Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2017.21555

94 (2017) 156–163
October

Synthesis of nanostructured ZnO/copper electrodes for nitrate electroreduction

N. Ait Ahmed[a,*], H. Hammache[a], M. Eyraud[b], L. Makhloufi[a], N. Gabouze[c]

[a]*Laboratoire d'Electrochimie, de Corrosion et de Valorisation Energétique (LECVE), Université de Bejaia, 06000 Bejaia, Algérie, email: naitahmed213@gmail.com (N. Ait Ahmed), houahammache@yahoo.fr (H. Hammache), laid_mak@yahoo.fr (L. Makhloufi)*
[b]*Aix-Marseille University, CNRS, MADIREL UMR 7246, équipe Electrochimie des Matériaux, 13397 Marseille Cedex 20, France, email: marielle.eyraud@univ-amu.fr (M. Eyraud)*
[c]*Centre de Recherche en Technologie des Semiconducteurs pour l'Energétique (CRTSE), 2, bvd. Frantz Fanon, B.P. 140 Alger 7 Merveilles, Alger, Algérie, email: ngabouze@yahoo.fr (N. Gabouze)*

Received 21 May 2017; Accepted 12 October 2017

ABSTRACT

In this work, ZnO thin films were electrochemically precipitated on copper electrode in zinc nitrate solution. The effects of the electrodeposition potential and time on the morphology, structure and electrocatalytic properties of ZnO towards nitrate reduction were studied. Surface morphology and structure were investigated by scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques. Voltammetric results show that under optimized ZnO electrodeposition conditions, the ZnO/Cu modified electrode exhibits interesting electrocatalytic performance towards nitrate reduction. A well-defined and reproducible peak with maximum current density was obtained for ZnO/Cu electrode elaborated at –1 V for 20 min electrodeposition time. Kinetic study by chronoamperometry is indicative of ammonia formation.

Keywords: ZnO; Electrodeposition; Modified electrode; Electrocatalysis; Nitrate reduction

1. Introduction

Nitrate reduction and determination is extremely important for environment and public health issues. The development of specific analytical methods for detection and destruction of nitrate is of great importance to limit pollution of the natural environment. Many methods are used to remove NO_3^- ions from contaminated water, such as reverse osmosis, photocatalytic, biochemical, chemical and electrochemical reduction [1–4]. Most of them involving complicated and time-consuming procedures. In contrast, electrochemical nitrate treatment can offer a promising and attractive solution due to its advantages regarding low cost effectiveness, convenience, ability to treat highly concentrated nitrate effluents and environmental friendliness [5,6].

As the products of nitrate electroreduction are critically dependent on the nature of the cathode material [7,8], several simple metal electrodes (nickel, platinum, graphite, glassy carbon, copper, etc.) have been widely used [9–14]. Compared to other materials, Cu metal has shown good catalytic character for this reaction [15–17], but required high potentials [18,19] and tend to be poisoned by the species formed during the electrochemical process [20]. This considerable drawback limits their use for large scale applications. To overcome these problems, the use of modified electrodes has received considerable attention in recent years. They offer many advantages, such as wider operational potential window, easy manufacture, low price, renewable surface and longer life time [21–23]. In the other hand, ZnO are the object of quickly growing in the last few years, due to its number of exciting properties [24–26]. It is a wide band gap semiconductor material with Eg ≈3.3 eV and large excitonic binding energy of ~60 meV [27]. It presents environmentally friendly properties without toxic by products [28], low price, high chemical and thermal stabilities. Due to these excellent properties, ZnO nanomaterials have been used as efficient electron mediators for the fabrication of electrochemical sensors. The electrochemical reduction

---

*Corresponding author.

of nitrate ions has been investigated over a large number of modified electrodes, as metallic modified electrode [29,30], conductive polymer modified electrode [31] or hybrid material [32]. For example, Cu/nafion/carbon nanofibers modified electrodes allowed high nitrate reduction rates into nitrogen species. To our knowledge, fewer research articles have been published on electro catalytic activity of ZnO towards nitrate.

The main objective of the present study is to elaborate ZnO copper modified electrode by electrodeposition method for the selective reduction of NO_3^- under neutral pH condition. The electrocatalytic activity of the as-prepared ZnO/Cu electrode is thoroughly investigated by cyclic voltammetry (CV) and chronoamperometry and compared with that of a pure Cu surface. The influence of ZnO electrochemical parameters (potential applied, time, temperature) was study on the nitrate reduction reaction. The morphology and structure of the ZnO films were also determined.

2. Materials and methods

2.1. Reagents and solutions

All chemicals were of analytical-reagent grade from Merck or Fluka and were used directly without further purification. All aqueous solutions were prepared with bi-distilled water (presenting high resistance ~18 MΩ). The supporting electrolyte used in all the experiments was 0.1 M KNO_3 or 0.1 M phosphate buffer solutions.

2.2. Apparatus

All the electrochemical experiments were carried out using a potentiostat/galvanostat (Autolab PGSTAT30) coupled with HP computer under "Voltamaster logitiel". The electrochemical cell was assembled with a conventional three-electrode system: a bare Cu or ZnO/Cu were employed as working electrodes. Platinum wire is used as auxiliary electrode and a saturated calomel electrode (SCE) as reference. All the potentials were expressed with respect to this reference.

The surface morphology of the modified electrode was investigated by a scanning electron microscope (SEM) (Hitachi, S-570). X-ray diffraction (XRD) analyses were performed on a Siemens D5000 diffractometer using filtered CuKα (λ = 0.15406 nm) radiation for 2θ angles between 30°and 40°. The diffractometer was operated at 40 kV, room temperature, with a scanning rate of 10°/min.

2.3. Preparation of the synthesized ZnO/Cu electrode

A wet electrochemical method was employed for the synthesis of ZnO thin films. They were elaborated from an electrolyte containing 5 10^{-3} M Zn $(NO_3)_2$, $6H_2O$ and 0.1 M KNO_3 at 70°C using various potentials (–0.6, –0.8, –1 and –1.2V/SCE) and different deposition times (5, 10, 15, 20, 25 and 30 min). The pH was fixed at 6.8.

Before the electrodeposition process, the massive Cu electrode was polished using 1200 grit emery paper, degreased with acetone, cleaned with twice distilled water and dried with a soft tissue paper. This Cu electrode was then used as the working electrode for the ZnO electrodeposition process.

3. Results and discussion

3.1. Electrochemical study of ZnO deposition

Prior to the development of ZnO by chronoamperometry, we found it useful to consider the voltammetric behavior of ZnO deposit. The cyclic voltammetry study was performed in a potential range of –0.5 to –1.6 V/SCE onto the copper substrate. The potential scan was initiated in the negative direction from the open circuit potential (OCP) at a scan rate of 8 mV s^{-1} (Fig. 1). We can see in Fig. 1 that the cathodic current begins to increase for a potential close to –0.4 V followed by a peak around –0.7 V and then reached a quasi-plateau in current until –1 V. This potential area corresponds to the reduction of nitrate ions into nitrite [16] (standard potential: –0.248 V/SCE). The last increase in current for potential more cathodic than –1 V corresponds to the water reduction reaction. No anodic peak appears in the return sweep, indicating that no metallic zinc deposit is formed. While Cu substrate presents a low over potential for nitrate reduction, the followed well-known mechanism [25] can be proposed: nitrate reduction producing hydroxide ions, induced precipitation of zinc hydroxide at electrode surface that is followed by its conversion in zinc oxide due to the temperature. The following reactions summarized this ZnO deposition process:

$$NO_3^- + H_2O + 2\,e^- \rightarrow NO_2^- + 2\,OH^- \quad (1)$$

$$Zn^{2+} + 2\,OH^- \rightarrow Zn\,(OH)_2 \quad (2)$$

$$Zn\,(OH)_2 \rightarrow ZnO + H_2O \quad (3)$$

Accordingly to elaborate the ZnO films, the potential window chosen was from –0.6 to –1.2 V, a more cathodic poten-

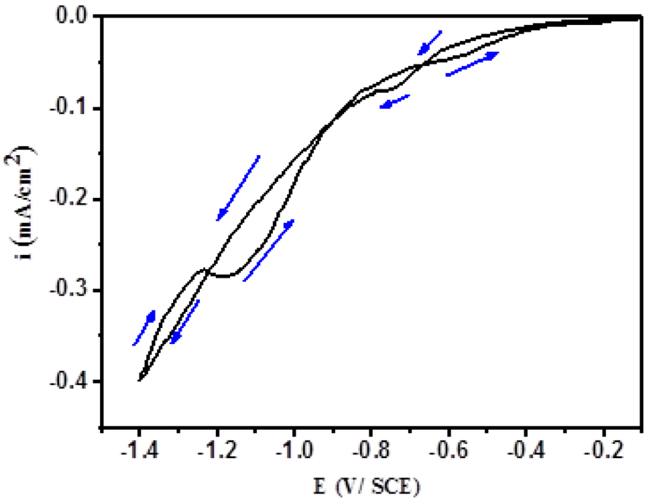

Fig. 1. Cyclic voltammogram of 5 mM Zn $(NO_3)_2$ + 0.1 M KNO_3 solution recorded using Cu electrode, pH = 6.8, T = 70°C, scan rate = 8 mV/s.

tial promoting higher deposition rates. The obtained current transients are illustrated in Fig. 2. After an initial sharp peak, the current decreases rapidly in the first few seconds due to the charge of the double layer which can be accompanied by the adsorption of ZnO at the interface. Then, the current stabilizes to form a plateau corresponding to the stability of ZnO. The more cathodic applied potential; the higher are the current plateau values leading to an increase in zinc oxide deposition with a probable water reduction at –1.2 V.

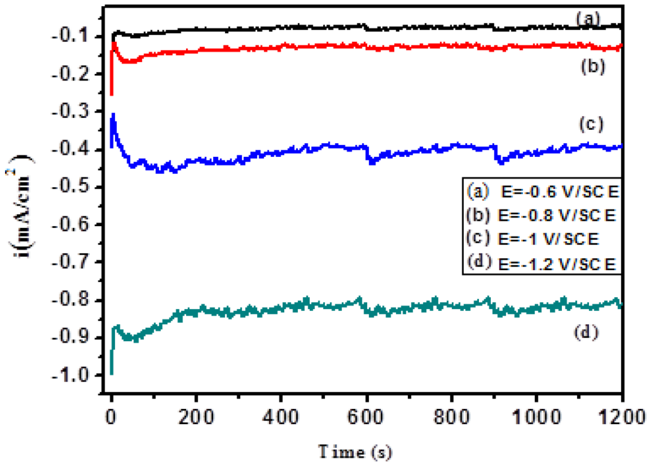

Fig. 2. Chronoamperometric response of Cu electrode in solution containing: [Zn $(NO_3)_2$] = 5 mM and [KNO_3] = 0.1 M at different potentials (a) –0.6; (b) –0.8; (c) –1 and (d) –1.2 V/SCE. pH = 6.8, T = 70°C, scan rate = 8 mV/s.

3.2. Morphological and structural properties of the synthesized ZnO thin films

SEM micrographs and XRD spectra for a selected ZnO/Cu electrodes synthesized at 20 min electrodeposition time are shown in Fig. 3 and Fig. 4 respectively. It can be noted that, the morphology of the deposit obtained at –0.6 V (Fig. 3a) presents a grain structure, with an inhomogeneous distribution. Increasing the potential at –0.8 V (Fig. 3b), the deposit becomes more compact and homogeneous, with a surface made of hexagonal shapes stems. For more cathodic potentials (Fig. 3c and d), the morphology changes to an oriented flower shape and each flower consists of petals. ZnO nanoflowers offer a large surface area that expects to enhance electrocatlytic activity. The layer appears more compact and more homogeneous at –1 V in comparison to –1.2 V where some lacks and heterogeneities can be attributed to the side reaction of water reduction.

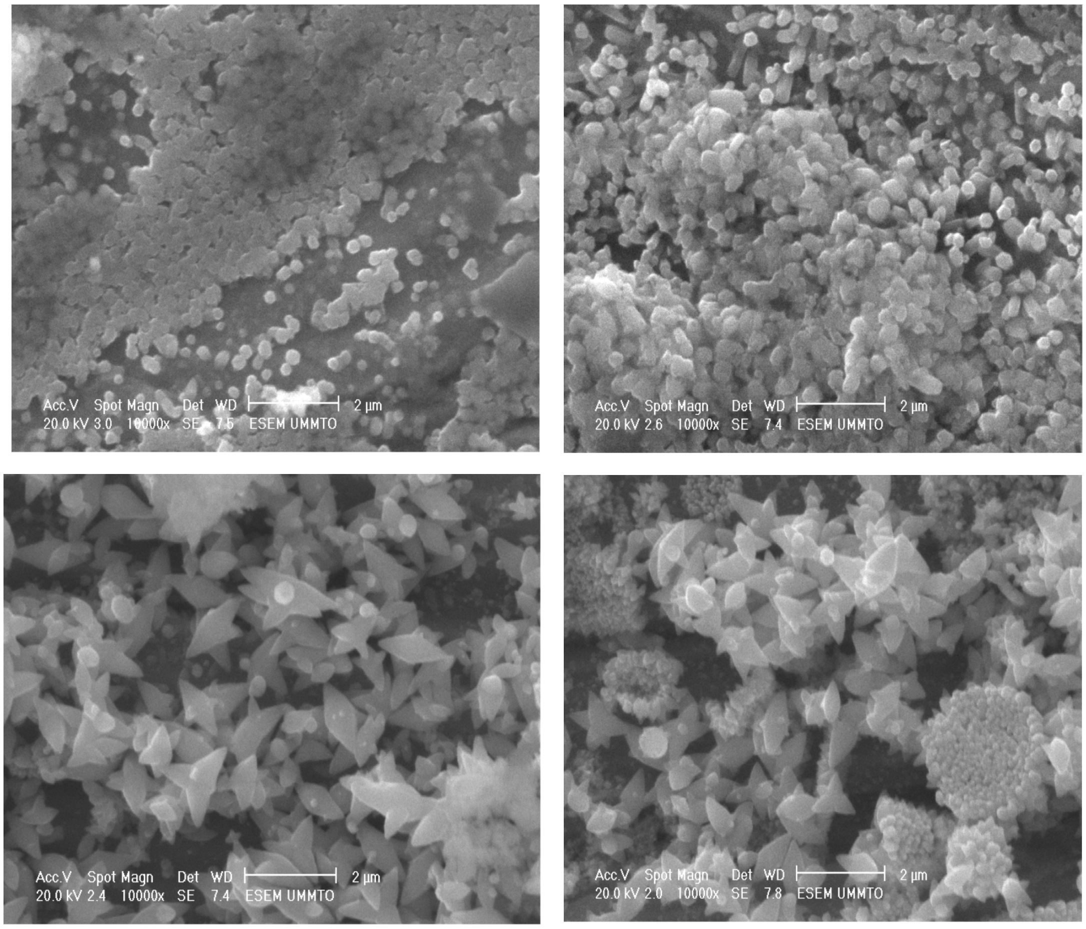

Fig. 3. SEM images of ZnO thin films obtained at different voltages: (a): –0.6 V, (b): –0.8 V, (c): –1 V and (d): –1.2 V, in 5 mM Zn $(NO_3)_2$ + 0.1 M KNO_3 solution, pH = 6.8, T = 70°C, on Cu electrode.

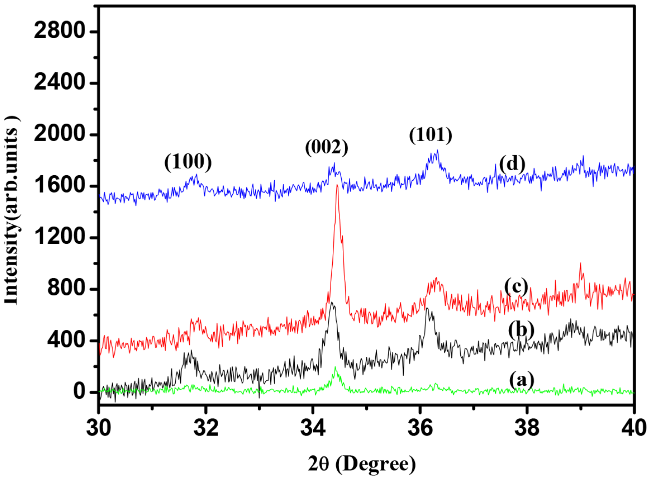

Fig. 4. XRD patterns of ZnO thin films obtained at different voltages: (a): –0.6 V, (b): –0.8 V, (c): –1 V and (d): –1.2 V, in 5 mM $Zn(NO_3)_2$ + 0.1 M KNO_3 solution, pH = 6.8, T = 70°C, on Cu electrode.

The XRD measurements confirm the formation of ZnO thin films on Cu substrate (Fig. 4). Three pronounced peaks for the respective 2θ values of 31.7, 34.4 and 36.3° are observed in the as-prepared samples. According to the 36–1451 JCPDS standard, they can be respectively indexed to the (100), (002), and (101) diffractions of the wurtzite-type ZnO crystal. No other diffraction peaks were detected. The sample electrodeposited at –1 V presents a significantly higher intensity of the (002) diffraction peak indicating that the ZnO flowers were preferentially oriented along the c-axis crystallographic direction.

3.3. Electrochemical behavior of nitrate ions on bare Cu and ZnO/Cu modified electrode

In order to evaluate the electrocatalytic behavior of the ZnO/Cu modified electrode towards nitrate reduction, we performed voltammograms in absence of NO_3^- ions on Cu electrode (Fig. 5a), in 0.01M KNO_3 electrolyte on bare Cu (Fig. 5b) and on ZnO/Cu modified electrodes (Fig.5.c). For the modified electrodes, ZnO deposits on Cu were obtained in 5 10^{-3} M Zn $(NO_3)_2$, $6H_2O$ + 0.1 M KNO_3 at 70°C, by chronoamperometry at –1 V for 20 min.

In NO_3^- solution (Figs. 5b and c), very broad reductive waves were observed from –0.4 V on the voltammograms recorded on both electrodes. They are followed by a new increase in current around –0.9 V due to the water reduction reaction. This wave was not performed from nitrate free electrolyte (Fig. 5a), thus can be attributed to the nitrate reduction, in good agreement with literature [16]. Moreover, this reaction is under mass transfer control of nitrate from the bulk solution to the electrode/solution interface, as indicated by the peak formation. This wave is more intense on the modified electrode in comparison to the Cu one. That can be explained by an increase of the electronic transfer due to the enhancement in the surface area or to an electrocatalytic activity between ZnO and nitrate. Compared to the bare Cu electrode, the ZnO/Cu modified electrode promoted then nitrates reduction.

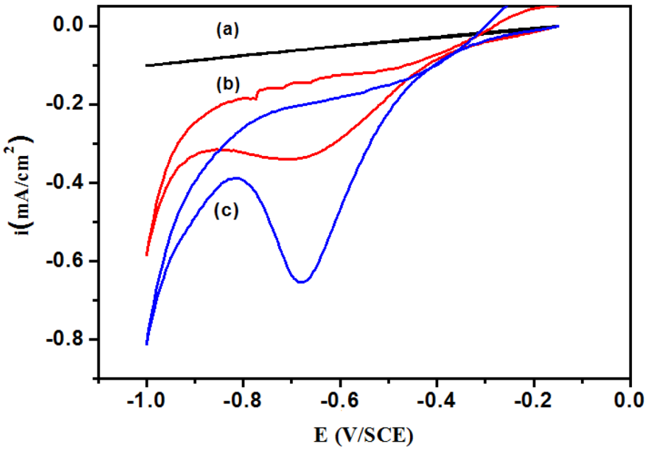

Fig. 5. Cyclic voltammograms obtained (a) on bare Cu electrode in [KCl] = 0.1 M; (b) on bare Cu electrode in ([KNO_3] = 0.01 M; (c) on ZnO/Cu modified electrode in [KNO_3] = 0.01 M, pH = 6.9. Scan rate = 8 mV/s.

3.4. Electrocatalytic reduction of nitrate onto ZnO/Cu modified electrode

It has already shown that the operating conditions have a direct effect on the morphology and properties of the deposits [13,24]. Thus, in the following parts the effects of electrodeposition time, bath temperature and deposition potential on the morphology and structure of the ZnO deposits were study as their possible influence on the electrocatalytic activity towards the nitrate reduction.

3.4.1. Effects on NO_3^- reduction of potentials and deposition times used for ZnO formation on Cu

ZnO deposits were obtained on Cu in 5 10^{-3} M $Zn(NO_3)_2$ + 0.1 M KNO_3 for different ZnO deposition times (5, 10, 15, 20, 25 and 30 min) at potential values of –0.6 V to –1.2 V. Figs. 6a, b, c and d show the curves performed in 0.01 M KNO_3 on these different ZnO/Cu modified electrodes. The cathodic reduction waves increased in the CVs with increasing electrodeposition time, suggesting that the morphology and the structure of the deposits have a great influence on the electrocatalytic activity of ZnO/Cu modified electrodes towards nitrate reduction. It can be observed whatever the potential used to form the ZnO deposits, that a 20 min ZnO electrodeposition time leads to sharper reduction peaks and higher current intensities for the nitrate reduction.

Fig. 6e was performed in nitrate solution, on the film obtained after 20 min at different potentials. The nitrate reduction wave increase with the potential until –1 V, and is quite stable between –1 and –1.2 V. This increase in electrocatalytic activity is probably due to the specific morphology shown by SEM analysis. At –1 V, the ZnO deposits are composed by dense flowers that covered the Cu substrate leading to the increase in the surface area. On the contrary, the electrocatalytic nitrate reduction decreases on the film at –1.2 V probably due to the poor morphology of ZnO because of water competing reaction.

Thus, ZnO optimum values towards nitrate reduction were determined to be 20 min and –1 V.

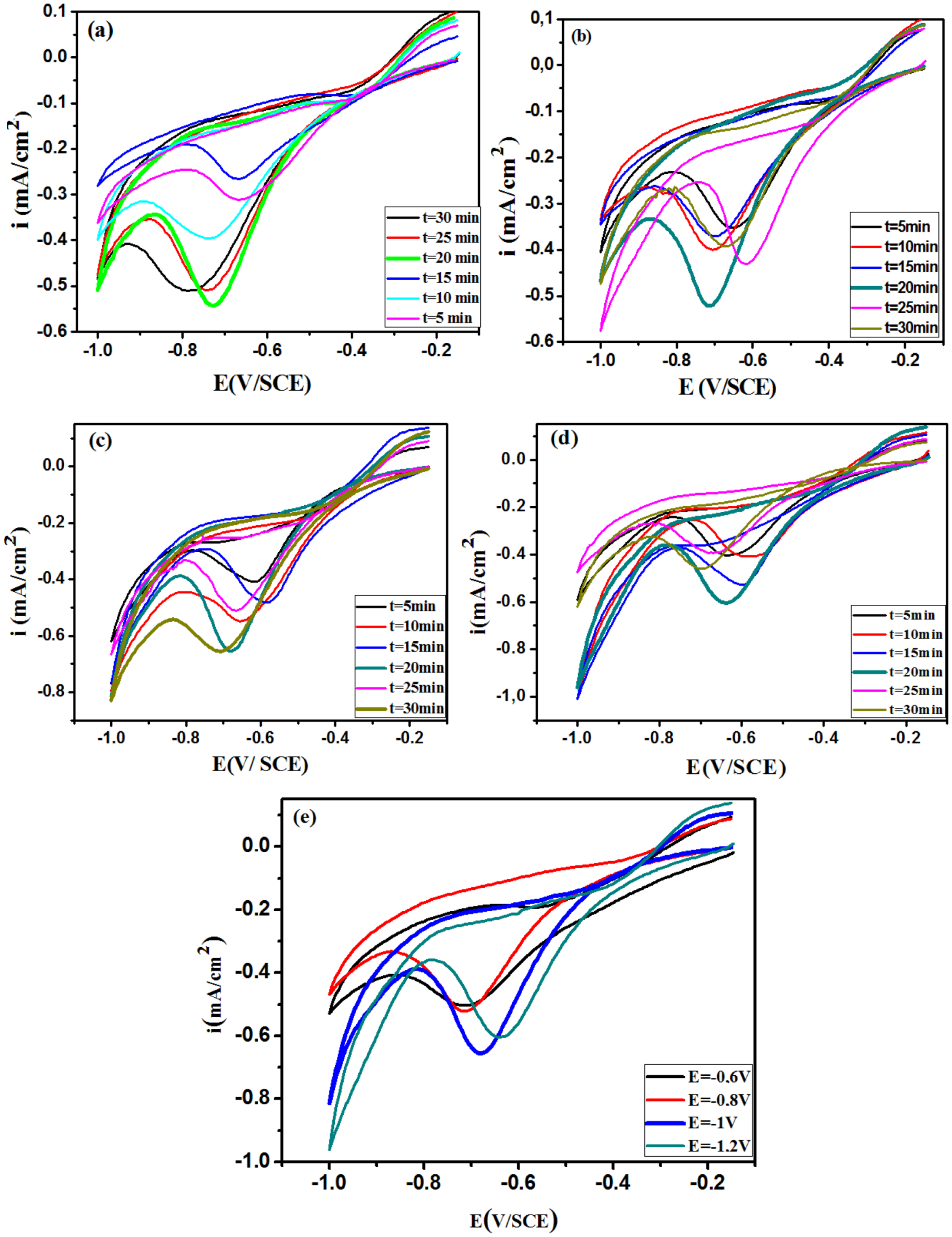

Fig. 6. Cyclic voltammograms in 0.01 M KNO_3 (pH = 6.9) on ZnO/Cu modified electrodes. Scan rate = 8 mV/s. ZnO deposits were obtained in 5 10–3 M $Zn(NO_3)_2$ + 0.1 M KNO_3 for different ZnO deposition times (5, 10, 15, 20, 25 and 30 min) at potential values of –0.6 V (a), –0.8 V (b), –1 V (c), –1.2 V (d). For (e): ZnO deposits were obtained for 20 min at different potentials (E = –0.6, –0.8, –1, –1.2 V).

3.4.2. Effects on NO_3^- reduction of temperatures used for ZnO formation on Cu

Fig. 7 shows the cyclic voltammetry performed in 0.01 M KNO_3 on different ZnO/Cu modified electrodes obtained in 5 10^{-3} M Zn $(NO_3)_2$ + 0.1 M KNO_3 at –1 V for 20 min and different temperatures. As can be seen from Fig. 7, an increase in temperature of the bath used to get the ZnO films results in an increase in the intensity of the peak of nitrate reduction. This result can be explained by a more efficient conversion of Zn $(OH)_2$ to ZnO during the ultimate step of the process (see reaction 3 in section 3.1).

ZnO deposits were elaborated on Cu electrode for the best electrochemical parameters determined previously: 5 10^{-3} M Zn $(NO_3)_2$ + 0.1 M KNO_3 at 70°C, –1 V for 20 min.

3.4.3. Electrochemical behavior of ZnO/Cu modified electrode in nitrate solution for different nitrate concentrations

The electroactivity towards nitrate reduction on the best ZnO/Cu modified electrode was then studied for different nitrate concentrations from 0.03 to 10 mM of KNO_3 (Fig. 8).

The cathodic peak current observed increases with increasing NO_3^- concentration in the solution. This catalytic peak current has a linear relationship with the concentration of NO_3^- in the range 0.03–10 mm with a correlation coefficient of 0.999 (see inset in Fig. 8). Electroreduction of NO_3^- onto this modified electrode can then be used as sensor for the determination of nitrate concentration in solution.

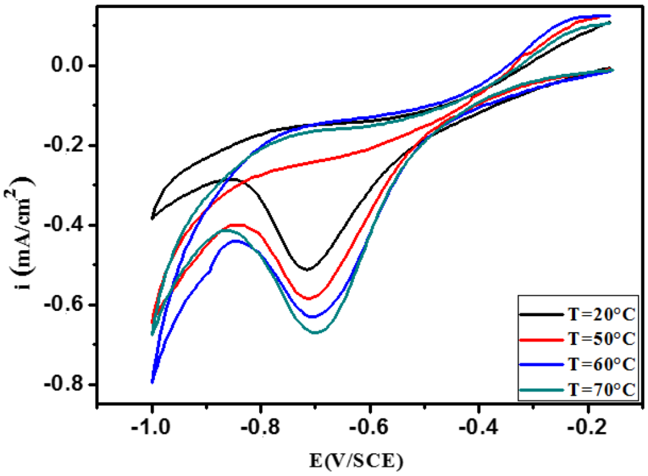

Fig. 7. Cyclic voltammograms on ZnO/Cu modified electrodes in 0.01 M KNO_3, (pH = 6.9). Scan rate = 8 mV/s. ZnO deposits were obtained in 5 10^{-3} M Zn $(NO_3)_2$ + 0.1 M KNO_3 at –1 V for 20 min at different temperatures.

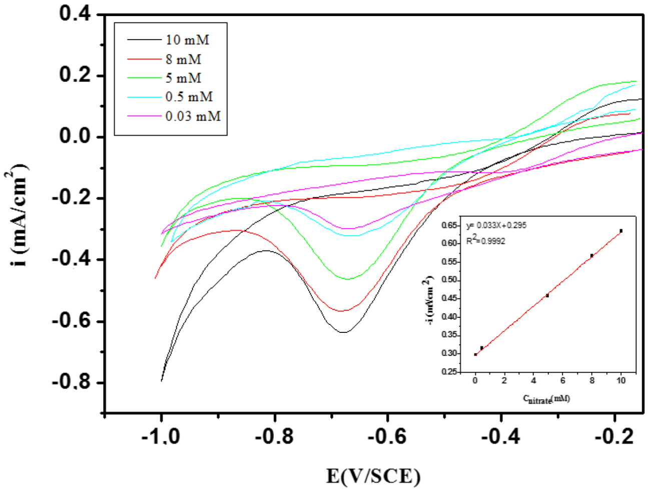

Fig. 8. Cyclic voltammograms on ZnO/Cu modified electrode for various $[KNO_3]$ = 0.03 to 10 mM, (pH = 6.9). Scan rate = 8 mV/s. ZnO deposit was obtained in 5 10^{-3} M $Zn(NO_3)_2$ + 0.1 M KNO_3 at 70°C, –1 V for 20 min.

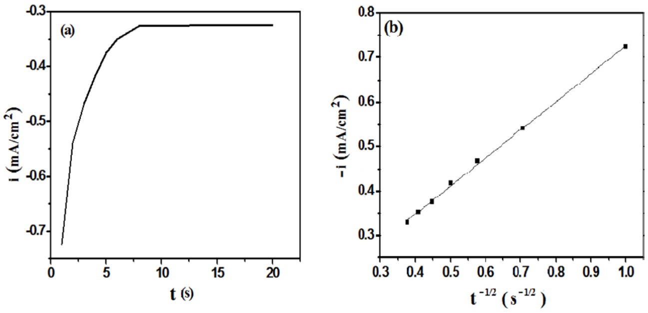

Fig. 9. (a) Chronoamperometric response on ZnO/Cu modified electrode in solution in 0.01 M KNO_3, (pH = 6.9) at E = –0.68 V/SCE. (b) Dependence of the current with $t^{-1/2}$.

3.4.4. Chronoamperometric measurement on ZnO/Cu modified electrode in nitrate solution

Fig. 9a illustrates the current versus time transients for the best ZnO/Cu modified electrode in 10 mM KNO_3 at a cathodic potential of –0.68 V/SCE. This potential is set at the maximum of the peak current for nitrate reduction determined previously (Fig. 6e). The shape of this transient corresponds to a deposit formation involving a direct reduction under diffusional control characterized by a slow decrease in current. Moreover, the current variation versus $t^{-1/2}$ being linear with a correlation coefficient of 0.9984 (Fig. 9b), the nitrate reduction effectively is under mass transfer controlled as presumed from Fig. 5. From the slope of this line, we can then estimate the total number of electrons transferred during the reaction of nitrate reduction using the Cottrell equation:

$$i = n\cdot F\cdot A\cdot D^{\frac{1}{2}}\cdot C_{NO3}{}^{-}\cdot \pi^{\frac{-1}{2}}\cdot t^{\frac{-1}{2}} \tag{4}$$

where *C* is the bulk concentration (mol·cm^{-3}), *F* the Faraday constant, *A* the electrode area, *D* the diffusion coefficient of nitrate in solution, *n* the number of electron transferred, *i* the current.

For $C_{NO_3^-}$ = 0.01 M and D = 2.10^{-5} cm^2·s^{-1} [5], we can then determine n equal to 7.901 (*n* = 8). In accordance with the number of electrons involved, it appears that on the ZnO/Cu modified electrode, nitrates are reduced in ammonia (reaction 4) rather than nitrogen (reaction 5) as mentioned on other electrode [32].

$$NO_3^- + 6\,H_2O + 8\,e^- \rightarrow NH_3 + 9\,OH^- \tag{5}$$

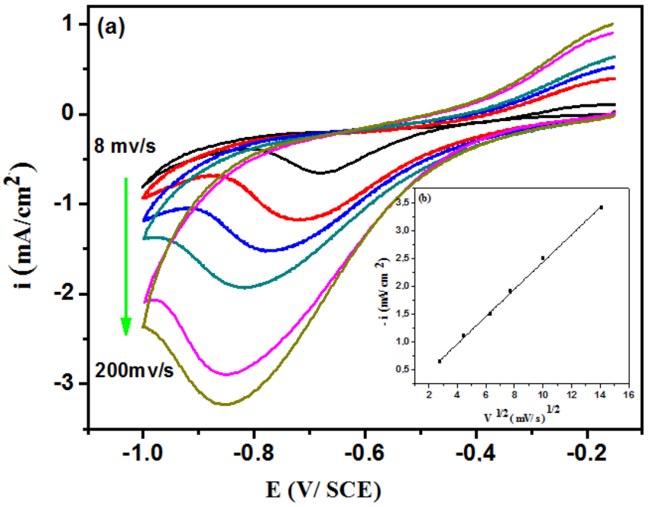

Fig. 10 (a). Cyclic voltammetry sweep curves on ZnO/Cu modified electrode in 0.01 M KNO_3 (pH = 6.9) at various scan rates from 8 to 200 mV/s and (b) the insert figure is the plot between the cathodic current versus the square root of the scan rate.

$$NO_3^- + 6\,H_2O + 10\,e^- \rightarrow 2\,N_2 + 12\,OH^- \qquad (6)$$

The one step reduction reaction was indicative of rapid NO_3^- reduction process. Moreover, the ZnO/Cu modified electrode might be used for ammonia synthesis, a useful product from the industrial point of view.

There are a number of reports in the literature of electrochemical reduction of nitrate containing solutions to ammonia. De et al. [33] have used cyclic voltammetric and Tafel slope determination to study the nitrate and nitrite ion reduction at the surface of an iridium-modified carbon fibre electrode in aqueous sodium perchlorate solutions at pH 7. They demonstrated a two-step nitrate reduction mechanism in which nitrate is first reduced to nitrite and then further reduced to ammonia. Scharifker et al. [34] have shown that nitrate reduction can be catalyzed during an electrodeposition process, specifically during electrodeposition of thallium from TI^{3+} solutions.

Cattarin [35] has investigated the reduction of nitrate and nitrite ions in 1 M sodium hydroxide (NaOH) supporting electrolyte, with both copper and silver electrodes. Electrolysis was performed at –1.4 V/SCE. At this potential nitrate is predominantly reduced to nitrite on silver electrodes, while ammonia is the predominant product for copper electrodes.

3.4.5. Effect of sweep rate on NO_3^- reduction

Fig. 10a shows the CV responses on ZnO/Cu electrode in 10 mM KNO_3 at different scan rates (8, 20, 40, 60, 100 and 200 mV/s). The nitrate reduction current increases with the increase of sweep rate and was proportional to the square root sweep rate (Fig. 10b), implying that the reduction process is effectively under diffusion controlled.

4. Conclusion

The development of specific analytical methods for the detection and destruction of nitrate is of great importance to limit pollution of the natural environment.

In this study, the reduction of nitrate ions in neutral conditions on copper electrodes modified by ZnO electrodeposited thin films was investigated. ZnO electrodeposition parameters such as potential and time have a great influence on the structure and morphology of the deposit.

ZnO/Cu modified electrodes has obviously electrocatalytic activity towards nitrate reduction. The best ZnO electrodeposition parameters for nitrate reduction were determine: at –1 V for 20 min and 70°C ZnO deposit presents an oriented polycrystalline structure with a flower morphology. The results are reproducible over a large nitrate concentration range from 0.03 to 10 mm. The determination of the quantity of electrons exchanged during nitrate reduction reaction proves ammonia formation that is a useful product from an industrial point of view. ZnO/Cu modified electrode might be used for ammonia synthesis as well as NO_3^- detection.

References

[1] Y.H. Kim, E.D. Hwang, W.S. Shin, J.H. Choi, T.W. Ha, S.J. Choi, Treatments of stainless steel wastewater containing a high concentration of nitrate using reverse osmosis and nanomembranes, Desalination, 202 (2007) 286–292.

[2] A. Elmidaoui, F. Elhannouni, M.A. Sahli, L. Chay, H. Elabbassi, M. Hafsi, D. Largeteau, Pollution of nitrate in Moroccan ground water: removal by electrodialysis, Desalination, 136 (2001) 325–332.

[3] R. Molinari, P. Argurio, L. Romeo, Studies on interactions between membranes (RO and NF) and pollutants (SiO_2, NO_3^-, Mn^{++} and humic acid) in water, Desalination, 138 (2001) 271–281.

[4] S. Aslan, A. Turkman, Combined biological removal of nitrate and pesticides using wheat straw as substrates, Process Biochem., 40 (2005) 935–943.

[5] D. Reyter, G. Chamoulaud, D. Bélanger, L. Roué, Electrocatalytic reduction of nitrate on copper electrodes prepared by high-energy ball milling, J. Electroanal. Chem., 596 (2006) 13–24.

[6] L. Durivault, O. Brylev, D. Reyter, M. Sarrazin, D. Bélanger, L. Roué, Cu–Ni materials prepared by mechanical milling: Their properties and electrocatalytic activity towards nitrate reduction in alkaline medium, J. Alloys Comp., 432 (2007) 323–332.

[7] K. Shimazu , R. Goto, K. Tada, Electrochemical reduction of nitrate ions on tin-modified platinum and palladium electrodes, Chem. Lett., 31 (2002) 204–205.

[8] J.W. Peel, K.J. Reddy, B.P. Sullivan, J.M. Bowen, Electrocatalytic reduction of nitrate in water, Water Res., 37 (2003) 2512–2519.

[9] A.L. Santos, L.J. Denier, H. Varela, The effect of ultra-low proton concentration on the electrocatalytic reduction of nitrate over platinum, Catal. Commun., 9 (2008) 269–272.

[10] S. Taguchi, J.M. Feliu, Electrochemical reduction of nitrate on Pt (S) [n (1 1 1) × (1 1 1)] electrodes in perchloric acid solution, Electrochim. Acta, 52 (2007) 6023–6033.

[11] M.T. de Groot, M.T.M. Koper, The influence of nitrate concentration and acidity on the electrocatalytic reduction of nitrate on platinum, J. Electroanal. Chem., 562 (2004) 81–94.

[12] S. Taguchi, J.M. Feliu, Kinetic study of nitrate reduction on Pt (1 1 0) electrode in perchloric acid solution, Electrochim. Acta, 53 (2008) 3626–3634.

[13] B. Keita, E. Abdeljalil, L. Nadjo, R. Contant, R. Belgiche, First examples of efficient participation of selected metal-ion-substituted heteropolyanions in electrocatalytic nitrate reduction, Electrochem. Com., 3 (2001) 56–62.

[14] D. Reyter, D. Bélanger, L. Roué, Study of the electroreduction of nitrate on copper in alkaline solution, Electrochim. Acta, 53 (2008) 5977–5984.

[15] K. Bouzek, M. Paidar, A. Sadilkova, H. Bergmann, Electrochemical reduction of nitrate in weakly alkaline solutions, J. Appl. Electrochem., 31 (2001) 1185–1193.

[16] N. Aouina, H. Cachet, C. Debiemme-Chouvy, T.T. Mai Tran, Insight into the electroreduction of nitrate ions at a copper electrode, in neutral solution, after determination of their diffusion coefficient by electrochemical impedance spectroscopy, Electrochim. Acta, 55 (2010) 7341–7345.

[17] E. Pérez-Gallent, C. Marta, I. Katsounaros, M.T.M. Koper, Electrocatalytic reduction of nitrate on copper single crystals in acidic and alkaline solutions, Electrochim. Acta, 227 (2017) 77–84.

[18] J.E. Newbry, M. Pilar Lopez de Haddad, Amperometric determination of nitrite by oxidation at a glassy carbon electrode, Analyst, 110 (1985) 81–82.

[19] A.Y. Chamsi, A.G. Fogg, Oxidative flow injection amperometric determination of nitrite at an electrochemically pre-treated glassy carbon electrode, Analyst, 113 (1988) 1723–1727.

[20] J.N. Barisci, G.G. Wallace, Development of an improved on-line chromatographic monitor with new methods for environmental and process control, Anal. Chim. Acta, 310 (1995) 79–92.

[21] K. Kalcher, J.M. Kauffmann, J. Wang, I. Svancara, K. Vytras, C. Neuhold, Sensors based on carbon paste in electrochemical analysis: a review with particular emphasis on the period 1990–1993, Electroanalysis, 7 (1995) 5–22.

[22] I. Svancara, K. Vytras, J. Barek, J. Zima, Carbon paste electrodes in modern electroanalysis (a review), Crit. Rev. Anal. Chem., 31 (2001) 311–345.

[23] A. Hamam, D. Oukil, H. Hammache, L. Makhloufi, B. Saidani, Polypyrrole coated cellulosic substrate modified by copper oxide as electrode for nitrate electroreduction, Surf. Rev. Lett., 22 (2015) 1550065.

[24] N. Ait Ahmed, H. Hammache, L. Makhloufi, M. Eyraud, S. Sam, A. Keffous, N. Gabouze, Effect of electrodeposition duration on the morphological and structural modification of the flower-like nanostructured ZnO, Vacuum, 120 (2015) 100–106.

[25] N. Ait Ahmed, M. Eyraud, H. Hammache, F. Vacandio, S. Sam, N. Gabouze, New insight into the mechanism of cathodic electrodeposition of zinc oxide thin films onto vitreous carbon, Electrochim. Acta, 94 (2013) 238–244.

[26] N. Ait Ahmed, G. Fortas, H. Hammache, S. Sam, A. Keffous, A. Manseri, Structural and morphological study of ZnO thin films electrodeposited on n-type silicon, Appl. Surf. Sci., 256 (2010) 7442–7445.

[27] S.J. Pearton, D.P. Norton, K. Ip, Y.W. Heo, T. Steiner, Recent advances in processing of ZnO, J. Vac. Sci. Technol. B, 22 (2004) 932–948.

[28] Y. Wang, J. Yang, H. Jia, M. Yu, H. Jin, Self-assembled urchin-like ZnO nanostructures fabricated by electrodeposition-hydrothermal method, J. Alloys Comp., 665 (2016) 62–68.

[29] M.A. Hasnat, M.A. Islam, S.M. Borhanuddin, M.R.U. Chowdhury, M. Machida, Influence of Rh on electrocatalytic reduction of NO_3^- and NO_2^- over Pt and Pd films, J. Molec. Catal. A: Chemical, 317 (2010) 61–67.

[30] M.A. Hasnat, N. Ahamad, S.M.N. Uddin, N. Mohamed, Silver modified platinum surface/H^+ conducting Nafion membrane for cathodic reduction of nitrate ions, Appl. Surf. Sci., 258 (2012) 3309–3314.

[31] X. Zhang, J. Wang, Z. Wang, Sh. Wang, Electrocatalytic reduction of nitrate at polypyrrole modified electrode, Synthetic Metals, 155 (2005) 95–99.

[32] M.Y. Chaika, E.V. Bulavina, T.A. Kravchenko, Hybrid electrode materials based on ion-exchange matrix containing copper nanoparticles and carbon fibers, for the electroreduction of nitrate ions, Nanotech. Russia, 10 (2015) 565–569.

[33] D. De, J.D. Englehardt, E.E. Kalu, Cyclic voltammetric studies of nitrate and nitrite ion reduction at the surface of iridiummodified carbon fiber electrode. J. Electro chem. Soc., 147 (2000) 4224–4228.

[34] B.R. Scharifker, J. Mostany, A. Serruya, Catalytic reduction of nitrate during electro deposition of thallium from Tl^{3+} solution, Electro chem. Commun., 2 (2000) 448–451.

[35] S. Cattarin, Electrochemical reduction of nitrogen oxyanions in 1 M sodium hydroxide solutions at silver, copper and $CuInSe_2$ electrodes, J. Appl. Electrochem., 22 (1992) 1077–1081.