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Efficient electrochemical reduction of nitrate to nitrogen on tin cathode at very high cathodic potentials

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Abstract

The electrochemical reduction of nitrate on tin cathode at very high cathodic potentials was studied in 0.1 M K_2SO_4, 0.05 M KNO_3 electrolyte. A high rate of nitrate reduction (0.206 mmol min^{-1} cm^{-2}) and a high selectivity (%*S*) of nitrogen (92%) was obtained at −2.9 V versus Ag/AgCl. The main by-products were ammonia (8%) and nitrite (<0.02%). Small amounts of N_2O and traces of NO were also detected.

As the cathodic potential increases, the %*S* of nitrogen increases, while that of ammonia displays a maximum at −2.2 V. The %*S* of nitrite decreases from 65% at −1.8 V to <0.02% at −2.4 V. The kinetic analysis indicated that the formation of nitrogen and ammonia proceeds through the intermediate nitrite.

The reduction follows first order kinetics for both nitrate and nitrite at more cathodic potentials than −2.4 V, while at less negative potentials the kinetics is more complicated.

The %Faradaic efficiency (%FE) of the reduction at −2.9 V was about 60% initially and decreased to 22% at 40 min.

A cathodic corrosion of tin was observed, which was more intensive in the absence of nitrate. At potentials more negative than −2.4 V, small amounts of tin hydride were detected.

Keywords: Nitrate; Electrochemical; Reduction; Tin; Hydride; Nitrogen; Corrosion

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1. Introduction

Nitrate-containing wastes can cause eutrophication of lakes, rivers, bays and seas, while a high concentration of nitrate in drinking water can cause serious health problems in humans. The reduction of nitrate to nitrogen gas by other methods apart from the biological, which cannot be applied in all cases, is a challenge for the researchers in this field [1].

Electrochemical methods are ideal for removing nitrate ions from concentrated aqueous solutions, that come out from reverse osmosis, ion exchange membranes, neutralized nitric acid wastes, as well as for solutions that contain other toxic compounds, such as nuclear wastes, in which the biological method cannot be applied [2].

Numerous efforts have been made so far, concerning the electrochemical reduction of nitrate on various metallic electrodes [3–24] and graphite [5,6,25,26]. It was proved that the conversion of nitrate to the nontoxic nitrogen gas is difficult since it is one of the eight possible products, NO_2, NO_2^-, NO, N_2O, N_2, NH_2OH, NH_3 and NH_2NH_2. When the supporting electrolyte is basic or neutral, the main by-products are nitrite and ammonia; furthermore, in acid electrolyte hydroxylamine and hydrazine have been also detected [27]. Nitrogen gas was detected on various metals and alloys, such as Cd (70–75%) [28], Pd–Cu (50%) [7], Pb (22%) [4], Sn85–Cu15 (34%) [29], Pd–Sn–Au (34%) [30], Sn–Pt (37%) [31] and Pd–Rh (94%) [32].

According to Ferapontova and Fedorovich [33] the rate of the reduction of the anions of the second group (BrO_4^-, BrO_3^-, NO_3^-, IO_4^- and others) is controlled by the simultaneous transfer of the electron and a proton from a proton donor through the reaction: $A^{z_A} + HB^{z_D} + e^- \rightarrow HA^{z_A} + B^{z_D - 1}$ (where HA = H_2O, H_3O^+, NH_4^+ and z_i the charge). The rate of the reduction depends on the cathodic potential, the structure of the double layer and the nature of the proton donor. High reduction rates of the anions of the second group were achieved at metals of high overpotential for hydrogen evolution at high

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cathodic potentials. For example, efficient reduction of nitrate to nitrogen on Pb [12] was carried out at cathodic potentials more negative than -2 V, while that of bromate [34] up to -2 V versus SCE. Even though tin alloys were studied for the reduction of nitrate, in our knowledge, pure tin has not been studied at high cathodic potentials.

This work includes preliminary experimental results on the electrochemical reduction of nitrate on a tin cathode. Even though at high cathodic potentials, where the rate of hydrogen evolution is high, ammonia is the predominant product [4,27,29,32] the present work shows that at high cathodic potentials, unexpectedly, the main product on tin is nitrogen gas having both a high *%S* (92%) and a high rate of formation.

2. Experimental

A Teflon cell (Fig. 1) having a total volume of 24 mL was used in all experiments. A Nafion 117 (H^+ form) cation exchange membrane divided the cell into two equal volume compartments. The heat transfer from the cell was achieved by two aluminum plates (10 cm × 10 cm × 0.5 cm) and the experiments were performed at ambient temperature. The compartment of the catholyte had an extra volume of 2 mL on the top, in order to secure that the electrolyte covered the whole surface of the cathode, despite the volume removed due to the sampling. Moreover, the cell had an extra free electrolyte volume of 2 mL on the top, to prevent a blow-away of the electrolyte due to the Helium stream. The tightness of the cell was achieved by Viton O-Rings. The geometrical area of the cathode was 6 cm^2 and the anode was a platinized Pt foil (Alpha Metal) of equal area. The potential was controlled by a Wenking POS 73 (Bank Elektronik) potentiostat and the reference was a saturated Ag/AgCl electrode. The voltammograms were obtained under nitrogen atmosphere in a conventional H type glass cell, using a tin foil having an apparent geometrical area of 0.2 cm^2, which was fitted in a Teflon tube. All chemicals were reagent grade (Aldrich) and the solutions were prepared using ultra pure water from a Sation 9000 apparatus.

The tin foil (Sigma–Aldrich 99.9%) was polished with abrasive grade 600-mesh paper and washed quickly with ultra pure water, before using it for the first time.

The composition of the catholyte was 0.1 M K_2SO_4 and 0.05 M KNO_3, unless otherwise stated.

2.1. Analytical methods

At specific time intervals, samples of 0.1 mL were withdrawn from the catholyte by a chromatography syringe and were analyzed, after the appropriate dilution. The determination of nitrate and nitrite was performed by both standard colorimetric methods [35] and ion chromatography (Dionex 4500i, AS9-HC column). The determination of ammonia was performed by fluorometry after its on-line derivatization with o-phthalaldehyde [36]. The possible formation of hydrazine and hydroxylamine was investigated by colorimetric methods [37,38].

In the steady-state electrolytic experiments the solution was degassed for about 30 min before applying the voltage by a stream of He having a constant flow rate of 15 mL min^{-1}. Moreover, the He stream withdrew the gaseous products from the cell during the electrolysis. No significant volume loss was observed in the catholyte due to the helium stream. The analysis of nitrogen and hydrogen was carried out by GC, using a molecular sieve 5 A column 1.8 m, 0.3175 cm i.d., and a thermal conductivity detector (TCD), at a constant temperature of 80 °C. The total volume of the produced nitrogen was calculated by the equation: $V_t = \int C_p R \, dt$, where V_t is the total volume of the produced nitrogen, C_p the point concentration of nitrogen in the gas stream and R is the flow rate of He.

In selected experiments, the gaseous products of the electrolysis were collected into a sampling bag and the nitrogen oxides (NO, NO_2 and N_2O) were analyzed by an Agilent Technologies GC–MS.

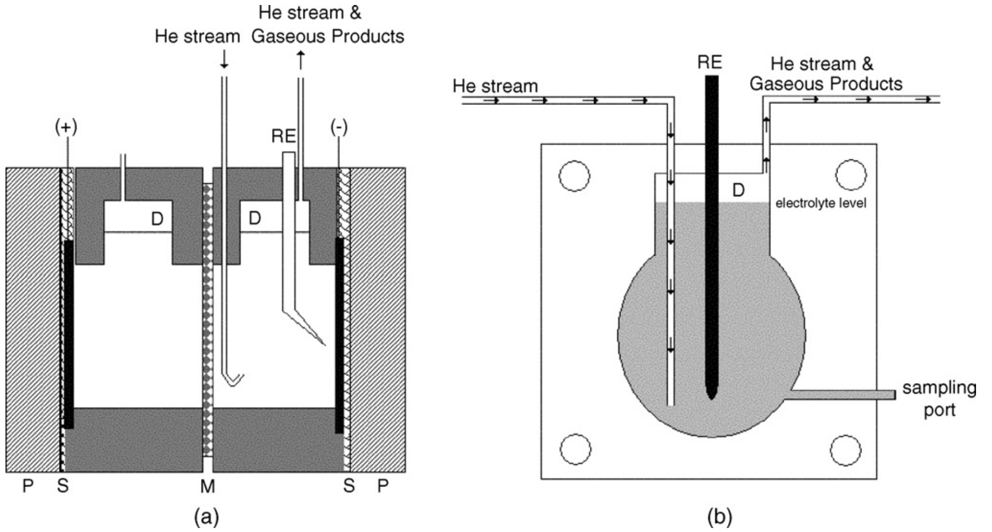

Fig. 1. (a and b) The electrolysis cell: (P) aluminum plates, (S) silicone gasket, (M) nafion membrane, (D) dead volume, (RE) reference electrode. The distance between the Luggin capillary and the cathode was about 1 mm.

The amount of ammonia which is presented in the experimental results is the sum of three parts: the catholyte, the anolyte as well as the ammonia which was trapped by bubbling of the outgoing gas stream in a solution of 1N H_2SO_4 [29]. It should be mentioned that up to 30% of the produced ammonia escaped from the catholyte due to the He stream.

The %removal efficiency (%RE) of nitrate and the %selectivity (%*S*) of the products were calculated by the equations:

$$\%\mathrm{RE} = \frac{n_\mathrm{o} - n}{n_\mathrm{o}} 100\%$$

$$\%S_i = p\frac{n_i}{n_\mathrm{o} - n} 100\%$$

where n_o is the initial mols of nitrate; n is the remaining mols of nitrate; n_i is the produced mols of compound i; p is mols of nitrate needed for the formation of 1 mol of compound i ($p = 1$ for nitrite, ammonia and $p = 2$ for nitrogen).

3. Results

Fig. 2 shows the cyclic voltammograms obtained for the reduction of nitrate and nitrite. In both cases a reversible peak was observed at −1.2 and −1.15 V. This peak was not observed in the voltammogram of the supporting electrolyte at 50 mV/s, but it was observable at scan rates higher than 100 mV/s. The peak was attributed to the oxidation/reduction of Sn^{2+} to Sn^{4+} (SnO_2 and/or $Sn(OH)_4$) species [39–41]. The increase of the peak current in the presence of nitrate and nitrite was attributed to the increased corrosion of tin, because they can be reduced, facilitating the cathodic reaction [41]. Moreover, an increase in the current density (cd) from −1.4 V in the case of nitrite and from −1.65 V in the case of nitrate was observed and it is remarkable that the cd of nitrite reduction is much higher than that of nitrate at any potential. The more negative potential required for the reduction of nitrate was attributed to the resonance structure of nitrate, which makes it more stable than nitrite.

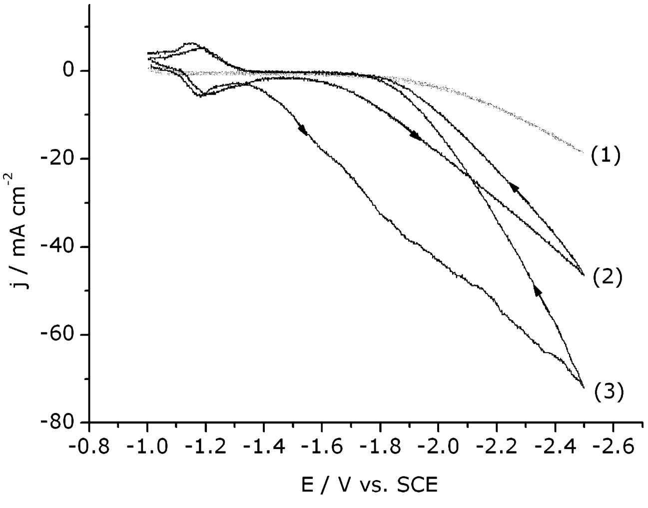

Fig. 2. Cyclic voltammograms in (1) 0.1 M K_2SO_4, (2) 0.1 M K_2SO_4/0.05 M KNO_3 and (3) 0.1 M K_2SO_4/0.05 M KNO_2 electrolyte, at a scan rate of 50 mV s^{-1}.

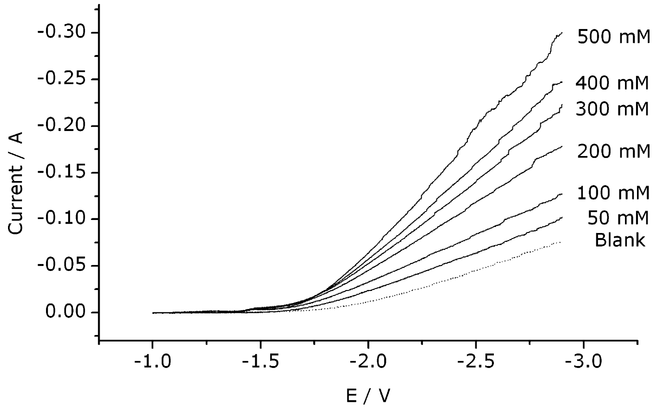

Fig. 3. Slow-sweep voltammograms at a scan rate of 5 mV s^{-1} of solutions containing various concentrations of nitrate in 0.1 M K_2SO_4.

Slow-sweep voltammograms with a 5 mV/s scan rate between −1.0 and −2.9 V were taken to determine the electrokinetic behaviour of nitrate. On the potential sweep in the negative direction the current increases gradually from −1.6 V and this increase depends on the concentration of nitrate (Fig. 3). The current density depends on both the potential and the concentration of nitrate and that implies that the reaction is not diffusion-controlled, which is in accordance with the results of the steady-state electrolytic experiments. From the slope of the diagram of log *j* versus log *C* (Fig. 4) the reaction order was calculated to be 0.63, 0.78, 0.91 and 0.93 at −2.0, −2.3, −2.7 and −2.9 V, respectively. A fractional reaction order was reported previously by other workers on Pt–Pd–Ge [22], Pd–Sn–Au [30] and Cu–Tl [42] and it was explained assuming a Temkin adsorption [5,27]. Recently, Casella and Contursi [43] reported a value of 1.25 for the reaction order on Pd–Sn in acid medium.

3.1. Constant potential electrolysis

The reproducibility of the batch electrolytic experiments was tested by carrying out several experiments at −2.9 V under the same conditions. An increase in the apparent rate constant of the nitrate reduction from 0.052 to 0.102 min^{-1} was observed by using the same electrode for three consecutive experiments

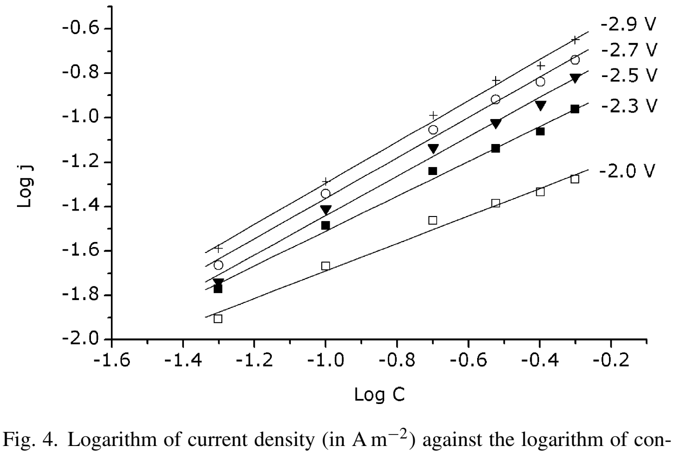

Fig. 4. Logarithm of current density (in A m^{-2}) against the logarithm of concentration (in mol L^{-1}) at various cathodic potentials.

Table 1
%RE of nitrate and %*S* of the products in three different experiments under the same conditions

Experiment	NO_3^- (%RE)	NO_2^- (%*S*)	NH_3 (%*S*)	N_2 (%*S*)	Apparent rate constant (min^{-1})
First	99.48	0.86	8.62	85.54	0.052
Second	99.28	<0.02	9.11	86.01	0.077
Third	99.78	<0.02	8.10	91.75	0.102
Final	99.64	<0.02	7.6	93.80	0.104

Potential −2.9 V vs. Ag/AgCl, electrolyte 0.1 M K_2SO_4/0.05 M KNO_3 and electrolysis time 2.5 h.

and it remained constant within the experimental error, when more experiments were performed (Table 1). The apparent rate constant was calculated assuming first order kinetics for the reduction of nitrate at this potential, as it was approximately estimated from Fig. 4 and confirmed by the electrolytic experiments. An experiment (final experiment in Table 1), which was performed by an electrode that had been previously used for the reduction of nitrate at all potentials mentioned in the following text, indicated no significant differences, as regards the rate and the %*S* of the products, in comparison to that of the third experiment. The reduction of nitrate took place rapidly and the %RE was more than 99% in all experiments performed at −2.9 V. An increase by a factor of 1.5 was also observed in the total electrolysis current between the first and the third experiment. The simultaneous increase in both the reaction rate and the electrolysis current was attributed to the increase of the specific area of the electrode, which was visible to the naked eye. Furthermore, the electrode surface darkened and lost its metallic lustre, while small particles of tin appeared in the catholyte. Fig. 5(a and b) shows the SEM photographs of (a) an unused and (b) an extensively used tin electrode. The great harshness of the surface of the used electrode compared with the smooth surface of the unused, leads to an increase of its specific area.

According to the Pourbaix diagram [44] at high cathodic potentials, tin can be converted to gaseous SnH_4 through the reaction: $Sn + 4H^+ + 4e^- \rightarrow SnH_4$. The equilibrium potential at pH = 0 is −1.074 V versus NHE. The potential depends upon the pH and the logarithm of the partial pressure of SnH_4, according to the Nernst equation:

$$E_0 = -1.074 - 0.059\mathrm{pH} - 0.0148\ \log p\mathrm{SnH_4}\ \text{versus NHE}$$

At pH > 7, the potential is calculated to be more negative than −1.487 V versus NHE or −1.709 V versus Ag/AgCl, assuming that the influence of the term $\log p\mathrm{SnH_4}$ is negligible. Given that our experiments were performed at much higher cathodic potentials, the formation of SnH_4 is possible. There are many references on the formation of tin hydride on various cathodes [45,46], but its formation on tin cathode was doubtable up to 1977 [47], since there was only one reference [48] where the cathodic corrosion of tin was attributed to the formation of SnH_4. Later studies speculated the possible formation of SnH_4 [49,50].

In order to investigate the observed cathodic corrosion of tin, some experiments were performed under conditions corresponding to that of the batch electrolysis; the electrode was left at open circuit conditions for 30 min (as it happens during degassing by the He) and afterwards a potential of −2.9 V was applied to the cell for 150 min. The gaseous products of the cell were passed through a glass tube containing 15 mL of 0.01 M silver nitrate solution, which is a trapping agent of tin hydride [48,51]. At specific time intervals, samples were withdrawn from the catholyte and were analyzed by atomic absorption in a graphite furnace. The analysis of the trapping solution after electrolysis for 180 min indicated that the concentration of tin in the presence of nitrate was 3.5 ppm, while in the absence of nitrate 4.5 ppm. It is worth to mention that tin was not detected in the trapping solution when the electrolysis was carried out at potentials less negative than −2.4 V. The presence of tin in the trapping solution is a strong indication that the formation of gaseous tin hydride takes place at potentials more negative than −2.4 V, contributing to the corrosion of tin, to a small extent.

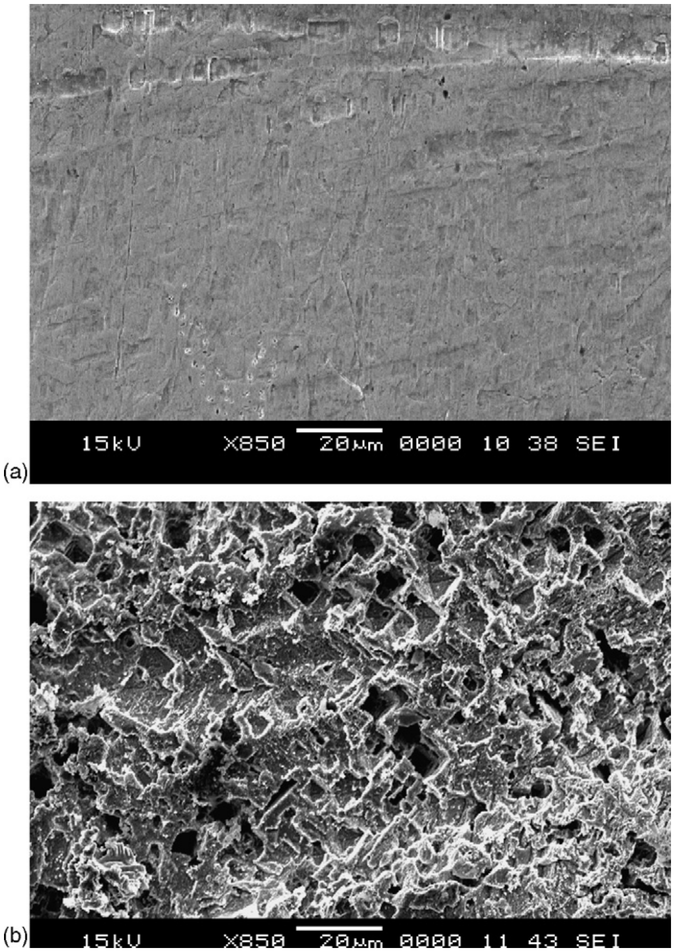

Fig. 5. SEM photograph of (a) an unused and (b) an extensively used for electrolysis tin cathode.

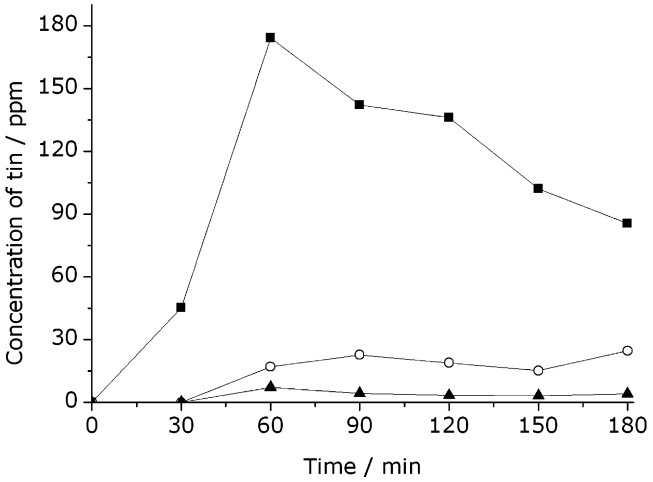

Fig. 6. Concentration of tin in the catholyte vs. time in (■) 0.1 M K_2SO_4, (○) 0.1 M K_2SO_4/0.05 M KNO_3 and (▲) 0.1 M K_2SO_4/0.05 M KNO_3 + 5 × 10^{-4} M $(NH_4)_2SO_4$ at −2.9 V vs. Ag/AgCl.

Fig. 6 shows that the concentration of tin versus time in the catholyte reaches a maximum after 60 min and afterwards it remains approximately constant, when the solution contains nitrate. A significantly higher concentration of tin was detected in the absence of nitrate, which was gradually decreased from 180 ppm at 60 min to 100 ppm at 180 min. It should be noted that, in this case, the concentration of tin in the trapping solution was also higher, as it is noticed above. The decreased corrosion of tin in the presence of nitrate was attributed to the decreased coverage of the surface of the tin cathode by adsorbed hydrogen due to the co-adsorption of nitrate.

Three different explanations have been given so far for the cathodic disintegration of tin: (a) formation of tin hydrides (SnH_2 and SnH_4). According to Salzberg and Mies [48], tin under cathodic polarization forms initially SnH_2, which is unstable and decomposes to metallic tin and SnH_4 via a disproportionation reaction: $2SnH_2 \rightarrow Sn + SnH_4$. The rate of disintegration is inversely proportional to the concentration of the supporting electrolyte and depends also on the nature of the cation in the order $Na^+ > K^+ > Li^+ \gg NH_4^+$. (b) Cathodic incorporation of alkali metals [52–56], which usually occurs at potentials by 1.4 V more positive than the potential of the deposition of each alkali metal and leads to the formation of intermetallic compounds between the tin cathode and the metal. The hydrogen evolution takes place via the discharge of alkali–metal after its chemical reaction with water, as follows [56]:

$$K(Sn) + H_2O \rightarrow Sn + H_{ads} + K^+ + OH^-$$

The change of the mechanism of the conventional hydrogen evolution reaction, leads to an increase of the overpotential of hydrogen by about 0.25 V. According to this hypothesis the rate of disintegration is expected to be proportional to the concentration of the supporting electrolyte. The latter is in contradiction with the first assumption of hydride formation. (c) Tin under cathodic polarization gives tin polyanions of the type $Sn_9{}^{4-}$, which consequently react with the surrounded water molecules to give hydrogen gas or hydrides and metallic tin [57]. The assumptions (a) and (c) are not in contradiction since the final result is the formation of tin hydrides and metallic tin.

According to Salzberg and Mies [48] a small concentration of ammonium in the catholyte limits the corrosion of tin. After that we performed an experiment in 0.1 M K_2SO_4, 0.05 M KNO_3 and 5 × 10^{-4} M $(NH_4)_2SO_4$. The experimental results showed that the concentration of tin in the catholyte was by 20 times lower than that without ammonium, as it is depicted in Fig. 6.

Since the specific area of the tin electrode that was used for the first time, is continuously increased during the electrolysis, we preferred to perform all the reported experiments in the following text using a tin cathode which had been already used for the reduction of nitrate (50 mM) at −2.9 V for three consecutive experiments. In this case, as we pointed out, the roughness factor of the electrode remains almost constant, even though the corrosion of tin is still taking place.

3.2. Reaction kinetics and influence of the potential

The concentration profile of nitrate versus time (Fig. 7) revealed that the reaction follows first order kinetics at −2.5 V, since the graph of the logarithm C/Co versus time (not depicted here), which is characteristic for first order reaction kinetics, is linear, with a correlation coefficient $R^2 = 0.975$. On the other hand, at −1.8 V more complicated kinetics is involved, which is in agreement with the slow-sweeping rate voltammetric measurements (Fig. 4). Moreover, when the electrolysis was performed at −2.5 V in the presence of 25 mM KNO_2 the apparent rate constant was 0.059 min^{-1}, while in the absence of nitrite was 0.061 min^{-1}, which denotes that the reduction of nitrate is not inhibited in the presence of nitrite, under these conditions.

The variation of the concentrations of the initial nitrate and the main products of electrolysis versus time is depicted in Fig. 8. The concentration of nitrite displays a maximum at 10 min, which is an indication that it is an intermediate product of a consecutive reactions mechanism, as it is previously proposed by other workers [4,29]. The concentrations of N_2 and NH_3 display

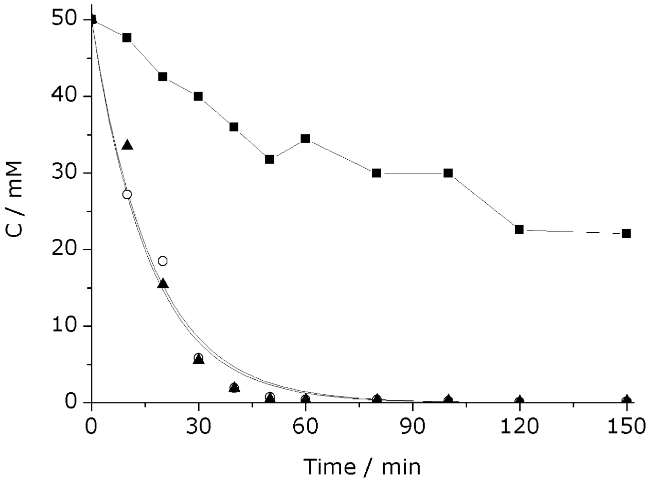

Fig. 7. Concentration profile of nitrate vs. time at: (■) −1.8 V in 0.1 M K_2SO_4/0.05 M KNO_3, (○) at −2.5 V in 0.1 M K_2SO_4/0.05 M KNO_3 and (▲) at −2.5 V in 0.1 M K_2SO_4/0.05 M KNO_3 + 0.025 M KNO_2.

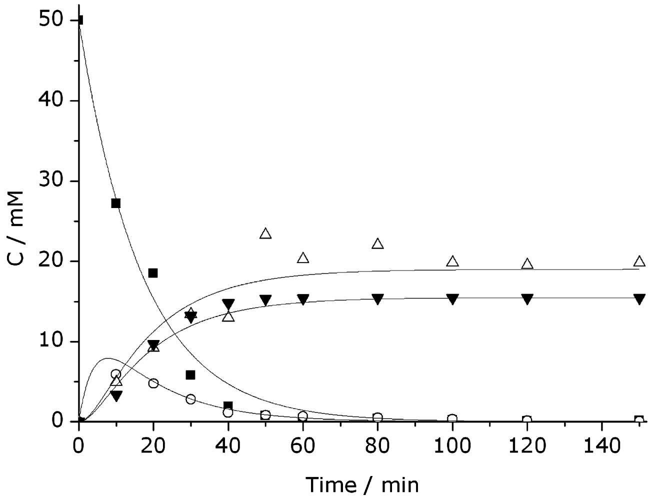

Fig. 8. Variation of the concentration of (■) nitrate, (○) nitrite, (△) ammonia and (▼) nitrogen vs. electrolysis time at −2.5 V. Electrolyte 0.1 M K_2SO_4/0.05 M KNO_3. The lines were drawn by non-linear regression based on the proposed model.

a sigmoidal form, which is characteristic for the final product of the above mentioned mechanism. The rate of production of both products increases simultaneously and this implies that these species are produced through a common intermediate. It should be noted that hydroxylamine and hydrazine were not detected, but the GC–MS analysis of the gaseous products indicated small amounts of N_2O and traces of NO.

In order to verify that nitrite is an intermediate for the formation of the final products, the reduction of 0.05 M KNO_2 was carried out at −2.5 V. The reduction of nitrite displays the same characteristics as those obtained for nitrate, since the main products were ammonia and nitrogen. The reduction follows first order kinetics, as in the case of nitrate.

According to the above, a consecutive reaction mechanism can describe the experimental results on tin at potentials more negative than −2.5 V, including first order kinetics for both nitrate and nitrite, as follows:

$$\mathrm{NO_3}^- \xrightarrow{k_1} \mathrm{NO_2^-}$$

$$\mathrm{NO_2}^- \xrightarrow{k_2} \mathrm{NH_3}$$

$$2\mathrm{NO_2}^- \xrightarrow{k_3} \mathrm{N_2}$$

Scott [58] published a paper describing the behaviour of some electrochemical reaction schemes, where the thermodynamics, the kinetics as well as the mass transfer were taken into account. Scott calculated the mathematical expressions for three cases:

(a) Redox reaction:

$$\mathrm{A} + n_1\mathrm{e} \underset{k_{\mathrm{b1}}}{\overset{k_{\mathrm{f1}}}{\rightleftharpoons}} \mathrm{B}$$

(b) Two redox reactions in series:

$$\mathrm{A} + n_1\mathrm{e} \underset{k_{\mathrm{b1}}}{\overset{k_{\mathrm{f1}}}{\rightleftharpoons}} \mathrm{B} + n_2\mathrm{e} \underset{k_{\mathrm{b2}}}{\overset{k_{\mathrm{f2}}}{\rightleftharpoons}} \mathrm{E}$$

(c) Two parallel redox reactions:

$$\mathrm{A} + n_1\mathrm{e} \underset{k_{\mathrm{b1}}}{\overset{k_{\mathrm{f1}}}{\rightleftharpoons}} \mathrm{B}, \quad \mathrm{A} + n_2\mathrm{e} \underset{k_{\mathrm{b2}}}{\overset{k_{\mathrm{f2}}}{\rightleftharpoons}} \mathrm{R}$$

In the case of nitrate reduction, the mechanism is a combination of the above mentioned systems.

The reduction of nitrate to nitrite can be described by the scheme (a), namely:

$$\mathrm{NO_3}^- + n_1\mathrm{e} \underset{k_{\mathrm{b1}}}{\overset{k_{\mathrm{f1}}}{\rightleftharpoons}} \mathrm{NO_2}^-$$

Since the reactions take place at high negative potentials, the term k_{b1}, which is the rate constant for the oxidation of nitrite to nitrate, is negligible.

Assuming first order kinetics, the reaction rate can be expressed as:

$$i_1 = n_1 F k_{\mathrm{f1}} C^{\mathrm{s}}_{\mathrm{NO_3}^-} \tag{1}$$

where the rate constant k_{f1} can be defined as an exponential function of the cathodic potential, and $C^{\mathrm{s}}_{\mathrm{NO_3}^-}$ is the surface concentration of nitrate.

By taking into account the mass transfer, the current for the transport of nitrate from the bulk to the surface is:

$$i_1 = n_1 F k_{\mathrm{L,NO_3}^-}[C^{\mathrm{b}}_{\mathrm{NO_3}^-} - C^{\mathrm{s}}_{\mathrm{NO_3}^-}] \tag{2}$$

where $k_{\mathrm{L,NO_3}^-}$ is the mass transfer coefficient for nitrate and $C^{\mathrm{b}}_{\mathrm{NO_3}^-}$ the concentration of nitrate in the bulk solution.

The surface concentration $C^{\mathrm{s}}_{\mathrm{NO_3}^-}$ can be eliminated, by combining Eqs. (1) and (2), so the final expression for the partial current density of the reduction of nitrate to nitrite is:

$$i_1 = \frac{n_1 F k_{\mathrm{f1}}}{1 + (k_{\mathrm{f1}}/k_{\mathrm{L,NO_3}^-})}[\mathrm{NO_3}^-] \tag{3}$$

The reduction of nitrite to either nitrogen or ammonia is described by Scott's scheme (c) as "Two parallel redox reactions".

$$\mathrm{NO_2}^- \xrightarrow{k_{\mathrm{f2}}} \mathrm{NH_3}$$

$$2\mathrm{NO_2}^- \xrightarrow{k_{\mathrm{f3}}} \mathrm{N_2}$$

The rate constants k_{b} given by Scott for the backward reactions were also assumed to be negligible.

In terms of kinetics and mass transfer parameters, the expressions for the partial current densities of the ammonia and nitrogen are:

$$i_2 = n_2 F k_{\mathrm{f2}} C^{\mathrm{s}}_{\mathrm{NO_2}^-} \tag{4}$$

$$i_3 = \frac{1}{2} n_3 F k_{\mathrm{f3}} C^{\mathrm{s}}_{\mathrm{NO_2}^-} \tag{5}$$

$$\frac{i_2}{n_2 F} + \frac{i_3}{n_3 F} = k_{\mathrm{L,NO_2}^-}(C^{\mathrm{b}}_{\mathrm{NO_2}^-} - C^{\mathrm{s}}_{\mathrm{NO_2}^-}) \tag{6}$$

where $k_{\mathrm{L,NO_2}^-}$ is the mass transfer coefficient for nitrite and $C^{\mathrm{b}}_{\mathrm{NO_2}^-}$ and $C^{\mathrm{s}}_{\mathrm{NO_2}^-}$ are the concentrations of nitrite in the bulk and on the surface, respectively.

The surface concentration of nitrite $C^{s}_{NO_2^-}$ can be eliminated, by combining Eqs. (4)–(6), so the expressions for the partial current densities can be written as:

$$i_2 = n_2 F \frac{(k_{f2}/X k_{L,NO_2^-})[k_{L,NO_2^-} - (k_{f3}/Y)]}{[1 - (k_{f2}k_{f3}/k^2_{L,NO_2^-})]XY}[NO_2^-] \tag{7}$$

$$i_3 = \frac{1}{2} n_3 F \frac{k_{f3}/Y}{[1 - (k_{f2}k_{f3}/k^2_{L,NO_2^-})]XY}[NO_2^-] \tag{8}$$

where:

$$X = 1 + \frac{k_{f2}}{k_{L,NO_2^-}}, \qquad Y = 1 + \frac{k_{f3}}{k_{L,NO_2^-}}$$

If the partial current densities of Eqs. (3), (7) and (8) are expressed in terms of reaction rate, the differential equations are:

$$\frac{d[NO_3^-]}{dt} = -\frac{k_{f1}}{1 + (k_{f1}/k_{L,NO_3^-})}[NO_3^-]$$

$$\begin{aligned}\frac{d[NO_2^-]}{dt} &= +\frac{k_{f1}}{1 + (k_{f1}/k_{L,NO_3^-})}[NO_3^-] \\ &\quad - \frac{(k_{f2}/X k_{L,NO_2^-})[k_{L,NO_2^-} - (k_{f3}/Y)]}{[1 - (k_{f2}k_{f3}/k^2_{L,NO_2^-})]XY}[NO_2^-] \\ &\quad - \frac{k_{f3}/Y}{[1 - (k_{f2}k_{f3}/k^2_{L,NO_2^-})]XY}[NO_2^-]\end{aligned}$$

$$\frac{d[NH_3]}{dt} = +\frac{[k_{f2}/(X k_{L,NO_2^-})][k_{L,NO_2^-} - (k_{f3}/Y)]}{[1 - (k_{f2}k_{f3}/k^2_{L,NO_2^-})]XY}[NO_2^-]$$

$$\frac{d[N_2]}{dt} = +\frac{1}{2}\frac{k_{f3}/Y}{[1 - (k_{f2}k_{f3}/k^2_{L,NO_2^-})]XY}[NO_2^-]$$

The terms before the concentrations are constant and they can be represented as apparent rate constants, namely:

$$k_1 = \frac{k_{f1}}{1 + (k_{f1}/k_{L,NO_3^-})}$$

$$k_2 = \frac{(k_{f2}/X k_{L,NO_2^-})[k_{L,NO_2^-} - (k_{f3}/Y)]}{[1 - (k_{f2}k_{f3}/k^2_{L,NO_2^-})]XY}$$

$$k_3 = \frac{k_{f3}/Y}{[1 - (k_{f2}k_{f3}/k^2_{L,NO_2^-})]XY}$$

Finally, the differential equations are:

$$\begin{aligned}\frac{d[NO_3^-]}{dt} &= -k_1[NO_3^-] \\ \frac{d[NO_2^-]}{dt} &= +k_1[NO_3^-] - k_2[NO_2^-] - k_3[NO_2^-] \\ \frac{d[NH_3]}{dt} &= +k_2[NO_2^-] \\ \frac{d[N_2]}{dt} &= +\frac{1}{2}k_3[NO_2^-]\end{aligned}$$

The solutions of the differential equations using Laplace transforms give the concentrations versus time:

$$\begin{aligned}[NO_3^-] &= [NO_3^-]_{initial}\, e^{-k_1 t} \\ [NO_2^-] &= k_1[NO_3^-]_{initial}\frac{e^{-(k_2+k_3)t} - e^{-k_1 t}}{k_1 - k_2 - k_3} \\ [NH_3] &= k_2 k_1[NO_3^-]_{initial}\frac{1}{k_1(k_2+k_3)}\left[1 + \frac{k_1\, e^{-(k_2+k_3)t} - (k_2+k_3)\, e^{-k_1 t}}{k_2 + k_3 - k_1}\right] \\ [N_2] &= \frac{1}{2}k_3 k_1[NO_3^-]_{initial}\frac{1}{k_1(k_2+k_3)}\left[1 + \frac{k_1\, e^{-(k_2+k_3)t} - (k_2+k_3)\, e^{-k_1 t}}{k_2 + k_3 - k_1}\right]\end{aligned}$$

The non-linear regression of the experimental results according to the above equations gives $k_1 = 0.059\ \mathrm{min}^{-1}$, $k_2 = 0.089\ \mathrm{min}^{-1}$ and $k_3 = 0.145\ \mathrm{min}^{-1}$, at −2.5 V. The obtained values from the proposed model fit well to the experimental data, as it is shown in Fig. 8, where the curves depict the predictions of the model.

The apparent rate constant k_1 increases as the potential becomes more negative even at very high cathodic values, as it is shown in Table 2, which verifies that the reduction of nitrate to nitrite is not limited by the mass transfer, which is in accordance with the voltammetric curves (Fig. 2).

Fig. 9 shows the %FE versus time at three different potentials. The %FE was calculated assuming 2, 8 and 10 electrons for the formation of nitrite, ammonia and nitrogen, respectively. At the first stages of electrolysis, the %FE is high in all cases (60–75%) and consequently decreases. The %FE at 40 min, where the %RE of nitrate is 99% at −2.9 V, is 22%. The decrease of the %FE, as the concentration of nitrate decreases, leads to a corresponding increase in the %FE of hydrogen, which was also confirmed by the GC analysis of the hydrogen in the outgoing gas stream. The low rate of hydrogen evolution at the first electrolysis steps, where the concentration of nitrate is high, leads to the conclusion that the evolution of hydrogen on tin cathode is strongly inhibited in the presence of nitrate.

Table 2
Apparent rate constant of the reduction of nitrate vs. potential

Potential (V)	Apparent rate constant (min^{-1})
−2.3	0.0335
−2.4	0.0532
−2.5	0.0614
−2.7	0.0787
−2.9	0.1041

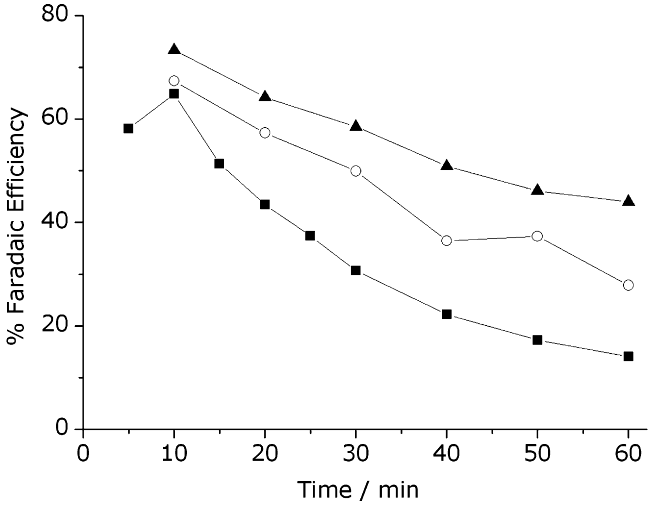

Fig. 9. %Faradaic efficiency of the reduction of nitrate against electrolysis time at (▲) −1.8 V, (○) −2.5 V and (■) −2.9 V. Electrolyte 0.1 M K_2SO_4/0.05 M KNO_3.

The influence of the cathodic potential on the product distribution and the %RE of nitrate is shown in Fig. 10. The %RE increases gradually and converges at 100% at more cathodic potentials than −2.5 V. The %*S* of nitrogen displays an almost linear increase between −1.8 V (15%) and −2.9 V (91.8%), while that of ammonia, after a maximum at −2.2 V (63.9%), decreases to 8.1% at −2.9 V. The form of the curve of ammonia is unexpected, since, as it is well known from previous works [4,27,29,32] the formation of ammonia, which is a hydrogenated product of the nitrate reduction, is favoured at high cathodic potentials. At potentials more negative than −2.4 V the sum of the %*S* of ammonia and nitrogen remains constant within the experimental error and this is an additional indication that nitrogen and ammonia are produced through a common intermediate. The %*S* of nitrite decreases from 65% at −1.8 V to almost 0.5% at −2.4 V and then converges at <0.02% at −2.9 V. However, when the reduction of nitrate takes place in an unbuffered electrolyte at current densities up to 120 mA cm^{-2} (at −2.9 V) a significant increase in the pH in the vicinity of the cathode is expected. In addition, an increase in the temperature of about 10 °C was observed in the cell due to the high current.

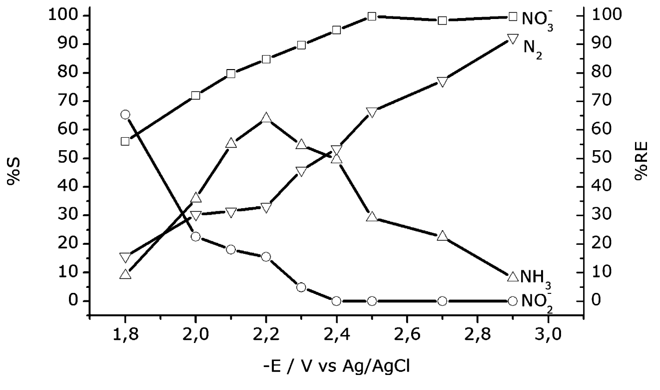

Fig. 10. Influence of the cathodic potential on the distribution of the main products of the reduction of nitrate. The electrolyte was 0.1 M K_2SO_4/0.05 M KNO_3 and the electrolysis time was 2.5 h.

In order to clarify the influence of the change of the temperature and the pH, two additional experiments were performed (at −2.9 V), using an electrode having an area of 2 cm^2 instead of 6 cm^2 (in order to have a lower total current) and the cell was placed in a thermostated water bath at 25 °C. In the first experiment, the supporting electrolyte was 0.1 M K_2SO_4 + 0.05 M KNO_3 and in the second, a buffer containing 0.1 M $KHCO_3$ and 0.1 M K_2CO_3 + 0.05 M KNO_3. No significant differences were observed between the two experiments, within the experimental error, since the %RE of nitrate was 95.9% in the unbuffered and 97.1% in the buffer, while the %*S* of NH_3, N_2 and NO_2^- were 7.0, 86.9 and 0.5% in the first experiment and 10.5, 84.9 and 0.36% in the second, respectively. These findings are reasonable since in both cases, in this pH region, the water molecule is the proton donor [33].

4. Discussion

The mechanism of the nitrate reduction is complicated, because of its multi-electron nature and the presence of a large number of intermediates. The presented data are insufficient to obtain the detailed mechanism of the reduction. At this point, we shall summarize the main experimental findings which are useful for the further discussion: (a) the reduction of both nitrate and nitrite at high negative potentials, follows first order kinetics, (b) the hydrogen evolution on tin is inhibited in the presence of nitrate as it is concluded from Fig. 9, (c) at cathodic potentials more negative than −2.4 V tin is converted to tin hydride to a small extent, (d) ammonia and nitrogen are produced through a common intermediate and (e) at potentials between −2.0 and −2.2 V ammonia is the main product, while at more negative potentials the %*S* of ammonia decreases and that of nitrogen displays a corresponding increase.

Based on the fact that the reduction follows first order kinetics for both nitrate and nitrite, a second intermediate must be involved, which is the precursor of ammonia and nitrogen formation. This intermediate is probably the adsorbed nitrogen monoxide, which was detected in our experiments and it has been already proposed by other authors [7,22,59] so the reaction scheme can be the following:

$$NO_3^- \rightarrow NO_2^- \rightarrow [NO]$$

$$2[NO] \rightarrow N_2$$

$$[NO] + 5[H] \rightarrow NH_3 + H_2O$$

$$Sn + 4[H] \rightarrow SnH_4$$

According to the scheme, nitrogen and ammonia are formed through the surface adsorbed [NO]. At potentials between −1.8 and −2.2 V the %*S* of ammonia increases as a result of the increase in the surface concentration of [H] since ammonia is a hydrogenated product. At more negative potentials the surface concentration of [H] is limited due to the formation of the hydrides of tin (SnH_2 and SnH_4) [48], leading to an increase in the %*S* of nitrogen.

If the incorporation of potassium into the tin cathode is assumed, we can arrive at similar conclusions, since the incorporation also limits the hydrogen evolution reaction [54], leading to a decreased %S of ammonia. Moreover, the fact that nitrogen was not produced in 0.1 M NH_4Cl + 0.05 M NH_4NO_3 or in 0.1 M $(NH_4)_2CO_3$ + 0.05 M NH_4NO_3 electrolyte at −2.9 V and the rate of the reduction of nitrate was much lower than that in a solution containing potassium under the same conditions shows that the presence of potassium plays an important role in the mechanism of the reduction as it was reported by Kabanov et al. [60]. The two phenomena (hydride formation and incorporation) may take place simultaneously and further work is required to define the degree of participation of each one in the corrosion of tin and in the mechanism of the reduction of nitrate. Furthermore, the ions of Sn^{2+} which are formed in the solution due to the corrosion of tin can play an important role in the overall process as it has been proposed by Safonova and Petrii [61] on Pt electrodes.

It is well known that the rate of the reduction of anions is strongly dependent on the nature of the cation and the concentration of the supporting electrolyte. This phenomenon was attributed initially to double layer effects by Frumkin et al. [62]. Later studies introduced the term “cationic catalysis” in order to extend this theory by taking into account the participation of ion pairs or bridge assisted electron transfer between the non reacting cation of the supporting electrolyte (K^+ or NH_4^+ in our case) and the reacting anion, especially in the interfacial reaction layer [63]. The formation of ion pairs possibly explains why nitrate anions are not repelled by the negatively charged electrode even at very high cathodic potentials. Further work is needed to clarify the role of the supporting electrolyte in the reduction of nitrate.

The corrosion of tin seems to be the most serious problem of the whole process, since the concentration of tin in the bulk solution is higher than the environmentally acceptable level. This problem could be treated further by applying a less negative potential after the removal of nitrate, in order to redeposit the dissolved tin. Otherwise, according to Salzberg and Mies [48], the presence of small amounts of some cations, such as cesium or rubidium in the catholyte can stop the corrosion at current densities up to 2.7 A/cm^2.

In conclusion, tin at high potentials is the most effective cathode, which has been reported in the literature so far for the electrochemical reduction of nitrate to nitrogen, since it combines both high %S for nitrogen and high rate of reduction, which could result to a low value of space-time in a flow-cell, namely to a small volume of the cathodic part of the reactor. The remaining concentrations at −2.9 V of both nitrate (6.8 ppm) and nitrite (<0.5 ppm) are under the maximum contaminant level (MCL) in wastewaters and potable water [64]. The concentration of the produced ammonia (68 ppm) is over the MCL, but this could be treated thereafter by using a paired electrolysis reactor, where the catholyte would be passed through the anodic compartment of the cell to convert the ammonia via its oxidation to either nitrate or nitrogen [65].

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