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Electrochemical removal of nitrate from waste water

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Keywords: Cu and CuSn electrodes, square wave voltammetry, electrochemical nitrate reduction, flow reactor

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Introduction

The removal of nitrate from waste water is a subject of intense research. The approach in our work is based on an electrochemical technique using efficient and selective electrocatalysts for nitrate reduction. The main advantages of the electrochemical approach are its versatility and simplicity in use, its low cost and its environmental friendliness. Therefore, electrochemical techniques must be developed to reduce adequately and specifically nitrate ions to harmless products such as nitrogen. The nitrate reduction mechanism is very complex and many intermediate species can be generated during the reduction. Consequently, a large number of cathode mate-

rials have been studied under various conditions. For a fast and simple detection of the products resulting from electrochemical nitrate reduction (ENR) square wave voltammetry (SWV) and cyclic hydrodynamic voltammetry (CHV) with rotating ring-disk electrode (RRDE) represent versatile analytical tools for the detection of reaction intermediates. It is known that copper and copper-tin alloys exhibit electrocatalytic activity towards nitrate reduction [1, 2, 3, 4, 5, 6] and therefore they were used in our studies. The group of Polatides et al. [7] reported that, by using a CuSn electrode at very negative potentials ($E = -2$ V vs. Ag/AgCl), nitrate can be removed up to 97%, with a selectivity of 35% for N₂ as a final product. The interest in CuSn coatings increased during

the last years due to their better corrosion and mechanical properties compared to pure copper or tin coatings. In general it is a major challenge to develop new methods for nitrate removal from waste waters in which biological alternative cannot be applied. Our work has been strongly influenced by the target application with a strong focus on the cathode material as one crucial parameter.

Experimental Section

Reagents

Sodium nitrate (Merck), sodium nitrite (Merck), copper (II) sulphate pentahydrate (Grüssing), sodium hydroxide (Merck), tin sulphate (Merck), copper (II) sulphate pentahydrate (Grüssing) and sulphuric acid (Merck) were of analytical grade and used as received without further purification. All solutions were prepared with 18.2 MΩ cm (25°C) Millipore Milli-Q® water. For all measurements on nitrate reduction 1 M NaOH was used as supporting electrolyte. All the measurements were performed in the presence of air. The pH value of the solution were recorded by a pH/Cond 340i (WTW, Germany) pH-meter.

Electrode materials

In order to study the influence of deposition parameters and bath composition on the electrodeposition of copper, tin and copper-tin alloys, potentiostatic and galvanostatic experiments were performed. Most of the characterization measurements have been chosen to gain further insight on the range of electroplating conditions in which adherent and uniform coatings can be produced. A number of techniques, including scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) were used to

provide the information on these coatings development processes.

Experimental setups

Voltammetric measurements were carried out using a BioLogic Potentiostat/Galvanostat model VSP (France). A standard glass cell with three electrodes was used. The counter electrode (CE) was an oxygen evolving dimensionally stable anode (Ti/IrO₂-Pt) and a Ag/AgCl/KCl_{sat} electrode was used as reference electrode (RE).

An electrochemical filter-press micro flow reactor (ElectroCell A/S, Denmark) was used for the electroreduction of nitrates. In both compartments a volume of 300 mL of solution was circulated. The cathode and anode chambers were separated by a Nafion® 324 (DuPont) cation selective – membrane (separator). A model electrolyte (0,1 M NaNO₃, 1M NaOH) was used in the cathodic compartment. The anolyte was 1.0 M NaOH. The anodic and cathodic compartments were of equal volumes (10 mL). Sealing of the cell was achieved by using rubber frames, specially designed for the reactor. The geometrical areas of the cathode and the anode were 10 cm² each and the distance between the two electrodes was 1 cm. The electrolytes were circulated through the cell compartments with a peristaltic pump (TC type, with two channels, Medorex, Germany) with a monitored flow rate. The determination of nitrate and nitrite was performed by ion chromatography (Dionex DX 100 with an anion column for AG 14A/AS14 A) after appropriate dilution. All measurements were performed at room temperature.

Experimental procedure

Model solutions containing nitrate ions were filled in the cathodic compartment of the flow cell. By applying direct current to the electrodes,

nitrate ions move towards the cathode by passing through a cationic selective membrane. In this way, we eliminated possible interferences such as nitrite oxidation at the anode. In order to analyse the nitrate and nitrite concentrations samples were taken from the cathode compartment at specific time intervals with a syringe. The total time of the experiments was 24 hours. The experiments were conducted in galvanostatic operation mode (Cu: -20 and -40 mA·cm⁻²; CuSn: -25 and -50 mA·cm⁻²).

Results and Discussion

1. Preparation and characterization of Cu and CuSn materials

One aim of this study was to develop a simple, environmentally friendly cupric-stannous plating

solution containing a minimum of components that can be electroplated at reasonable rates at room temperature and can be used for ENR. The results discussed in [8] allowed us to establish the specific parameters concerning the electrodeposition of the individual metals and their alloys. Potentiostatic and galvanostatic experiments were performed to study the influence of parameters on the electrodeposition of Cu, Sn and CuSn alloys. SEM images taken for CuSn deposits indicate significant changes in their surface morphology with changing electrodeposition parameters (Fig. 1). As can be seen in Figure 1 (A and B) the CuSn deposits have a uniform surface morphology when galvanostatic deposition is used.

For the potentiostatic deposition at $E = -0.5$ V vs. Ag/AgCl (Fig. 1C) the surface morphology of the deposits is more rough. This roughness could be

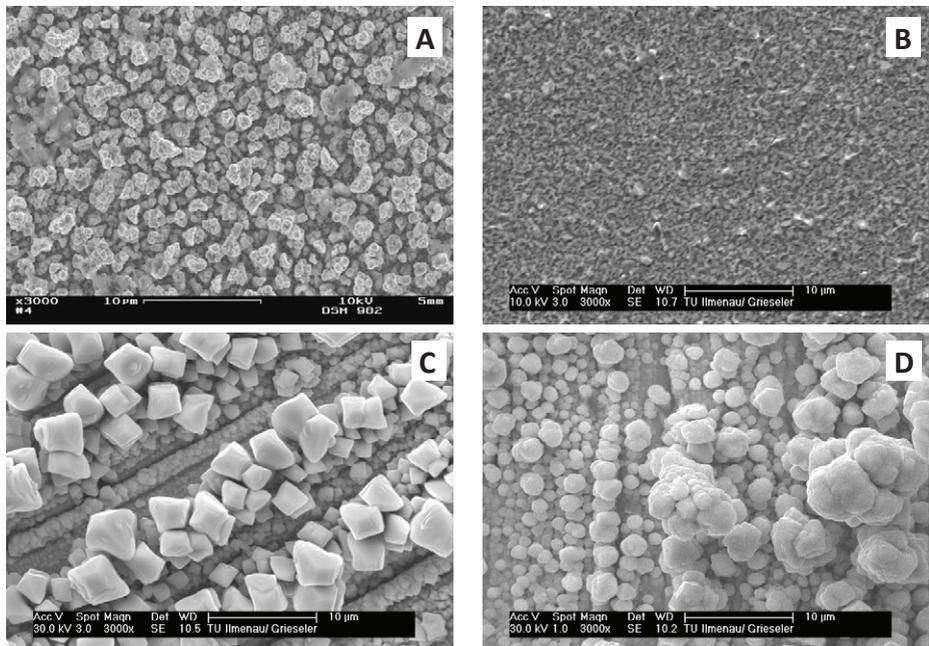


Fig. 1: SEM micrographs showing the surface morphologies of CuSn films obtained at $i = 80$ mA/cm² (A), $i = 120$ mA/cm² (B), $E = -0.5$ V (C) and $E = -0.6$ V (D) with stirring (2000 rpm)

related to the fact that, at $E = -0.5\text{V}$ the deposition of tin just starts. This assumption is in correlation with the CV studies presented in [8]. At more cathodic potentials (Fig. 1D) more uniform and dense deposits are obtained. Moreover, the SEM measurements showed that the CuSn deposits are more uniform if potentiostatic deposition is applied. Analyzing the CuSn deposits obtained under galvanostatic and potentiostatic conditions via EDX showed that the highest tin percentage in the deposit (73%) was obtained at $E = -0.6\text{ V}$ (Tab. 1).

Tab 1: Correlation between potential and CuSn content for the obtained deposits

E (V vs. Ag/AgCl)	Cu (wt %)	Sn (wt %)
Bath composition		
0.1 M CuSO_4 + 0.8 M SnSO_4 + 1 M H_2SO_4 + 0.2 M HBF_4		
-0.5	42	58
-0.6	27	73
-0.7	29	71

An electrode material with high Sn content was obtained. In the following the properties of the electrode material will be discussed for electrochemical reduction process.

2. Detection of electroactive products

After synthesis and characterization of copper, tin and copper-tin alloy, the copper and copper-tin electrode material were chosen as cathode materials for the reduction of nitrate from model nitrate solutions. The objective of this part was to establish the optimal conditions for the detection of the electroactive species resulting from ENR. For a fast and simple detection of the products resulting from ENR, square wave voltammetry (SWV) and cyclic hydrodynamic voltammetry (CHV) with rotating ring-disk electrode (RRDE)

represent versatile analytical tools. In order to evaluate the possibility of electrochemical detection of the electroactive products resulting from ENR in alkaline media, we performed preliminary studies in mono-component solutions using the standard addition method. Measurements were performed with the disk electrode disconnected; the detection of the individual species was carried out at the Pt ring electrode. In mono-component solutions, well defined oxidation peaks of nitrite, hydroxylamine and ammonia (see Fig. 2, 3, 4) were recorded using both techniques. Figures 2, 3, 4-A and B, which we report here for clarity, were published and discussed in our previous papers [9, 10]. A comparative study on the influence of Cu and CuSn alloys on ENR and the stability of the electrode materials (Fig. 5 A and B) in the presence and absence of nitrate was discussed in our previous paper [10].

Figure 2 A and B show the cyclic and square wave voltammograms recorded at the Pt ring electrode in 1 M Na_2SO_4 in the presence of different concentrations of NO_2^- . For clarity, figures present only the positive potential ranges from the corresponding anodic scan.

In mono-component solutions, depending on the concentration, the oxidation peak potential of hydroxylamine was between +1.1 and +1.3 V for CHV (Fig. 3A) and between +1.0 and +1.1 V for SWV (Fig. 3B), respectively.

Anodic sweeps recorded in the presence of different concentrations of ammonium are presented in Figure 4. At pH 11 the concentration ratio between NH_3 and NH_4^+ is 40 [11]. Thus, ammonium can be electrochemically detected via ammonia oxidation.

Comparing hydroxylamine and nitrite oxidation, we observed only a relatively small difference (from 100 to 200 mV) between the peak potentials evaluated by CHV and SWV. Taking into account that the hydroxylamine oxidation process is faster at the Pt electrode, the decrease

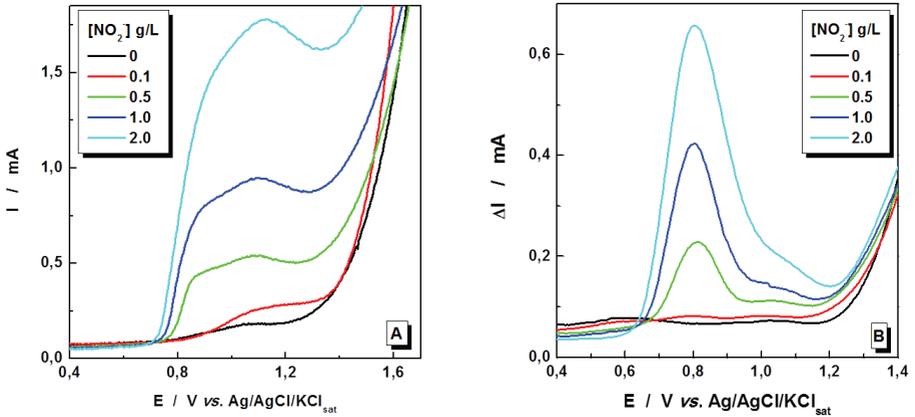


Fig. 2: Dependence of the anodic peak current on the NO_2^- concentration by CHV (A) and SWV (B) Experimental conditions: Start potential = -1.5 V and end potential = 2.0 V, $\omega = 1000$ rpm, disk electrode disconnected; CHV: $v = 500$ mV s^{-1} ; SWV: wave amplitude = 50 mV; wave period = 10 ms; wave increment = 5 mV.

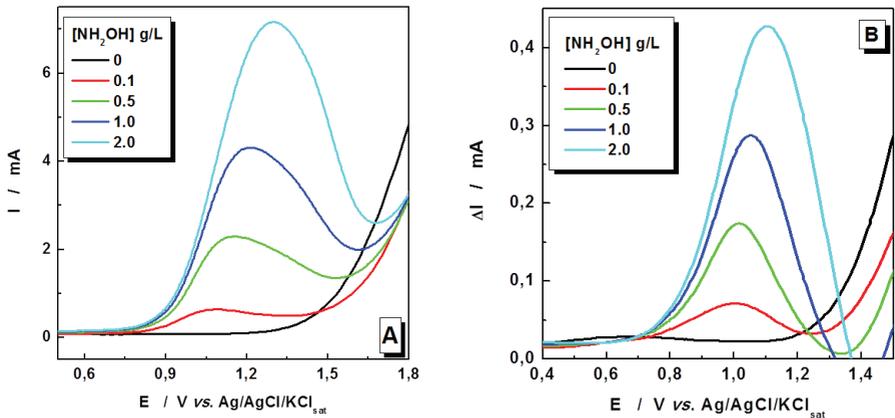


Fig. 3: Anodic peak currents dependence with NH_2OH concentration by CHV (A) and SWV (B) at Pt ring electrode. Experimental conditions: see Figure 1.

of this difference supports the previous explanation. SWV (Fig. 4B) measurements revealed well defined peaks for ammonia oxidation at ring potentials between +1.2 and +1.5 V, demonstrating that SWV is better suited for the electrochemical detection of ammonia. In conclusion, three different peak potentials could be identified for

the oxidation reactions: +0.8 V for NO_2^- , +1.0 V for NH_2OH and approximately +1.3 V for ammonia. Figure 5 presents details of the currents recorded at the Pt ring electrode during the anodic scans for two different disk potentials: -1.3V for Cu and -1.5V for CuSn electrode, respectively. Measurements were performed by recording eight succes-

sive cycles without refreshing of the Cu and CuSn layers. It can be observed that for the selected potentials, every first cycle indicates a maximum electrocatalytic activity, which decreases rapidly in the following sweeps. Moreover, after the first cycle, the peak potentials for the currents at the Pt ring electrode shift to more positive values. This indicates a blocking of the disk surface. The decrease of the copper electrode electroactivity

after the first cycle may be related to the adsorption of hydrogen and nitrate reduction products. Based on the above discussed results and by reactivating the surface of the Cu and the CuSn electrode before each experiment, we started a detailed study concerning the influence of the polarization potential of the electrode on the ENR product composition. Only the anodic portions of every first cycle are presented (Fig. 6). A decrease

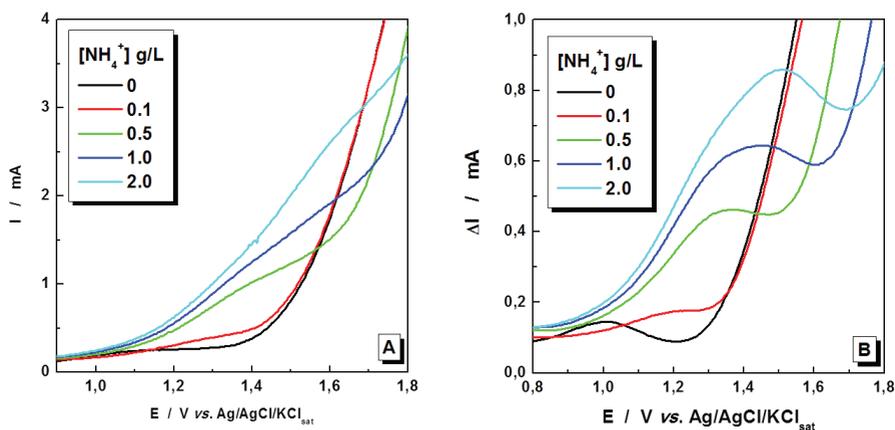


Fig. 4: Anodic peak current dependence with NH_4^+ concentration by CHV (A) and SWV (B) at Pt ring electrode.

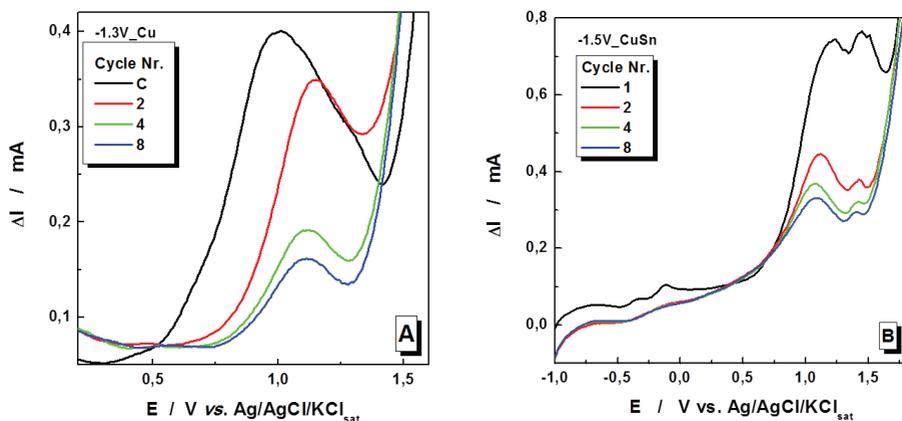


Fig. 5: Current signals at the Pt ring electrode at different potentials of the Cu (A) and CuSn (B) disk electrodes: (A) -1.3 V and (B) -1.5 V in 2 g/L NO_3^- solution containing 1 M Na_2SO_4 (pH 11) as supporting electrolyte

of the disk potential to more negative potentials causes an increase in the recorded ring currents. Depending on the disk potential, the currents recorded at the ring electrode correspond to the oxidation of different intermediate or final products of nitrate reduction.

In the case of the CuSn electrode (Fig. 6) the electrocatalytic activity of the electrode material is improved. Two distinct signals (peaks) are observed. Based on the results obtained in mono-component solutions, the peak at ca. 1.0 V can be attributed to the oxidation of nitrite (see Fig. 2) and hydroxylamine (see Fig. 3). For disk potentials more negative than -0.5 V, a clear signal, corresponding to ammonia oxidation, can be observed at ring potentials starting at 1.3 V. Bouzek et al. [12] and Gootzen et al. [13] concluded that from all possible products that are formed during the nitrate reduction only nitrite and hydroxylamine are sensitive towards oxidation at the platinum ring electrode and other possible products like NH_4^+ , N_2 and N_2O are not susceptible towards oxidation at the platinum

ring electrode. Contrarily, Endo et al. [14] studied the oxidation of ammonia on a disk electrode and concluded from RRDE experiments that two kinds of intermediates involved in the anodic oxidation of ammonia on platinum could be detected in situ; one can then be reduced (probably NO_x) and another can be further oxidized (such as NH_2OH).

3. Direct reduction in electrochemical flow reactor

As a part of the evaluation of electrode materials, voltammetric experiments were performed on two electrode materials. Linear sweep voltammetry (LSV) measurements were performed at a Cu and CuSn ($\text{Cu}_{27}\text{Sn}_{73}$) electrodes in the absence and presence of nitrate (Fig. 7 A and B). The differences between the two voltammograms were attributed to the electrocatalytic effects specific of each electrode material. The potential was swept in the cathodic range until hydrogen evolution occurred.

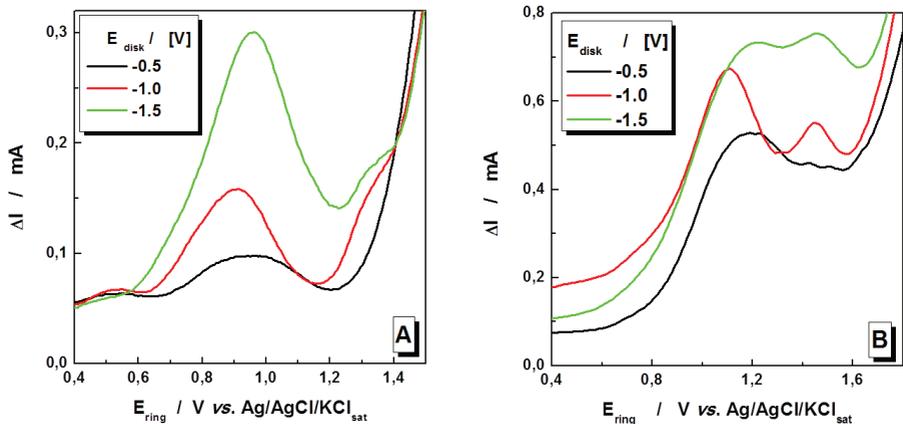


Fig. 6: Influence of the polarization potential on the oxidation currents recorded by SWV at a Cu (A) and CuSn (B) disk electrode. Experimental conditions: Start potential = -1.5 V and end potential = 2.0 V, $\omega = 1000$ rpm, wave amplitude = 50 mV; wave period = 10 ms; wave increment = 5 mV. The Cu and CuSn plated disk electrode was polarised at different constant potentials as indicated in the legends

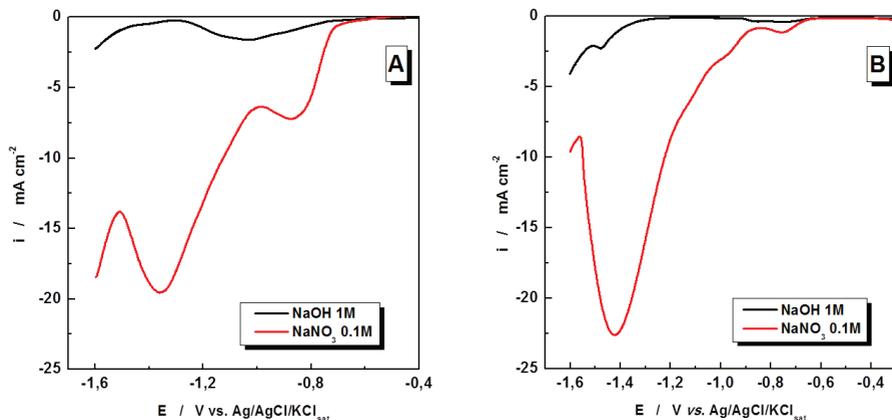


Fig. 7: Linear sweep voltammograms at a Cu (A) and CuSn (B) electrode in 1M NaOH (black line) in presence of 0.1M NaNO₃ (red line). Scan rate: 10 mV s^{-1} .

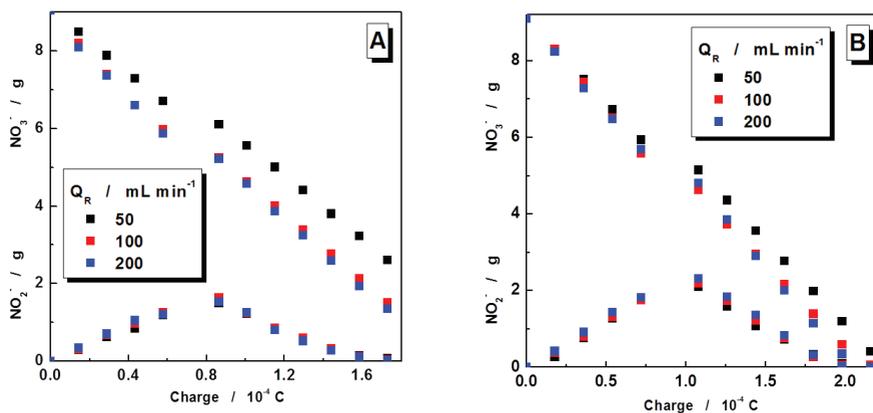


Fig. 8: Evolution of the concentration of NO_3^- and NO_2^- vs charge. Experimental conditions: 0.1 M NaNO₃ in 1 M NaOH electrolyte solution; (A) -20 mA cm^{-2} at a Cu electrode and (B) -25 mA cm^{-2} at a CuSn electrode.

A comparison between the two electrode materials, shows an enhancement of the nitrate reduction when CuSn is used. This is explained by the faster start of the electroreduction process (-0.7 V in Fig. 7B vs. -0.9 V in Fig. 7A). In order to analyse the reaction associated with the peaks, measurements involving prolonged electrolysis were performed at the current densities: (A) -20 mA cm^{-2} at a Cu

electrode and (B) -25 mA cm^{-2} at a CuSn electrode (Fig. 8).

After 24 h of electrolysis, at the Cu cathode the final concentration of nitrate reaches 1 g/L and it is totally eliminated at the CuSn cathode. The nitrite concentration increases at the Cu electrode and after that, is further diminished under the Maximum Permissible Contaminant Level (MPCL) of 50 mg/L after 24 h of electrolysis.

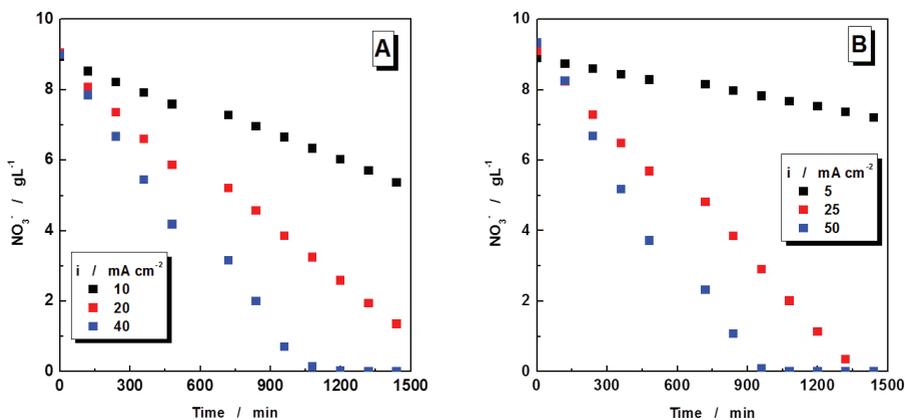


Fig. 9: Concentration profile of nitrate vs. time at a Cu (A) and CuSn (B) electrode. Experimental conditions: flow rate of 200 mL·min⁻¹; electrolyte: 0.1 M NaNO₃ + 1 M NaOH.

ENR was further investigated at even higher current densities in order to establish optimized working parameters. For this purpose, prolonged electrolyses were carried out at -40 mA cm⁻² at a Cu electrode and -50 mA cm⁻² and CuSn electrode, results presented in [8]. The obtained results show that at the same charge ($\sim 0.29 \cdot 10^{-4}$ C·cm⁻²) and flow rate (200 mL·min⁻¹), for the Cu electrode, a period of 18 h is sufficient to reduce the nitrate below the MPCL, while for the CuSn electrode, after 14 h the ENR is completed. Thus, we can conclude that at higher current density values, the ENR is more effective at the CuSn electrode. For cost evaluation of the ENR process, is important to identify the most efficient electrode material. Figure 9 A and B show the concentration decrease of nitrate at Cu and CuSn electrodes, respectively, obtained at a flow rate of 200 ml min⁻¹, from a solution containing 0.1 M NaNO₃ in 1 M NaOH, at three current densities. In order to reach the MPCL, the prolonged electrolyses need to perform a conversion degree for nitrate of at least 99.5%.

At the Cu electrode the MPCL was reached at -40 mA·cm⁻² after 20 h. On the other hand, for the CuSn electrode, at -25 mA·cm⁻², the MPCL was

reached after 22 h, while at the highest current density (-50 mA·cm⁻²) the MPCL was reached after 18 h.

The key parameters: energy consumption (W_s) and current efficiency (η_f) which describe the ENR process were evaluated. All the values were calculated at a flow rate of 200 mL·min⁻¹ and until the MPCL was reached (Fig. 10).

The obtained energy consumption (W_s) values are about the same on both electrode materials and increase almost linearly with the increase of the current density, from 2 kWh/kg NO₃⁻ to 16 kWh/kg NO₃⁻. The calculated W_s values (at higher current densities) are in accordance with those obtained by Katsouranos et al. [15], who succeeded to remove nitrate from an alkaline medium at an energy consumption value of 16.5 kWh/kg NaNO₃ at a Sn electrode. Similarly, Reyter et al. [16] studied the electroreduction of nitrate at a Cu electrode and obtained an energy consumption value of 25 kWh/kg NaNO₃. The current efficiency values decrease during the electrolysis by ca. 10%. Our results are in accordance with those of Reyter et al. [16] who observed a decrease of the current efficiency with the time. For the Cu material after 30 min of electrolysis a

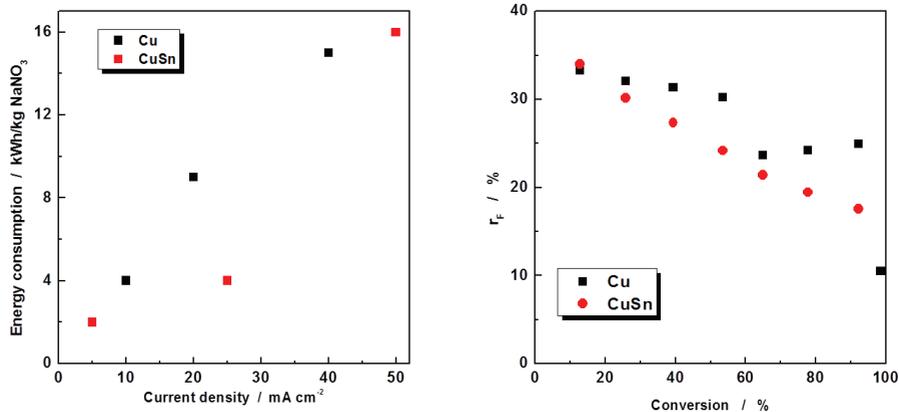


Fig. 10: Energy consumption (W_s) and current efficiency (r_f) values for the ENR at Cu and CuSn electrodes, obtained in synthetic nitrate solutions.

current efficiency of 30% was obtained, with a decrease to 20% after 180 min electrolysis.

Conclusions

The reduction process of nitrate at copper based electrodes was investigated. The CV studies allowed us to establish the specific parameters concerning the electrodeposition of the individual metals and their alloys. It was demonstrated that the products resulting from ENR in alkaline media can be detected by the CHV and SWV technique at Cu and CuSn plated Pt electrodes. Moreover, using SWV ammonium can be electrochemically detected with good accuracy. An enhancement of the electrocatalytic activity of Cu by alloying it with Sn was observed. On the two investigated types of cathode materials (Cu and CuSn), the concentration of nitrate was reduced electrochemically to the maximum permissible limit (50 mg/L) with a energy consumption in the range of 2 – 16 kWh/kg NaNO₃ at a CuSn cathode. In our test the energy consumption are comparable and even smaller compared to values reported in literature. An identical quantity of nitrate, was reduced at the

CuSn cathode below the permissible limit (99.5% conversion), in 18 h while at the Cu cathode the process needed 20 h. The current efficiency is about 35% corresponding to a conversion of 99.5%. Comparisons between these two electrodes indicate definite advantages in using the CuSn alloy for nitrate and nitrite reduction. Electrochemical removal of nitrate and nitrite has been demonstrated in a laboratory scale flow reactor under different operating conditions. In the used flow reactor the nitrate/nitrite reduction efficiency was improved with an increase in the current density and operation of the cell in a divided configuration.

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