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Influence of nitrate concentration on its electrochemical reduction on tin cathode: Identification of reaction intermediates

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ABSTRACT

The influence of the concentration of nitrate in the range between 100 and 62,000 mg L^{-1} $NaNO_3$ in NaCl solutions was studied under constant potential electrolysis at −2.8 V vs. Ag/AgCl. The rate of the reduction follows Langmuir–Hinshelwood kinetics, according to which zero order kinetics is followed at concentrations higher than 0.3 M whereas first order at lower concentrations.

The selectivity to nitrogen increases from 70 to 83% as the concentration of nitrate increases from 100 to 1500 mg L^{-1} and it remains almost constant for higher nitrate concentrations, whereas that of ammonia exhibits the opposite trend decreasing from 25 to 11%. The % Faradaic Efficiency (%FE) increased with the increase of the concentration of nitrate from 25% at 0.1 M to 78% at 1 M when 95% of nitrate was reduced in both cases. At high concentrations of nitrate, hyponitrite and hydroxylamine were detected as intermediates of the reduction and a reaction scheme which is in agreement with the experimental results has been proposed.

The hydrogen evolution in our conditions probably takes place through the discharge of the cation of the supporting electrolyte instead of the Volmer–Tafel mechanism and the reduction of nitrate proceeds through electrochemical hydrogenation.

1. Introduction

The main aim of the electrocatalytic methods for the reduction of nitrate is the treatment of wastewaters, such as the low-level nuclear wastes and the brine resulting from the regeneration of ion exchange resins, where the biological method cannot be applied [1]. The ideal electrochemical method should combine: (i) high rate of conversion of nitrate and high selectivity towards nitrogen gas, (ii) high current efficiency, (iii) low operating cost and (iv) applicability in any composition of wastes. The most common problem of the reduction of nitrate is the formation of side-products such as nitrite, ammonia and hydroxylamine, which are much more toxic than the removed nitrate [2–9].

In previous papers, it was proved that nitrate can be converted to dinitrogen with both high rate and high selectivity (~92%) on a tin cathode at very negative potentials (−2.5 to −2.9 V vs. Ag/AgCl) [10]. It was also found that the rate of the reduction increases as the concentration of the supporting electrolyte and the crystallographic radius of its cation increases [11]. A possible explanation was given by the theory of cationic catalysis, according to which the cation of the supporting electrolyte forms a virtual ion pair with the nitrate anion at the outer Helmholtz plane (oHp), before the electron transfer. The non-charged ion pair cannot be repelled by the negatively charged electrode and this explains why the rate of the reduction increases even at so negative potentials. In a recent study on Pt–Sn cathode [12], the authors reported a similar selectivity for nitrogen and ammonia, to that on pure tin [11].

The concentration of nitrate which can be found in wastes and water may vary; for example, the concentration of nitrate in contaminated drinking water is about 1.5×10^{-3} mol L^{-1} [1,7], the wastes from the regeneration of the ion exchange resins contain about 15×10^{-3} mol L^{-1} [13] and the concentration of nitrate in low-level nuclear wastes exceeds 1 mol L^{-1} [14]. Moreover, the concentration of nitrate can influence the rate of the reduction and the distribution of the products, as it has been previously reported [2,15–28]. For these reasons, the study of the influence of the concentration of nitrate is of great importance.

It has been proved that the reduction on various metallic electrodes proceeds through the intermediate nitrite, but the subsequent steps leading to the formation of the final products such as ammonia, nitrogen, nitrous oxide, hydroxylamine, etc., are yet to be defined [29]. The formation of other products like HNO, $N_2O_2{}^{2-}$, $N_3{}^-$ and NH_2NO_2 as possible key intermediates has been specu-

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lated in some papers regarding the chemical, electrochemical or biological reduction of nitrate or nitrite [29–35].

This paper includes experimental results on the influence of the concentration of nitrate on the rate of the reduction and on the distribution of the products. In addition, it was found that hydroxylamine and hyponitrite participate in the reaction mechanism which in our conditions proceeds through electrochemical hydrogenation (EH).

2. Experimental

A Teflon electrochemical cell equally divided into two volumes by a Nafion 117 (H^+ form) cation exchange membrane was used in all experiments. The geometrical area of the tin cathode (Sigma–Aldrich, 99.9%) was 2 cm^2 and the anode was a platinized Pt foil (Alpha Metal) of 6 cm^2. The potential was controlled by a Wenking POS73 (Bank Elektronik) potentiostat and the reference was a saturated Ag/AgCl electrode.

The determination of nitrate and nitrite was performed by Ion Chromatography (Dionex 4500i, AS9-HC) equipped with a UV detector. The analysis of hydrazine and hydroxylamine was carried out by colorimetric methods [36,37]. Ammonia was determined by fluorometry after its online derivatization with *o*-phthalaldehyde [38]. A helium stream having a constant flow rate of 12 mL min^{-1} withdrew the gaseous products of the electrolysis. The dilution of the gaseous stream mainly due to the hydrogen evolution as well as to the nitrogen production was taken into account in the calculations. The determination of the instant concentration of hydrogen, nitrogen and nitrous oxide in the outgoing gaseous stream from the electrolytic cell was performed by Gas Chromatography (Agilent Technologies, 6820), using a Molecular Sieve 13X column 1.8 m, 2.2 mm i.d., and a thermal conductivity detector (TCD). The temperature of the column was kept constant at 100 °C for 1.5 min and thereafter it was increased with a rate of 30 °C min^{-1} up to 180 °C where it was kept constant for 4 min. The total volume of the produced gaseous species was calculated by integrating the instant concentration curve of each product. The UV spectra were recorded by a Hitachi U-1900 spectrophotometer and the infrared spectra by a Thermo Scientific Nicolet IR200 spectrometer using KBr pellets.

More information about the experimental section and the calculation of the selectivity can be found in [10].

3. Results

3.1. Voltammetry

The slow-sweep cyclic voltammograms obtained in solutions of various concentrations of nitrate are depicted in Fig. 1. The concentration of the supporting electrolyte (NaCl) varied so that both the initial ionic strength and the concentration of the sodium cations were constant in all solutions, since the rate of the reduction is influenced by the concentration of the alkalimetal cation [11]. Moreover, all the experiments were performed in unbuffered solutions of sodium chloride, because the brine wastes coming from the regeneration of the ion exchange resins usually contain about 2 M NaCl [39]. The cathodic current density increases as the initial concentration of nitrate increases, in the whole potential range studied.

3.2. Intermediates of the reduction

It has been already proved [10,11] that the reduction on Sn is more efficient at very negative potentials, because both the rate of the reduction and the selectivity towards nitrogen are higher. For that reason, the batch electrolytic experiments were performed at −2.8 V vs. Ag/AgCl at constant ionic strength (2 M).

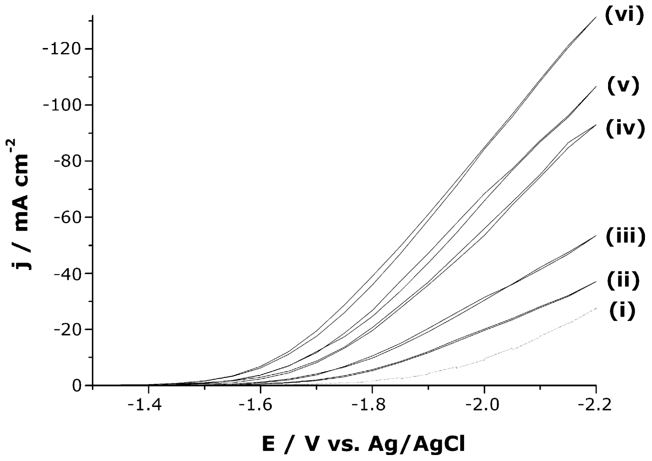


Fig. 1. Cyclic voltammograms in various concentrations of nitrate. Electrolyte: *x* M $NaNO_3$ + (2 − *x*) M NaCl, *x* = (i) 0, (ii) 0.05, (iii) 0.10, (iv) 0.25, (v) 0.50, and (vi) 1.0. Scan rate: 2 mV s^{-1}.

Fig. 2 shows the concentration profile of the initial nitrate (1 M $NaNO_3$) and the products of the electrolysis vs. time. The main gaseous products were nitrogen (85.7%) and N_2O (6%). Ammonia, which is an undesirable by-product, reaches a selectivity of 8.9%, while hydroxylamine was not detectable in the final solution. The concentration of nitrite vs. time is characteristic of an intermediate product in a consecutive reaction mechanism [40] and its final selectivity was 0.16% (1.52×10^{-3} mol L^{-1}). During the electrolysis, a significant loss of mass balance of the N-containing species vs. time was observed, the shape of which is similar to that of nitrite, having a maximum (250 mM) at 90 min, while the maximum of nitrite is displayed at 60 min. The fact that the maximum of the loss of mass is displayed after the maximum of nitrite implies that some intermediates subsequent to the formation of nitrite are involved in the reaction mechanism. The intermediates remain in the catholyte for a long period of time and continuously react to give the final products. After electrolysis time of 210 min there is no loss of mass balance, within the experimental error. The latter excludes the possibility of the formation of a gaseous product, such as nitrogen oxide (NO), which has a low solubility in

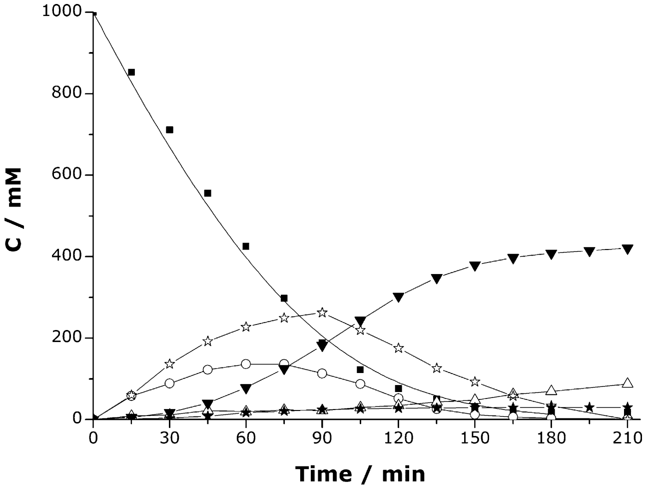


Fig. 2. Concentration profile of (■) nitrate, (○) nitrite, (△) ammonia, (▼) nitrogen and (★) nitrous oxide at −2.8 V vs. Ag/AgCl. (☆) Represents the loss of mass balance. Electrolyte: 1 M $NaNO_3$ + 1 M NaCl.

Table 1
Possible intermediates of the reduction of nitrate having oxidation number lower than +3

Name and formula		Oxidation number	Properties and detection method	Refs.
Hyponitrate or trioxodinitrate (Angeli's salt)	$N_2O_3^{2-}$	+2	Relatively stable in pH > 4. Decomposes to $N_2O_2^{2-}$ and NO_2^- $\lambda_{max} = 248$ nm (at pH 14)	[42,43]
Hyponitrite	$N_2O_2^{2-}$	+1	Relatively unstable in pH 3–13. $\lambda_{max} = 248$ nm (at pH 14) gives yellow precipitate with Ag^+ in acetate buffer	[42,44–47]
Nitramide (or nitroamine)	NH_2NO_2	+1[a]	Decomposes rapidly to N_2O in basic solution, $\lambda_{max} \sim 207$ nm	[42,48]
Hydrazoic acid	HN_3	+1/3	Gives white precipitate with Ag^+ ($K_{sp} = 2.8 \times 10^{-9}$), $\lambda_{max} = 210$ nm	[49,50]
Dinitramide	$NH(NO_2)_2$	+7/3[a]	Stable in pH 0–14, $\lambda_{max} = 210$ and 284 nm	[51]
Hydrazine	N_2H_4	−2	Reacts with *p*-dimethylaminobenzaldehyde to give a stable yellow colour with $\lambda_{max} = 458$ nm	[36]
Hydroxylamine	NH_2OH	−1	Reacts with 8-hydroxyquinoline and gives indooxine with $\lambda_{max} = 705$ nm	[37]

[a] Nitramide and dinitramide contain N atoms in different oxidation states.

water ($\sim 1.6 \times 10^{-3}$ mol L^{-1} [41]) and, if it was formed, it would have escaped from the solution. In addition, the analysis of the gaseous products by Drägger tubes showed only traces of NO. Furthermore, a loss of charge balance was also observed in parallel to that of mass balance during the same time interval. For example, the charge that passed after 90 min (calculated by the integral of the current) was 3747 C, while the charge consumed for the formation of the determined products was 2338 C, which means a loss of charge of about 37%.

According to the above discussion and given that there are no stable compounds in aqueous solution with oxidation numbers between +5 and +3, apart from nitrate and nitrite, the unknown intermediates is expected to have an oxidation number lower than +3. Some possible intermediates which may be involved in the reduction process are shown in Table 1.

The presence of hydrazoic acid and hydrazine was ruled out by performing analysis of the catholyte during the electrolysis by ion chromatography [50] and colorimetry [36], respectively. Even though hydroxylamine was not detectable as a final product it was detected as an intermediate and its concentration profile vs. time is shown in Fig. 3. The analysis of hydroxylamine was carried out by two ways: the method of 8-quinolinol [37] and that of Ferrozine [52], which are based on the conversion of hydroxylamine to the stable 5,8-quinolinequinone-5-(8-hydroxy-5-quinolylimide) known as indooxine (705 nm) and on the reduction of the trivalent iron by hydroxylamine, respectively. The first method is more reliable under our conditions because some reducing agents such as hyponitrites [53] and trioxodinitrate [54] could also reduce trivalent iron, causing a false-positive test.

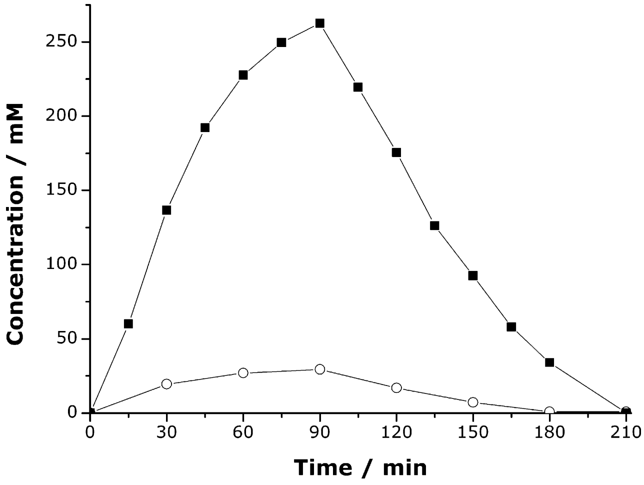


Fig. 3. Concentration of hydroxylamine (○) and loss of mass balance (■) vs. time. Potential: −2.8 V vs. Ag/AgCl. Electrolyte: 1 M NaCl + 1 M $NaNO_3$.

The observed loss of mass balance cannot be attributed to hydroxylamine only since it corresponds to about 10% of the mass loss, even if its actual concentration in the catholyte may be somewhat higher due to its reaction with nitrite during the time of analysis (about 7 min) to give N_2O [55]:

$$HNO_2 + NH_2OH \rightarrow N_2O + 2H_2O \qquad (1)$$

The reaction (1) shows that the actual concentration of nitrite may also be underestimated.

In order to verify if another intermediate apart from hydroxylamine is involved in the reduction mechanism the UV spectra of the catholyte were recorded (Fig. 4) at specific time intervals during the electrolysis. The absorbance at 240–270 nm increases with time ($\lambda_{max} = 243$ nm) proving that at least one more intermediate is formed. The species which absorb in this region are $N_2O_3^{2-}$ and $N_2O_2^{2-}$ ($\lambda_{max} = 248$ nm for both at pH 13). The shift in the λ_{max} to 243 nm can be attributed to the fact that the UV spectra of $N_2O_3^{2-}$ and $N_2O_2^{2-}$ are pH-dependent [56,57] and the λ_{max} moves to lower wavelengths ($\lambda_{max} < 248$ nm) as the pH decreases due to the participation of the absorptions of the anions $HN_2O_3^-$ and/or $HN_2O_2^-$.

Given that $N_2O_2^{2-}$ precipitates with Ag^+ in the form of $Ag_2N_2O_2$ in acetate buffer [46] a new experiment was performed in 0.5 M

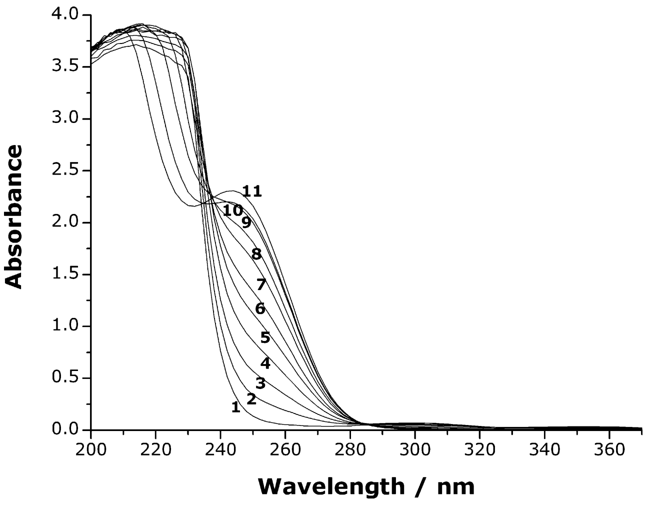


Fig. 4. UV spectra (100× dilution of the catholyte) during the electrolysis (−2.8 V vs. Ag/AgCl) at (1) 0, (2) 10, (3) 20, (4) 30, (5) 40, (6) 50, (7) 60, (8) 70, (9) 80, (10) 90, and (11) 100 min. Electrolyte: 1 M NaCl + 1 M $NaNO_3$.

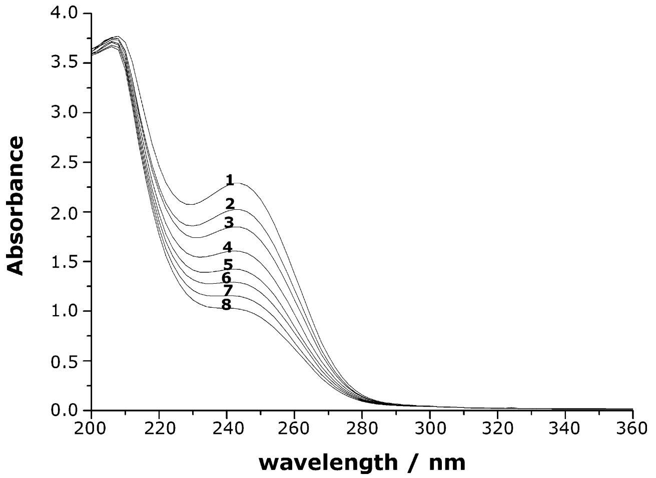


Fig. 5. UV spectra (100× dilution) after stopping the electrolysis at 100 min, for (1) 0, (2) 10, (3) 20, (4) 30, (5) 40, (6) 50, (7) 60, and (8) 70 min.

$CH_3COONa + 0.5$ M $CH_3COOH + 1$ M $NaNO_3$ at −2.8 V. After 90 min, 2 mL of a solution of 0.1 M $AgNO_3$ were added in an equal volume of the catholyte and a canary-yellow precipitate was obtained. The IR spectrum of the precipitate shows characteristic bands at 880, 1010, 1410 and 1605 cm^{-1} which correspond to $Ag_2N_2O_2$ [58,59]. In order to clarify if the detected hyponitrite is a secondary product of the decomposition of trioxodinitrate through the reactions [42,43]:

$$H_2N_2O_3 \rightleftharpoons HNO_2 + HNO \quad (2)$$

$$2HNO \rightarrow H_2N_2O_2 \quad (3)$$

the absorbance at 248 nm was measured (after 90 min of electrolysis) and the solution of the catholyte was immediately acidified with 2 M HCl at pH < 1, where hyponitrous acid is stable while trioxodinitrate decomposes rapidly to give nitric oxide [43]. After 30 min the pH of the solution was adjusted to its initial pH by a 2 M KOH solution and the absorbance at 248 nm was measured again. The comparison of the two absorbencies, by taking into account the dilutions made, indicated no significant change. Therefore, it is concluded that trioxodinitrate is probably not present in the catholyte.

When the electrolysis was stopped after 100 min, the absorbance at 243 nm decreased (Fig. 5), while nitrous oxide was still formed for 1 h due to both the reaction (1) and the nitrous acid-catalyzed decomposition of hyponitrite [42]:

$$H_2N_2O_2 \rightarrow N_2O + H_2O \quad (4)$$

The possible formation of nitramide under our conditions cannot be ruled out since it rapidly decomposes to N_2O by a base-catalyzed reaction [42] and only in situ methods can be applied for its detection. Moreover, the formation of dinitramide in a considerable concentration does not seem possible since no absorption peak was observed at 284 nm [51].

At this point we would like to comment the analytical methods used in many works on the electrochemical reduction of nitrate which do not include direct determination of the dinitrogen and the authors deduce its amount from the mass balance, namely by the simple subtraction of the produced ammonia and nitrite from the removed nitrate. In this case, the formation of other species such as NO, N_2O, NH_2OH, $H_2N_2O_2$, etc., which can have a considerable yield is ignored and this has been already criticized by Brylev et al. [60]. For example, in the present work, the concentration of hyponitrite, hydroxylamine and nitrous oxide during the electrolysis was about 30% and in some papers, N_2O was the predominant final product (yield 75%) [61]. It should also be noticed that the analyses of the samples taken during the reduction of nitrate must be performed without undue delay, in order to reduce the experimental error due to reactions between the products (e.g. hydroxylamine and nitrite), chemical decomposition of hyponitrite, etc. Moreover, the standard method of analysis of nitrate which is based on the direct measurement of the absorbance at 220 nm [62] cannot be used in the case of reduction of nitrate since other species such as nitrite and hyponitrite have an absorbance at the same wavelength.

3.3. *Influence of the concentration*

Fig. 6 shows the decay of C/C_O vs. time, in three different initial concentrations of nitrate at −2.8 V. At high concentration, e.g. 1 M, the reduction follows zero order kinetics at the first 75 min, while at 0.1 M it can be sufficiently described by first order kinetics, in accordance with previous results [7,9,11,63]. Zero order kinetics for high concentrations of nitrate has already been reported in previous papers [9,20] and it was attributed to the saturation of the electrode surface by the electroactive species, namely to the blocking of the active electrode surface sites. The reaction rate is then controlled only by the electron transfer and not by the diffusion of the ions to the surface of the electrode. A mathematical expression for the influence of the concentration on the rate of the reduction of nitrate by Langmuir kinetics which assumes that nitrate ion is adsorbed on the electrode surface has been given by De et al. [3] and Reyter et al. [64].

Our experiments were performed at a very negative potential (−2.8 V), where nitrate cannot be adsorbed directly on the electrode surface due to the strong repulsion by the likely charged electrode. In previous papers on the electrochemical reduction of anions such as persulfate [65,66] or anions of the type XO_3^-, for example, bromate, iodate, etc. [67,68] it was proposed that the anion reaches the electrode via the formation of a virtual ion pair between the cation of the supporting electrolyte and the reduced anion which is located at the oHp or at a distance from the electrode farther than the oHp [69,70]. Based on this hypothesis we explained in a previous paper why the rate of the reduction of nitrate increases even at so negative potentials [11].

Assuming that the adsorption of nitrate takes place at the oHp through the formation of ion pairs, an expression similar to the well known Langmuir model can be obtained as follows.

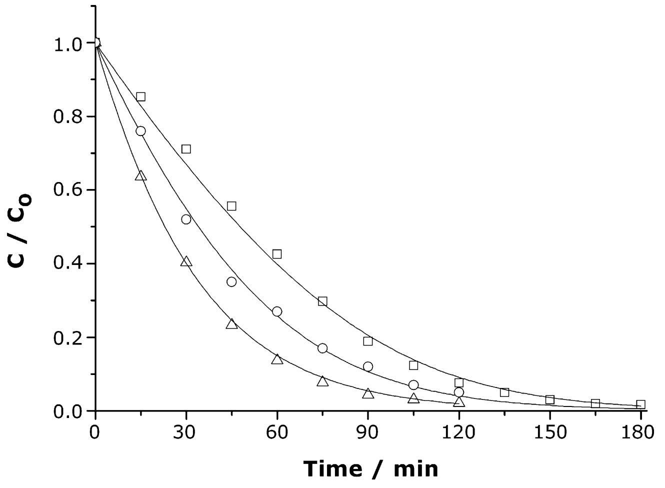


Fig. 6. C/C_O vs. time during the reduction of x = (□) 1 M (○) 0.5 M and (△) 0.1 M $NaNO_3$ at −2.8 V vs. Ag/AgCl. Electrolyte: x M $NaNO_3 + (2 - x)$. The points show the experimental data and the lines the simulation based on the Eq. (12).

The reduction occurs according to the scheme:

$$M^+ + NO_3^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M\cdots NO_3 \xrightarrow{k} \text{Products} \tag{5}$$

The rate of the formation of ion pairs (ion-pair association) is determined by:

$$r_1 = k_1[M^+][NO_3^-]\left(1 - \frac{N}{N_O}\right) \tag{6}$$

while the rate of the dissociation of the ion pair:

$$r_2 = k_{-1}[M\cdots NO_3] \tag{7}$$

The rate of the reduction of nitrate is:

$$r_3 = -\frac{d[NO_3^-]}{dt} = k[M\cdots NO_3] = k\frac{N}{N_O}[M^+] \tag{8}$$

where N represents the number of the metal cations that have formed ion pair with nitrate and N_O the total number of the metal cations that are located at the oHp. The steady-state approximation for the ion-pair yields:

$$\begin{aligned} \frac{d[M\cdots NO_3]}{dt} &= r_1 - r_2 - r_3 = k_1[M^+][NO_3^-]\left(1 - \frac{N}{N_O}\right) \\ &\quad - k_{-1}[M\cdots NO_3] - k[M\cdots NO_3] = 0 \\ \text{and } k_1[M^+][NO_3^-]\left(1 - \frac{N}{N_O}\right) &= (k_{-1} + k)[M\cdots NO_3] \\ &= (k_{-1} + k)\frac{N}{N_O}[M^+] \end{aligned} \tag{9}$$

The expression that gives the ratio N/N_O, is:

$$\frac{N}{N_O} = \frac{k_1[NO_3^-]}{k_1[NO_3^-] + k_{-1} + k} \tag{10}$$

The combination of Eqs. (8) and (10) gives:

$$-\frac{d[NO_3^-]}{dt} = k\frac{k_1[NO_3^-]}{k_1[NO_3^-] + k_{-1} + k}[M^+] \tag{11}$$

Assuming that the rate-determining step is the charge transfer, $k \ll k_1[NO_3^-] + k_{-1}$ and the rate of the reduction is determined by:

$$-\frac{d[NO_3^-]}{dt} = k[M^+]\frac{K[NO_3^-]}{1 + K[NO_3^-]} \tag{12}$$

where $K = k_1/k_{-1}$ is the ion association constant, which shows the tendency of nitrate to form ion pairs.

According to Eq. (12), the reduction follows zero order kinetics when the concentration of nitrate is high, because $1 + K[NO_3^-] \approx K[NO_3^-]$, while it follows first order kinetics when the concentration of nitrate is sufficiently low so that $1 + K[NO_3^-] \approx 1$. At intermediate values of $K[NO_3^-]$, a fractional reaction order must be expected. The expected dependence of the reaction order on the concentration of nitrate (Eq. (12)) has been observed in our experiments (Fig. 6), where the reaction order at the first stages of electrolysis in 1 M $NaNO_3$ solution was zero while in 0.1 M $NaNO_3$ was one.

This model fits well to all the experimental data, as it is depicted in Fig. 6, where the curves were drawn by non-linear regression fit to Eq. (12). The obtained values were $k = 4.56\ min^{-1}\ cm^{-2}$ and $K = 1.85\ M^{-1}$; the latter is similar to the value of the association constant ($K = 1.43\ M^{-1}$ at zero ionic strength) given by Damaskin et al. [71]. These values can also sufficiently describe the concentration decay of nitrate at all concentrations studied in the range between 1.5×10^{-3} and $45 \times 10^{-3}\ mol\ L^{-1}$ as it is depicted in Fig. 7, where the curves were drawn by non-linear regression fit to Eq. (12).

The selectivity to nitrogen (Fig. 8), as it is defined in [10], increases from 70 to 83% as the concentration of nitrate increases from 1.5×10^{-3} to $25 \times 10^{-3}\ mol\ L^{-1}$ and consequently it remains almost constant within the experimental error, whereas the selectivity to ammonia exhibits the opposite trend. The selectivity to nitrite was not dependent on the concentration of nitrate in the range examined. It should be mentioned that there was no loss of mass balance within the experimental error (±5%) when the concentration of nitrate was low.

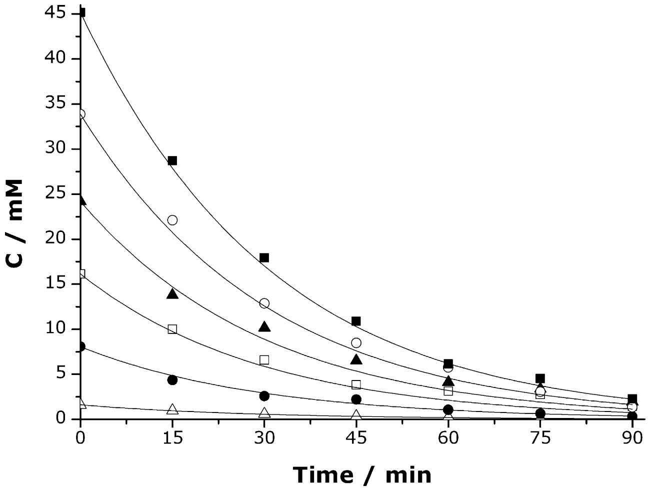


Fig. 7. Concentration decay of nitrate in (△) 1.5×10^{-3}, (●) 8×10^{-3}, (□) 15×10^{-3}, (▲) 25×10^{-3}, (○) 35×10^{-3} and (■) $45 \times 10^{-3}\ mol\ L^{-1}$. Ionic strength: 2 M. Potential: −2.8 V vs. Ag/AgCl.

3.4. *Influence of the concentration of nitrate on the hydrogen evolution*

It is known for many years that the amount of the evolved hydrogen during the electrolysis of concentrated solutions of nitric acid depends on the concentration of nitric acid as well as on the applied current density [72]. A similar dependence between the concentration of nitrate and the evolved hydrogen was also observed in our study as it can be seen in Fig. 9(a). Hydrogen was not detected in the outgoing gas stream from the electrolytic cell for 105 min at 1000 mM, for 30 min at 500 mM, while at 100 mM the hydrogen evolution started immediately at the beginning of the electrolysis. The form of the curve of hydrogen can be explained if it is assumed that the reduction of nitrate takes place through EH. At the begin-

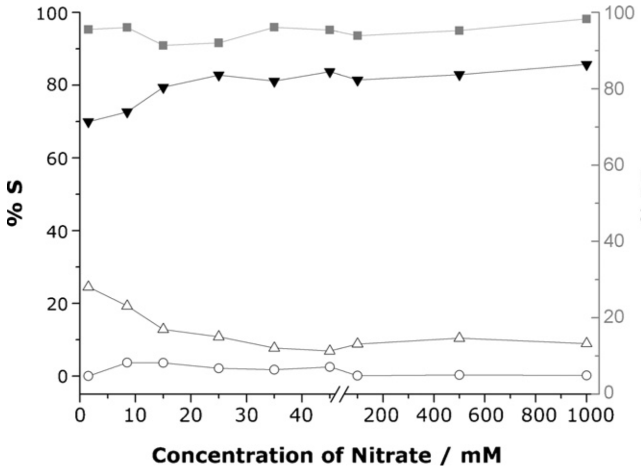


Fig. 8. Selectivity to (▼) nitrogen, (△) ammonia and (○) nitrite during the reduction of nitrate, as a function of the initial concentration of nitrate when 95% of the initial nitrate was removed. Ionic Strength: 2 M, potential: −2.8 V vs. Ag/AgCl.

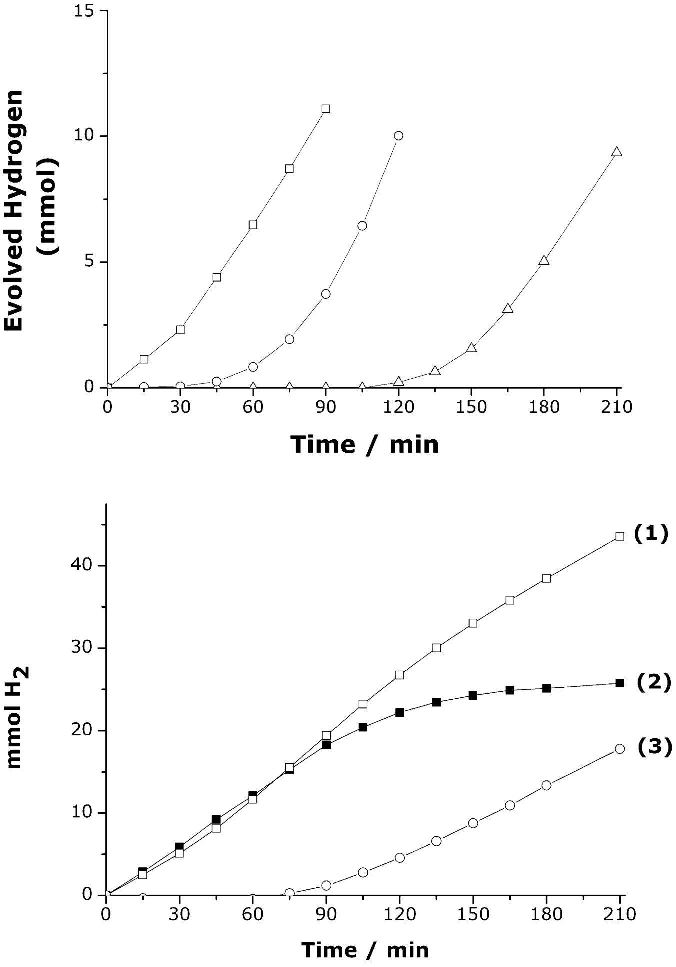


Fig. 9. (a) Evolved hydrogen vs. time during the reduction of x = (□) 0.1 M, (○) 0.5 M and (△) 1 M $NaNO_3$. Supporting electrolyte: x M $NaNO_3$ + (2 − x) M NaCl. Potential: −2.8 V vs. Ag/AgCl. (b) Curve (1): Theoretical amount of hydrogen if all the charge passed was consumed for the production of hydrogen. Curve (2): Required amount of hydrogen if all reactions took place through electrochemical hydrogenation. Curve (3): Difference between the curves (1) and (2) which shows the estimated amount of the evolved hydrogen. Supporting electrolyte: 1 M $NaNO_3$ + 1 M NaCl. Potential: −2.8 V vs. Ag/AgCl.

ning of the electrolysis, the concentration of nitrate is high enough so that the evolved hydrogen is totally consumed for the reduction of the nitrate and/or its intermediates. At longer electrolysis times, the concentration of nitrate is significantly lower and thus the produced hydrogen is partially consumed for the reduction of nitrate while the excess is released and is detectable in the gaseous stream.

Fig. 9(b) shows the amount of hydrogen that would be produced if the passed charge was totally consumed for the production of hydrogen (curve 1) and the required amount of hydrogen if all reactions (13)–(18) took place through EH (curve 2):

$$NO_3{}^- + H_2 \rightarrow NO_2{}^- + H_2O \tag{13}$$

$$NO_3{}^- + 2H_2 \rightarrow \tfrac{1}{2}H_2N_2O_2 + H_2O + OH^- \tag{14}$$

$$NO_3{}^- + 2H_2 \rightarrow \tfrac{1}{2}N_2O + \tfrac{3}{2}H_2O + OH^- \tag{15}$$

$$NO_3{}^- + \tfrac{5}{2}H_2 \rightarrow \tfrac{1}{2}N_2 + 2H_2O + OH^- \tag{16}$$

$$NO_3{}^- + 3H_2 \rightarrow NH_2OH + H_2O + OH^- \tag{17}$$

$$NO_3{}^- + 4H_2 \rightarrow NH_3 + 2H_2O + OH^- \tag{18}$$

The difference between the curves (1) and (2) represents the expected amount of the evolved hydrogen (curve 3). The curves (1) and (2) almost coincide up to 90 min, which is in agreement with the fact that hydrogen was not evolved at the first stages of electrolysis, whereas at electrolysis times longer than 90 min there is a difference between the two curves which corresponds to the evolved hydrogen. The fact that this curve is qualitatively similar to the experimentally taken in Fig. 9(a), leads to the conclusion that the produced hydrogen participates in the reaction mechanism, even though it is difficult to explicitly decide which steps of the reduction involve EH. Similar conclusions to that obtained in 1 M solution as regards the hydrogen evolution can be drawn at lower concentrations of nitrate which means that reduction takes place through EH in all the concentrations studied. The unusually high selectivity for nitrogen formation obtained in our experiments can be possibly related to the characteristically high selectivity of one product of the reactions which take place through EH [73].

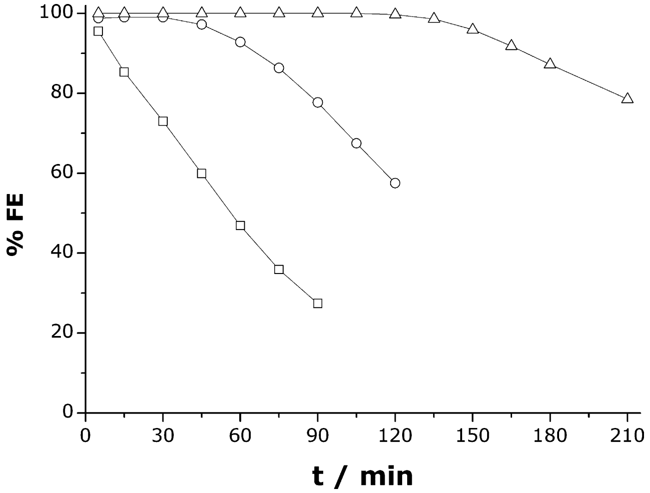


Fig. 10. % Faradaic Efficiency vs. time during the reduction of x = (□) 0.1 M, (○) 0.5 M and (△) 1 M $NaNO_3$. Supporting electrolyte: x M $NaNO_3$ + (2 − x) M NaCl. Potential: −2.8 V vs. Ag/AgCl.

The % Faradaic Efficiency (%FE) of the reduction of nitrate (Fig. 10) was calculated according to the equation:

$$\%FE = \frac{Q_{tot} - Q_{H_2}}{Q_{tot}} \times 100\% \tag{19}$$

where Q_{tot} is the total charge passed and Q_{H_2} is the charge consumed for the amount of hydrogen which was determined by Gas Chromatography. The %FE is about 100% in the first 120 min of electrolysis in 1 M of nitrate and then decreases to 78% at 210 min. On the other hand, the %FE decreases almost linearly in 100 mM of nitrate, reaching 25% after 90 min of electrolysis. The high %FE obtained when the concentration of nitrate was 1 M has a great importance for the treatment of nuclear wastes which contain about 1.8 M $NaNO_3$ and 0.55 M $NaNO_2$ [14], where the %FE is expected to be higher than 80%.

4. Discussion

The mechanism of the electrochemical reduction of nitrate is very complicated because nitrogen can form a large number of stable compounds and unstable intermediates during its transition from nitrate (+5) to ammonia (−3). Based on mechanisms proposed previously [28,30] the following reaction scheme (Scheme 1) can explain our experimental results.

The first step of this scheme is the conversion of nitrate to nitrite which proceeds through NO_2 formation as it has been proposed by other studies [27,74]. The further reduction of nitrite to nitroxyl (NOH) involves the intermediary formation of nitric oxide

[28,32] which, as it is well known, can be converted either electrochemically [75–78] or chemically by hydrogen [79] to the NOH radical. Thereafter, nitroxyl can either be reduced to form NH_2OH and NH_3 or dimerize rapidly with a second order rate constant in the range $2–8 \times 10^9\ M^{-1}\ s^{-1}$ [42] to give hyponitrous acid ($H_2N_2O_2$), which has been detected in our experiments. The hyponitrous acid is stable at moderate acidity as well as its dianion ($N_2O_2{}^{2-}$) but the monoanion ($HN_2O_2{}^{-}$) is unstable and decomposes in a pH-dependent mechanism to give N_2O [42].

$$HN_2O_2{}^- \rightarrow N_2O + OH^- \qquad (20)$$

An additional amount of N_2O can be formed through the reaction between hydroxylamine and nitrite (1). Nitrous oxide has a moderate solubility in water (~24 mmol L^{-1} [80]) and can be further reduced to N_2 [28,81]:

$$N_2O + H_2O + 2e^- \rightarrow N_2 + 2OH^- \qquad (21)$$

In order to examine whether hyponitrite is the main intermediate for the formation of nitrogen, a new experiment was performed at −2.8 V in 0.1 M NaOH + 0.05 M $Na_2N_2O_2$ solution, where hyponitrous dianion ($N_2O_2{}^{2-}$) is relatively stable ($k = 10^{-6}\ s^{-1}$) [44]. The reduction was followed by measuring the absorbance at 248 nm. The products were N_2O and N_2 in a ratio N_2O:N_2 of about 30:1. The ratio N_2O:N_2 during the reduction of nitrate was about 1:14, indicating that only a small part of nitrogen is produced through the reduction of N_2O and that there is an alternative path for the production of nitrogen. Moreover, neither ammonia nor hydroxylamine was detected, which implies that these compounds are not produced through electrochemical reduction of hyponitrite. This confirms that the monomer NOH is the precursor for their formation and not the dimmer hyponitrite [75,76].

Even though there are numerous works on the reduction of nitrate by various methods, e.g. chemical, biological, etc., the mechanism of the formation of nitrogen during the reduction of nitrate is not known yet. The presented experimental results are clearly not enough to give a sufficient explanation for the dominant way for the production of nitrogen. According to the literature the following reactions can lead to the formation of nitrogen [82,42,45,30]:

$$NH_2 + NO \rightarrow NH_2NO \rightarrow N_2 + H_2O \qquad (22)$$

$$NOH + NH_2OH \rightarrow N_2 + H_2O \qquad (23)$$

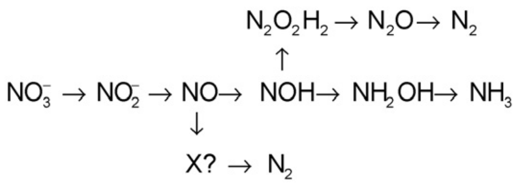
$$NO + 2H^+ + 2e^- \xrightarrow{-H_2O} N_{ads} \xrightarrow{+N_{ads}} N_2 \qquad (24)$$

In addition to the aforementioned reactions, other reactions between the detected compounds in the solution can also participate in the formation of nitrogen [83,82]:

$$H_2N_2O_2 + HNO_2 \rightarrow N_2 + NO_3{}^- + H^+ + H_2O \qquad (25)$$

$$NO_2{}^- + NH_4{}^+ \rightarrow N_2 + 2H_2O \qquad (26)$$

However, the rate of the reactions (25) and (26) is low at ambient conditions in comparison to the observed rate of nitrogen formation, so the reactions (25) and (26) cannot be considered as the dominant path. Based on the above, the reactions (22)–(24) seem to be the most probable paths for the formation of dinitrogen.



Scheme 1.

Furthermore, homogeneous reaction between Sn^{2+}, which is present in the catholyte due to the cathodic corrosion of tin [10], and nitrogen-containing species such as $NO_3{}^-$ [84,85] or NO [86] can play an important role in the overall mechanism. It should be noted that the weight loss of the tin cathode when the electrolysis was performed in 1 M solution for 210 min was 8 mg.

The above described experimental results showed that the evolved hydrogen participates in the reaction mechanism. Two mechanisms have been proposed for the hydrogen evolution reaction (HER) at high overvoltages; the classical Volmer–Tafel and the chemical one. The latter proceeds through the discharge of the cation of the supporting electrolyte as follows [87,88]:

$$Sn + Na^+ + e^- \rightarrow Sn(Na) \qquad (27)$$

$$Sn(Na) + H_2O \rightarrow Sn + Na^+ + \tfrac{1}{2}H_2 + OH^- \qquad (28)$$

The HER through cation discharge is favored in alkaline solutions, high overvoltages and high concentrations of supporting electrolyte. A detailed description of the HER on sp metals, such as Sn and Pb, through the cation discharge has been given by Kabanov and co-workers [89,90] who proved that the cation discharge starts at potentials even by 1.5 V more positive than the equilibrium potential of the alkali metal at room temperature. The formed intermetallic compound (e.g. Sn(Na)) can reduce a component of the solution such as water molecule, nitrate or nitrite by a chemical reaction. When the reduction takes place through the intermetallic compound the rate of the reaction has a linear dependence on the potential [89]. The experimental data presented in the Table 2 of a previous work [10] follow this condition, since the plot of the rate constant vs. *E* gives a linear dependence ($R^2 = 0.9825$), which is in agreement with the theory of the HER through cation discharge.

5. Conclusions

The influence of the initial concentration of nitrate on the rate of its reduction can be adequately described by a simple Langmuir–Hinshelwood kinetic model. The hydrogen evolution possibly takes place through the cation discharge instead of conventional Volmer–Tafel mechanism and the evolved hydrogen participates in the reaction mechanism. Hyponitrite and hydroxylamine were detected as intermediates of the reduction.

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