a result of the potentiodynamic scanning experiments an operating window for the cathodic reduction of nitric acid could be defined. The cathodic reduction was initiated at the start of a production experiment by the addition of 0.01 M $NaNO_2$ to the nitric acid catholyte. Due to the reduction of nitric acid, the nitrous acid concentration increased in the catholyte of the batch electrolytic cell. However, the nitrous acid concentration that can be obtained this way is limited. This is illustrated in Fig. 7 during a 30 h production test.

The nitrous acid produced is subject to decay to nitric oxide and nitric acid, according to the equation:

$$3\,HNO_2 \overset{K}{=} 2\,NO + H^+ + NO_3^- + H_2O \qquad (12)$$
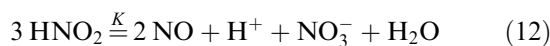
Theoretically, a maximum nitrous acid concentration will be established, depending on the value of the equilibrium constant K, the partial gas pressure of

Fig. 5. Limiting current density as a function of HNO_2 concentration at 60 °C. Platinized titanium cathode. Electrolyte composition $1.0 \text{ M } H^+ + 1.0 \text{ M } NO_3^-$.
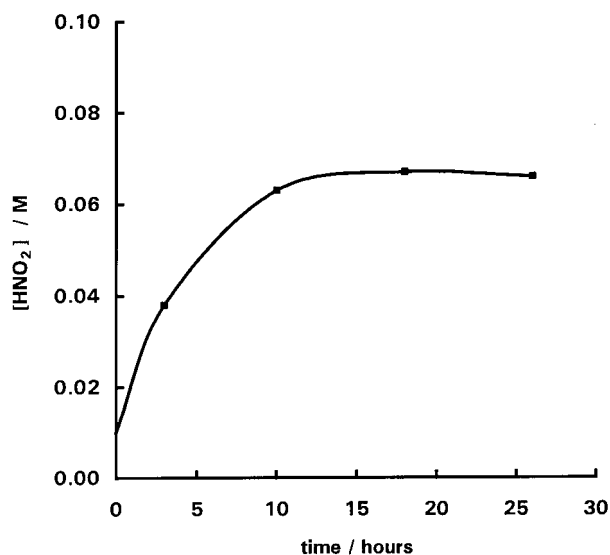
Fig. 7. Nitrous acid concentration as a function of time in a batch cell, 80 °C. Platinized titanium cathode. Current density 150 A m^{-2}. Initial electrolyte composition 1.0 M H$^+$ + 2.2 M NO$_3^-$ + 0.01 M HNO$_2$.

NO (P_{NO}), and the activities of H$^+$ and NO$_3^-$. The H$^+$ and NO$_3^-$ assay, given in Fig. 7, combined with extrapolated literature values for K [19] and P_{NO} [15] yield an equilibrium nitrous acid concentration of 0.07 M HNO$_2$. This is in close accordance to the experimentally determined maximum. Additional nitrous acid losses occurred at this concentration, since it was observed that nitric oxide evolved as a result from the reduction of nitrous acid at the cathode, according to Reaction 11.

4. Conclusion

Electrochemical reduction of nitrate in acidic nitrate solutions has been investigated in the range 0.45–2.70 M H$^+$, 0.0–0.1 M HNO$_2$, 0.5–2.0 M NO$_3^-$ and 20–80 °C at several cathode materials. Potentiodynamic scanning experiments with a platinized titanium cathode yielded limiting current densities of 0–300 A m^{-2} at cathode potentials of +950–+700 mV vs SHE. At cathode potentials less than +700 mV vs

SHE, cathodic reduction of nitrous acid to nitric oxide took place. A linear relation between the nitrous acid concentration and the limiting current density was found in this experimental range. The proton concentration, nitrate concentration, temperature and cathode material are other parameters which govern the cathodic reduction. Nitrous acid can be produced by cathodic reduction of nitric acid in a membrane cell. However, the maximum concentration of nitrous acid that can be produced by cathodic reduction of nitrate in acidic nitrate solutions is limited by two reactions; decay of nitrous acid to nitric acid and nitric oxide and cathodic reduction of nitrous acid to nitric oxide.

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