Electrochemical reduction of nitrate and nitrite in simulated liquid nuclear wastes

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ABSTRACT

The electrochemical reduction of nitrate and nitrite in simulated low-level nuclear wastes containing 1.8 M $NaNO_3$ + 0.55 M $NaNO_2$ + 1.16 M NaOH was studied under galvanostatic polarization on tin and bismuth cathodes. The rate of the reduction of nitrate was about the same on both metals. The selectivity (%S) to ammonia was similar on the two metals (12% at 450 mA/cm^2) and that to nitrogen 82% on Sn and 72% on Bi. On the other hand, the %S to nitrous oxide was lower on Sn (8%) than that on Bi (18%) under the same conditions. The current efficiency (%CE) on both metals was 80% when the 99% of the initial nitrogen was removed. The %CE gradually decreases as the concentration of the nitrogen containing species in the solution decreases during the electrolysis. The energy consumption for the removal of 1 g of N was 100 W h at 450 mA/cm^2 but it can be significantly reduced by a better design of the electrolysis cell. The presence of chromate in the electrolyte, which is a known inhibitor of the cathodic reduction of nitrate, has no influence on the rate of the reduction and the distribution of the products.

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1. Introduction

The liquid nuclear wastes are mainly divided into two categories: the high-level nuclear wastes (HLW) and the low-level nuclear wastes (LLW) which are characterized by high and low radioactivity respectively. The HLW contain high concentrations of HNO_3 (in the order of 2–7 M), while the LLW about 1.6–2.2 M $NaNO_3$ + 0.4–0.6 M $NaNO_3$ + 1.1–1.5 M NaOH [1,2]. Apart from nitrate and nitrite, both types of wastes contain other ionic species as it is shown in Table 1. A flow sheet of the process for treating liquid radioactive wastes has been presented by Prasad et al. [3] in which a necessary step is the removal of nitrate and nitrite [1–3].

The treatment of the LLW can be performed by electrochemical reduction of nitrate and nitrite to the non-toxic nitrogen gas [1,3–11]. An ideal electrochemical method must combine (i) selective conversion of nitrate and nitrite to nitrogen; (ii) high rate of reduction; (iii) high current efficiency (%CE); and (iv) low energy consumption. Additionally, the method must be uninfluenced by the presence of the other ions, especially by chromate which, as it is known [12], hinders the electroreductions which take place in alkaline solution. However, it is difficult to find a method which fulfils all the above requirements, because several by-products can be formed during the reduction of nitrate such as ammonia, nitrous oxide and hydroxylamine. Moreover, the rate of the reduction and the %CE are usually low leading to high energy consumption.

It has been found that high overpotential metals such as tin and bismuth are promising cathodes for the electrochemical conversion of nitrate to nitrogen, since they combine both high rates of reduction and selectivity (%S) to nitrogen which is ranged between 80% and 90% [13–16].

This paper deals with the electrochemical removal of nitrate and nitrite ions from simulated solutions of LLW on Sn and Bi under galvanostatic operation, which is more preferable in the industry.

2. Experimental

The electrolytic experiments were performed in a Teflon constructed cell which was divided by a Nafion 117 (H^+ form) membrane into two compartments of equal volume (10 mL). The cathode was a tin foil (Sigma–Aldrich, 99.9%) or a bismuth plate, which was prepared by melting granulated bismuth (99%, BDH Laboratory reagents) followed by cooling at ambient temperature. The anode was a platinized platinum foil (Alpha Metal). The geometrical area of the cathode and the anode was 2 and 6 cm^2 respectively and the distance between the two electrodes was 2 cm. All the experiments were carried out under galvanostatic operation.

A helium stream, having a constant flow rate of 12 mL/min withdrew the gaseous products of the electrolysis (H_2, N_2, and N_2O) from the cell and their analysis 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 up to 180 °C

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Table 1
Typical composition of high- and low-level nuclear wastes [1,2].

High-level radioactive wastes		Low-level radioactive wastes	
Component	Concentration (M)	Component	Concentration (M)
HNO_3	2	$NaNO_3$	1.80
$UO_2(NO_3)_2 \cdot 6H_2O$	0.0076	$NaNO_2$	0.55
$Ba(NO_3)_2$	0.0207	NaOH	1.16
$RbNO_3$	0.0074	$NaAl(OH)_4$	0.31
$Pd(NO_3)_2$	0.018	Na_2SO_4	0.14
$Y(NO_3)_3 \cdot 5H_2O$	0.0084	Na_2CO_3	0.16
$Ce(NO_3)_3 \cdot 6H_2O$	0.033	NaCl	0.22
$Nd(NO_3)_3 \cdot 6H_2O$	0.0434	NaF	0.015
$Fe(NO_3)_3 \cdot 9H_2O$	0.038	Na_2SiO_3	0.0038
$Ni(NO_3)_3 \cdot 6H_2O$	0.006	Na_3PO_4	0.0085
$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	0.069	Na_2CrO_4	0.0033
$Sr(NO_3)_2$	0.0165	$NaB(C_6H_5)_4$	0.0026
$CsNO_3$	0.0371	$Na_2[Ru(NO)(NO_2)_4(OH)]$	$4.5 \cdot 10^{-5}$
$ZrO(NO_3)_2 \cdot 2H_2O$	0.069	$HgCl_2$	$2.2 \cdot 10^{-6}$
$Rh(NO_3)_3$	0.008		
$La(NO_3)_3 \cdot 6H_2O$	0.0319		
$Eu(NO_3)_3 \cdot 5H_2O$	0.0019		

where it was kept constant for 4 min.

The analysis of nitrate and nitrite was performed by ion chromatography (DIONEX 4500i, AS9–HC) equipped with a UV detector, while that of ammonia by fluorometry [17]. The gaseous stream after the GC analysis was bubbled into a 1N H_2SO_4 solution in order to trap the produced ammonia which escaped from the cell. More information about the experimental setup has been given previously [13].

3. Results and discussion

3.1. Treatment of low-level radioactive wastes

Fig. 1(a) and (b) shows the concentration decay of nitrate on tin and bismuth respectively, obtained by steady state electrolysis of a solution containing 1.8 M $NaNO_3$ + 0.55 M $NaNO_2$ + 1.16 M NaOH, at different current densities. The concentration of nitrate vs. time, in all experiments, can be described by a pseudo-first-order kinetic equation:

$$C = C_o e^{-kt} \tag{1}$$

The insets in Fig. 1(a) and (b) show that the rate constant k increases almost linearly with the increase of the current density and that the rate of the reduction is about the same on the two metals. The fact that the rate does not depend on the nature of the metal, can be explained by assuming that the reduction of nitrate takes place far from the electrode surface, as it has been described in a previous work [14] and this leads to a weak interaction between the electrode and the reduced nitrate. In such cases, the rate of the reduction is expected to be almost independent of the nature of the metal electrode [18]. It should be noticed, that unpublished results from our laboratory have shown that the rate of the reduction on several sp metals (Sn, Bi, Pb, Al and In) at very negative potentials, does not depend on the electrode material but only on the potential of zero charge (pzc) of each metal. The pzc of Sn (−0.43 V) and Bi (−0.39 V) differs only by 40 mV [19] and this can explain why the rate of the reduction was found to be about the same on the two metals.

The concentration of nitrite initially increases, reaches a maximum and consequently decreases (Fig. 2(a) and (b)). The form of this curve is characteristic of an intermediate product in a consecutive reaction mechanism:

$$NO_3^- \rightarrow NO_2^- \rightarrow Products \tag{2}$$
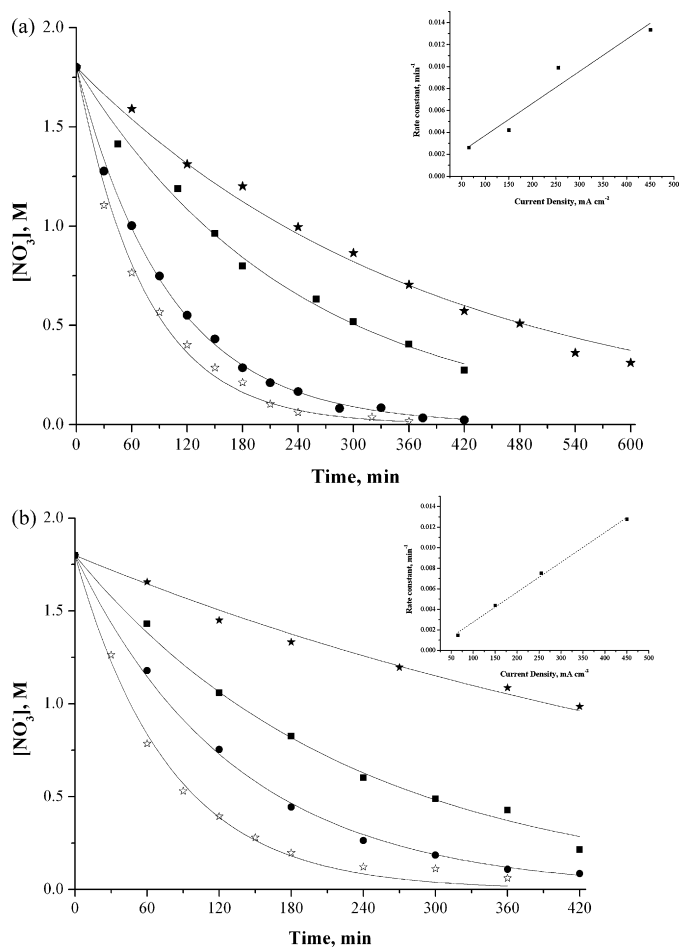
Fig. 1. Concentration profile of nitrate vs. time on (a) Sn and (b) Bi at (★) 65, (■) 150, (●) 255, and (☆) 450 mA/cm². The kinetic rate constant vs. the current density is displayed in the inset. Electrolyte: 1.8 M $NaNO_3$ + 0.55 M $NaNO_2$ + 1.16 M NaOH.

The profile of nitrite vs. time is different on the two metals, given that the height of the maximum of nitrite on tin decreases as the current density increases, while the opposite happens on bismuth.

The shape of these curves can be described by the model of the electrochemical reaction sequences [20]:

$$A \xrightarrow{\alpha_1} B \xrightarrow{\alpha_2} C \tag{3}$$

where α_i the transfer coefficient of the reaction i. According to this model, the maximum concentration of the intermediate B depends on the applied potential and the transfer coefficients α_1 and α_2:

$$C_{B,\max} = \left[\frac{e^{(\alpha_2 - \alpha_1)\theta}}{\mu} \right]^{\frac{\mu}{\mu - e^{(\alpha_2 - \alpha_1)\theta}}} \tag{4}$$

where θ is the dimensionless potential and μ is a selectivity parameter for C_A at zero potential. Eq. (4) shows that if $\alpha_2 - \alpha_1 > 0$, then the $C_{B,\max}$ decreases as the potential shifts to more negative values, as it is depicted in Fig. 2(a) and thus $\alpha_{2,Sn} > \alpha_{1,Sn}$. On the other hand, if $\alpha_2 - \alpha_1 < 0$ the $C_{B,\max}$ increases as the potential shifts to more negative values, as it is depicted in Fig. 2(b) and this means that $\alpha_{1,Bi} > \alpha_{2,Bi}$.

After prolonged electrolysis, when the % conversion of nitrate is >80% the final concentration of nitrite, which has practical importance, was about the same on the two metals. For example, at 250 mA/cm² after 420 min the 85% of nitrate was removed and the concentration of nitrite was 0.48 M on Sn and 0.42 M on Bi.

(a)

(b)
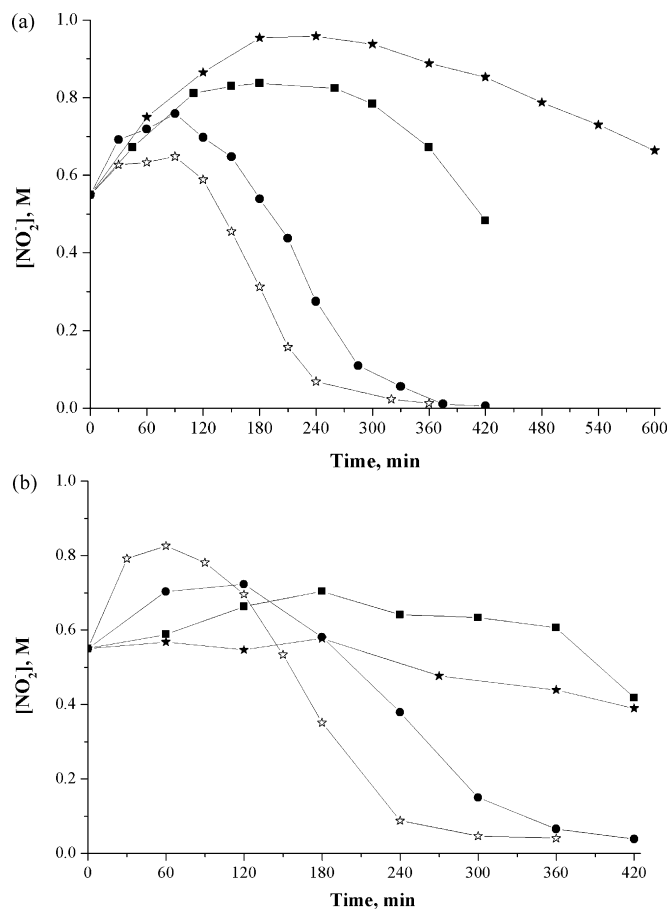
Fig. 2. Concentration profile of nitrite vs. time on (a) Sn and (b) Bi at ($\star$) 65, ($\blacksquare$) 150, ($\bullet$) 255, and ($\star$) 450 mA/cm^2. The kinetic rate constant vs. the current density is displayed in the inset. Electrolyte: 1.8 M NaNO$_3$ + 0.55 M NaNO$_2$ + 1.16 M NaOH.

The %S of each product was calculated according to the equation:

$$\%S = p \frac{n_i}{n_0 - n} 100 \tag{5}$$

where n_0 is the initial mols of nitrate; n is the remaining mols of nitrate; n_i is the produced mols of the i compound and p is the mols of nitrate needed for the formation of 1 mol of the i compound ($p = 1$ for nitrite and ammonia and $p = 2$ for nitrogen and nitrous oxide). Fig. 3 shows the %S of nitrogen, nitrous oxide and ammonia, when the 90% of initial N was reduced. The %S to nitrogen increases from 58 to 82% on tin and from 53 to 72% on bismuth, as the current density increases from 65 to 450 mA/cm^2. On the contrary, the %S to nitrous oxide decreases from 32 to 8% on tin and from 38 to 18% on bismuth, within the same interval. The %S to ammonia does not depend on the nature of the electrode and it was between 6 and 12%.

The %CE was calculated on the basis of the amount of hydrogen which was measured by GC, by assuming that the remaining electrical charge was consumed for the reduction of the nitrogen containing species. The calculation was based on the equation:

$$\% \text{CE} = \frac{Q_T - Q_{H_2}}{Q_T} 100 \tag{6}$$

where Q_T the (current density)(electrode area)(time) is the total charge and Q_{H_2} is the charge consumed for the hydrogen evolution reaction (calculated by the Faraday law). The %CE depended on the % removal efficiency (%RE) of the nitrogen containing species. At 450 mA/cm^2 the %CE was about 100% for the first 3 h of the electrolysis, where the %RE was 80%. At longer electrolysis times, when the
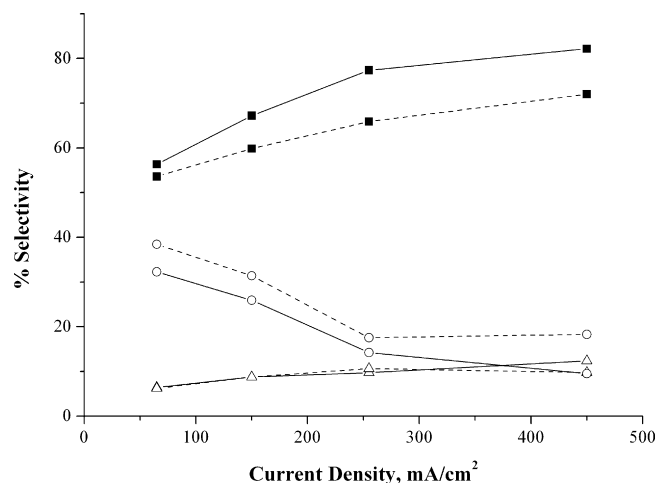

Fig. 3. % Selectivity to ($\blacksquare$) nitrogen, ($\bigcirc$) nitrous oxide and ($\triangle$) ammonia vs. current density on (—) Sn and (– – –) Bi cathode. Electrolyte: 1.8 M NaNO$_3$ + 0.55 M NaNO$_2$ + 1.16 M NaOH.

%RE was 99%, the %FE was decreased to about 70% (Fig. 4). It has been shown previously [15] that the reduction of nitrate at very negative potentials takes place through electrochemical hydrogenation, namely the hydrogen which is produced on the cathode reduces the initial nitrate and nitrite. At the beginning of the electrolysis, the concentration of these species in the solution is high enough so that the produced hydrogen is totally consumed for their reduction and this leads to a CE of 100%. As the electrolysis proceeds, the concentration of nitrate and nitrite decreases and the produced hydrogen is only partially consumed for their reduction. The excess of the hydrogen escapes from the cell leading to a decrease in the %CE.

However, the total %CE which was calculated from Eq. (6) corresponds to the sum of the %CEs of all the reduction products. The %CE of the reduction of nitrate to nitrite can be obtained as follows.

The instant concentration of nitrate, C, was calculated by Eq. (1), by using the rate constant which was shown in Fig. 1. The amount of nitrate which was removed is

$$N \text{ (mols)} = (C_0 - C)V \tag{7}$$
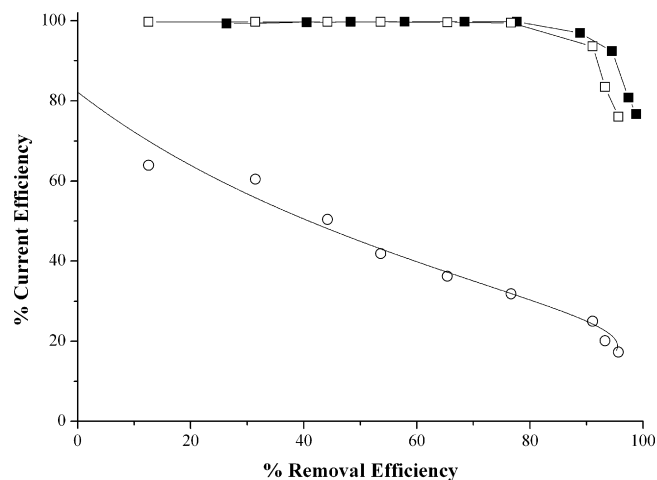
Fig. 4. % Current efficiency vs. the % removal efficiency of the nitrogen containing species on ($\blacksquare$) Sn and ($\square$) Bi at 450 mA/cm^2. The line shows the simulated %CE of the reduction of nitrate to nitrite on Bi based on Eq. (9) and ($\bigcirc$) the obtained %CE from the experimental data. Electrolyte: 1.8 M NaNO$_3$ + 0.55 M NaNO$_2$ + 1.16 M NaOH.

(a)

(b)
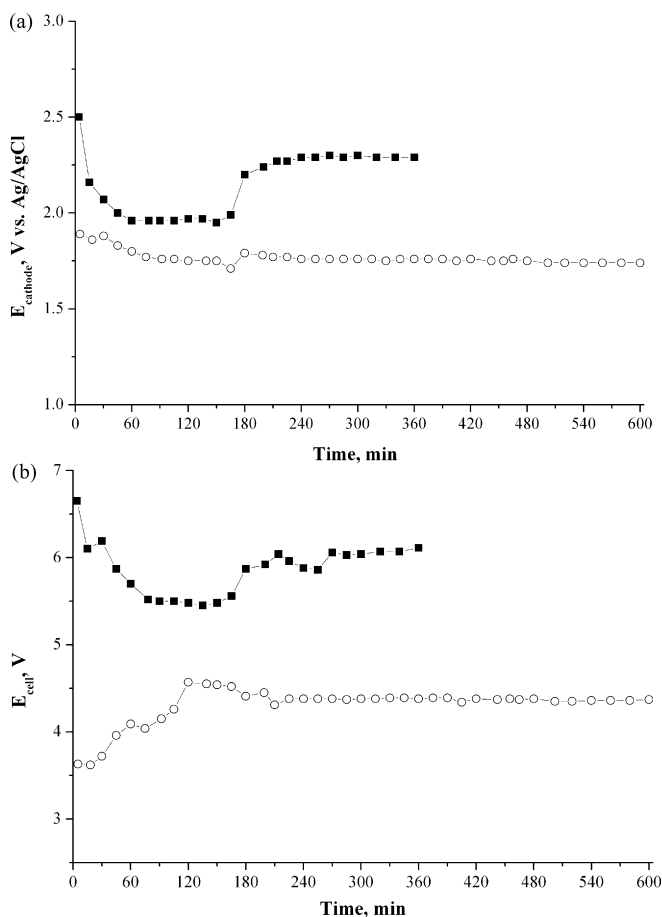
Fig. 5. Variation of (a) the potential of the cathode vs. Ag/AgCl and (b) the cell voltage on Sn at (○) 65 and (■) 450 mA/cm². Electrolyte: 1.8 M NaNO₃ + 0.55 M NaNO₂ + 1.16 M NaOH.

where V is the volume of the catholyte. The charge consumed for the reduction of nitrate to nitrite, Q, according to Faraday's law is

$$Q = NFn \tag{8}$$

where $n = 2$ is the number of electrons which corresponds to the reduction of nitrate to nitrite and F the Faraday's constant. The %CE of the reduction of nitrate to nitrite is

$$\%CE = \frac{Q}{Q_T} 100 \tag{9}$$

The line in Fig. 4 represents the simulated %CE of the reduction of nitrate to nitrite at 450 mA/cm² on Bi, as it was calculated by the aforementioned methodology and the points the %CE which was calculated on the basis of the concentration of nitrate which was determined analytically. As it is shown in Fig. 4, the simulated curve can adequately predict the experimental data.

As it is expected, the potential of the cathode vs. Ag/AgCl as well as the voltage of the cell varied during the electrolysis, in order to keep a constant current density. The variation of the potential of the cathode vs. Ag/AgCl and the cell voltage are depicted in Fig. 5(a) and (b) respectively, on Sn cathode. The same characteristics were observed on Bi, as well.

Table 2 shows the energy consumption, expressed as the ratio of the energy consumed to the mass of the reduced N (W h/g_N). The energy consumption is about the same on both metals and increases almost linearly with the increase of the current density, from about 25 W h/g_N at 65 mA/cm² to 100 W h/g_N at 450 mA/cm². Even though the energy consumption is reasonable, it can be further reduced by shortening the distance between the electrodes.

Table 2
Energy consumption vs. the current density. Electrolyte: 1.8 M NaNO₃ + 0.55 M NaNO₂ + 1.16 M NaOH.

| Current density (mA/cm²)	Energy consumption (W h/g_N)	
	Sn	Bi
65	29.1	22.6
150	43.9	39.2
255	60.3	50.6
450	97.0	98.6

It should be mentioned that the method can also be applied in HLW. However, the solution must be neutralized prior to the electrolysis, given that in such an acidic environment (2–7 M HNO₃), the production of hydroxylamine nitrate, which is highly explosive, is favoured [21].

3.2. Reduction of nitrate and nitrite in the presence of chromate

In a previous work [14] it has been proved that the presence of salts in the supporting electrolyte which cannot be electrodeposited on the electrode accelerates the reduction of nitrate. Thus, low concentration of salts such as NaCl, NaF, and Na₂SO₄ which are present in the LLW (Table 1) does not inhibit the reduction but, on the contrary, it is expected to lead to a small increase in its rate.

Duarte et al. [9] found that chromate in concentrations higher than 6.7×10^{-5} M hinders the electroreduction of nitrate and nitrite due to the electroreduction of Cr^{6+} to Cr^{3+} which thereafter forms an insoluble film of $Cr(OH)_3$ on the electrode surface [1,9,12]. Given that the LLW contain much higher concentration of chromate (about 3.3×10^{-3} M), a hindering of the reduction must be expected.

In order to clarify the role of chromate under our conditions, a new experiment was performed at 450 mA/cm² in a solution containing 1.8 M NaNO₃ + 0.55 M NaNO₂ + 1.16 M NaOH + 3.3×10^{-3} M Na₂CrO₄. The rate of the reduction and the distribution of the products were found to be about the same within the experimental error, compared to that in the absence of chromate. The formation of the film of $Cr(OH)_3$ which hinders the reduction is not possible in this case because the potential was negative enough for the reduction of Cr^{3+} to Cr, which is then deposited on the cathode [22]. The presence of chromium on the electrode was confirmed by EDS analysis (Fig. 6). The pzc of Cr is -0.45 V [19] which is close to that of Sn (-0.43 V) and this can explain why the presence of Cr on the electrode surface does not change measurably the rate of the reduction of nitrate.
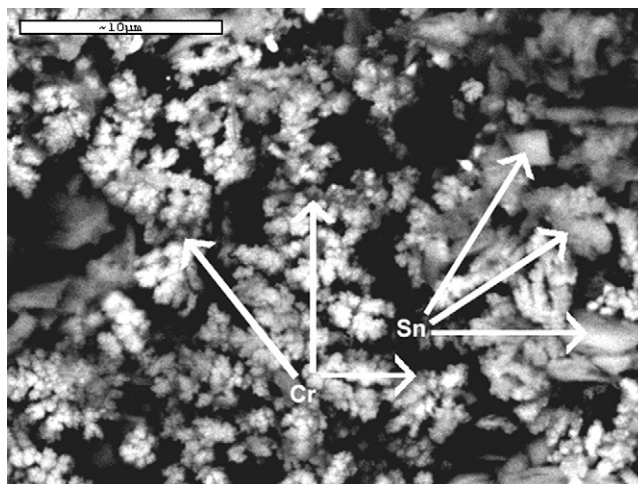
Fig. 6. SEM photograph of a tin electrode which was used for the electrochemical reduction of nitrate in the presence of chromate.

4. Conclusion

The electrochemical reduction of nitrate on Sn and Bi cathodes in simulated LLW was studied under galvanostatic polarization. The main conclusions of the work are

(1) The rate of the reduction of nitrate is about the same on Sn and Bi and it increases with the increase of the current density.
(2) The %S to N_2 and NH_3 increase as the current increases, while that to N_2O follows the opposite trend. The %S to NH_3 is the same on the two metals, while that of N_2 is higher on Sn. At $450 \, mA/cm^2$ the %S to N_2, N_2O and NH_3 was 82, 8 and 12% respectively on Sn.
(3) The %FE depends on the %RE of the nitrogen containing species and it is about 70% when the 99% of the initial nitrate and nitrite was reduced.
(4) The voltage of the cell and the potential of the cathode vs. Ag/AgCl increase as the current density increases. The energy consumption is about proportional to the applied current density.
(5) The presence of chromate does not hinder the reduction of nitrate under our conditions.

Acknowledgements

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