

Study of Electrocatalytical Reduction of Nitrate on Copper Electrode

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Abstract

This work aims to investigate the electro reduction of nitrate at copper electrode in HClO₄ medium by the linear sweep voltammetry and conductivity measurement methods. Two charge transfer steps were detected, the first one corresponding to adsorption and reduction of nitrate to nitrite and the second step consists of reducing nitrate to monoxide of nitrogen.

Keywords: electroreduction, nitrate, copper, linear sweep voltammetry, conductivity, square wave voltammetry.

Introduction

Pollution of ground and surface waters by nitrates is a wide spread and serious problem. Heavy utilization of artificial fertilizers has been known to cause penetration of large quantities of nitrates into ground and surface waters [1]. The nitrate has to be removed since its high concentration has a detrimental effect on environment and also limits the usage of water in industry. This contamination mainly due to liver stock faeces, industrial waste, or chemical fertilizers, represents a risk not only on aquatic ecosystems [2], but also for the human health [3, 4]. The maximum allowable concentration of nitrate as NO₃⁻ in drinking water, according to the world Health Organization recommendations, is 50 mg/L [5]. Several processes, including biological [6] and physico-chemical methods [7-10], are known for removing NO₃⁻ ions from contaminated water. However, these techniques present considerable drawbacks, such as low reaction

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rate, continuous monitoring, large amount of by-products, costly H₂ consumption or catalyst elaboration, which are hardly acceptable for large scale applications. In contrast, the electrochemical reduction of NO₃⁻ represents an attractive and promising solution due to its convenience, environmental friendliness, and low cost effectiveness [11]. A number of basic electrochemical research works related to nitrate ion reduction have been reported in the last two decades [12, 13]. Several works have been made to design active, selective electrodes. Single crystals [14], water-soluble porphyrins [15] and other modified electrodes [16, 17], and conductive polymers [18] have been extensively studied. Even at a monometallic electrode nitrate electroreduction is very complex, and strongly depends on the experimental conditions.

In the present work, the performance of electroreduction of nitrate on copper electrode has been investigated.

Experimental

Cyclic voltammetry, linear sweep voltammetry and square wave studies have been used to investigate the nitrate reduction reaction on a copper electrode in 0.1 M HClO₄ (pH~3-4) solution. A conventional three-electrode system consisting of a copper plate (1 cm²) as working electrode, platinum as counter electrode and SCE as reference electrode was used. The preparation of the working electrode surface consisted of polishing with emery paper, degreasing with acetone, washing with distilled water, followed by pickling in 50% HNO₃ solution, and washing with double distilled water.

Electrochemical experiments were performed using a Voltalab Potentiostat (model PGSTAT 100, Eco Chemie B. V. Utrecht. The Netherlands) driven by the general purpose electrochemical systems data processing software (Votala Master 4 software). A pH-meter (Radiometer Copenhagen, pHM210, Tacussel, French) was used for measuring pH values.

The solutions were prepared using chemically pure reagents and double distilled water and were not de-aerated because the oxygen reduction peak is separated from the nitrate reduction wave by several millivolts, and all measurements were made at room temperature (18 °C). The nitrate was added as NaNO₃.

Results and discussion

Cyclic and linear sweep voltammetry data

Fig. 1 (curve a) shows the Linear Sweep Voltammogram (LSV) of a copper electrode in 0.1 M HClO₄. No peak appears. The LSV of copper in presence of nitrate in 0.1 M HClO₄ (curve b) shows an abrupt increase of the cathodic current due to the nitrate reduction.

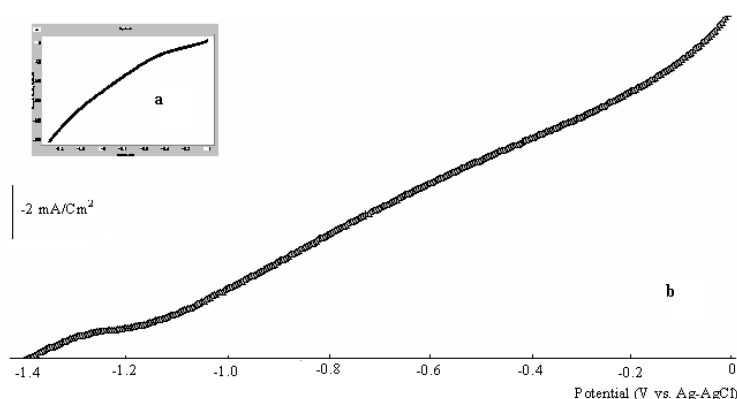


Figure 1. Linear sweep voltammogram of a Cu electrode in 0.1 M HClO₄ (curve a) and in presence of 0.235 M NaNO₃ (curve b). Scan rate: 50 mV.s⁻¹.

Fig. 2 shows the LVS's of copper in 0.1 M HClO₄ containing 0.235 M NaNO₃ as a function of the scan rate. The cathodic peak was shifted to more negative potentials as the scan rate increases. The number of electrons involved in the reduction peak can be determined for irreversible system by [19]:

$$j_p = -(2.99 \times 10^5)n(\alpha nc)^{1/2}AD^{1/2}v^{1/2}C \quad (1)$$

where A is the electrode surface area (1 cm²), C the bulk nitrate concentration (mol cm⁻³), D the nitrate diffusion coefficient (2 x 10⁻⁵ cm² s⁻¹), v the potential scan rate (Vs⁻¹), j_p the peak current (A), α the charge transfer coefficient, nc the number of electrons transferred in the rate determining step and n is the number of electrons involved for the considered reaction.

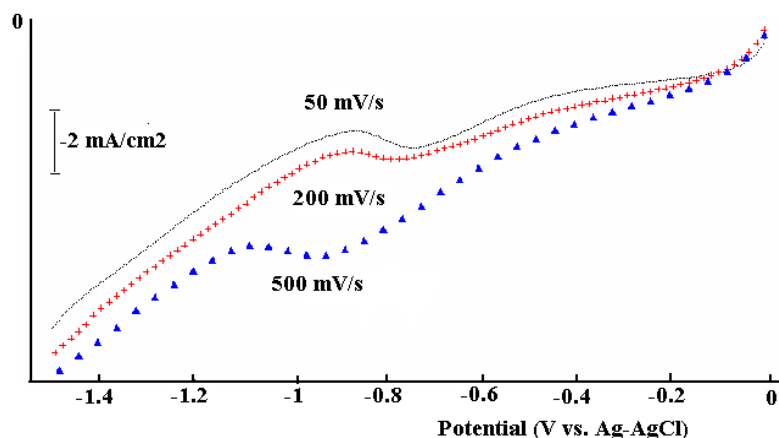


Figure 2. Linear sweep voltammograms of a Cu electrode recorded at different scan rates (50, 200 and 500 mV.s⁻¹) in 0.1 M HClO₄ + 0.235 M NaNO₃.

Equation 1 is valid in case where the interfacial process is controlled by the diffusion step; this hypothesis is verified by the diagram of impedance recorded for copper electrode in 0.1 M HClO₄ + NO₃⁻ solution (Fig. 3).

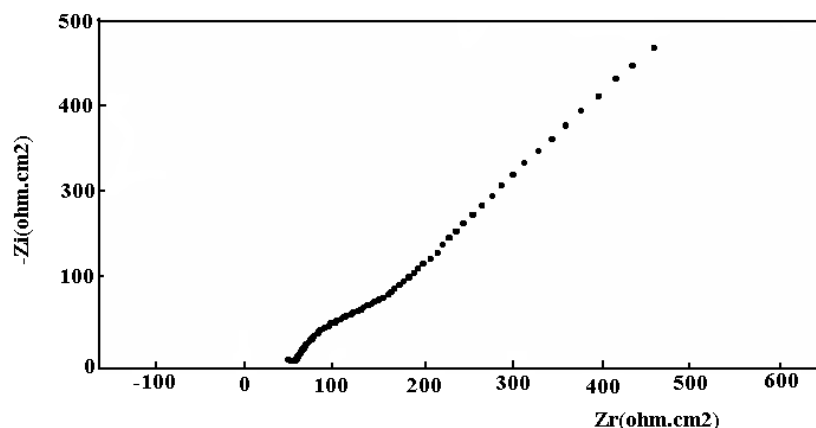


Figure 3. Electrochemical impedance spectra of Cu electrode in 0.1 M HClO₄ in the presence of 0.235 M NaNO₃. Scan rate: 50 mV.s⁻¹. 0.1 M HClO₄ + 0.235 M NaNO₃.

The LSV (Fig. 4) of copper in presence of nitrate recorded at 100 mV/s (scan rate) shows two reduction waves associated to reduction of nitrate or intermediates: an inflexion (C1) at about -0.58 V and a distinct peak (C2) at about -0.72 V.

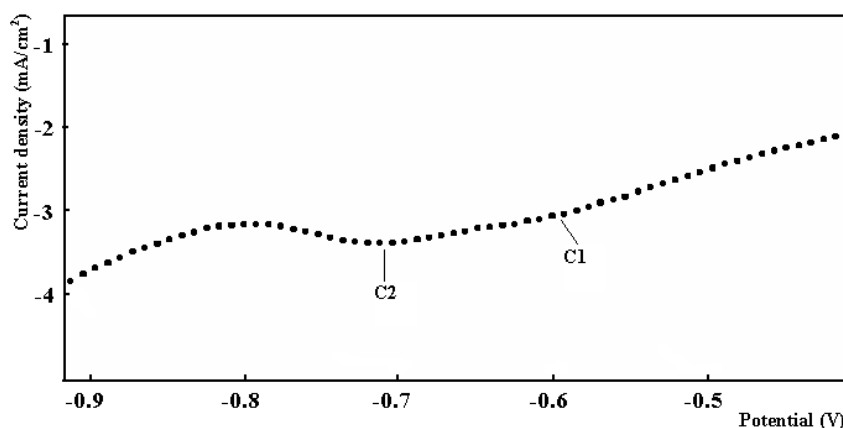
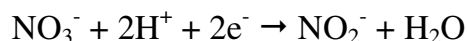


Figure 4. Linear sweep voltammogram of a Cu electrode in 0.1 M HClO₄ in presence of 0.235 M NaNO₃. Scan rate: 100 mV.s⁻¹.

At more negative potentials the current increases on account of hydrogen evolution reaction. The LSV obtained in presence of 0.01 M nitrite (NO₂⁻) in 0.1 M HClO₄ (Fig. 5 curve a) presents a similar shape except that currents are smaller, and that the C1 peak at -0.58 V does not appear, which may suggest that the inflection C1 is due to the reduction of the nitrate (NO₃⁻) to nitrite (NO₂⁻) through the following reaction:



The similarity of peak C2 in the presence of nitrate or nitrite suggests that it results from the reduction of nitrite.

A plot of the C2 peak potential (E_p) as a function of the $\ln v$ (v scan rate) is shown in Fig. 6, analyzing the dependence of the C2 peak potential (E_p) and of the $\ln v$ (v scan rate) in accordance with the relation:

$$E_p = E^\circ - RT/\alpha F [0.780 + \ln(D^{1/2}/K^\circ) + \ln(\alpha F v/RT)^{1/2}] \quad (2)$$

where E° is the formal potential of reaction, D the nitrate diffusion coefficient ($2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), v the potential scan rate (Vs^{-1}), α the charge transfer coefficient. At 298 K, $\alpha = 0.75$.

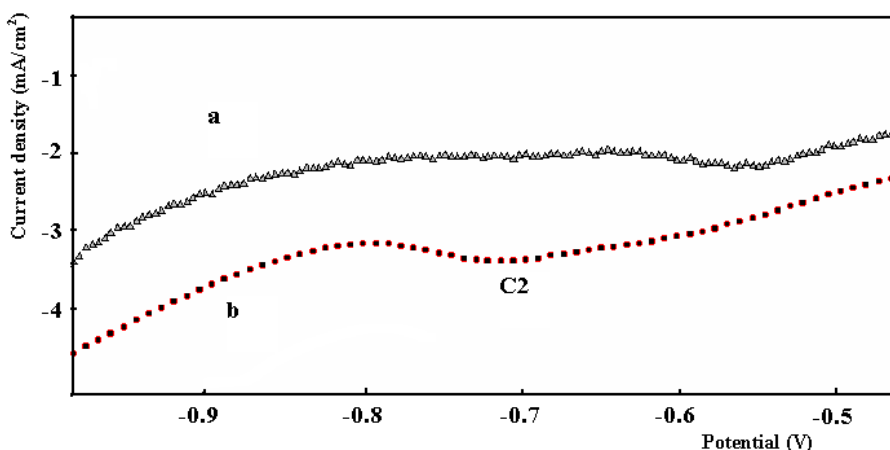


Figure 5. Linear sweep voltammograms of a Cu electrode in 0.1 M HClO_4 in presence of 0.235 M NaNO_3 (curve b) or 0.01 M NaNO_2 (curve a). Scan rate: $100 \text{ mV}\cdot\text{s}^{-1}$.

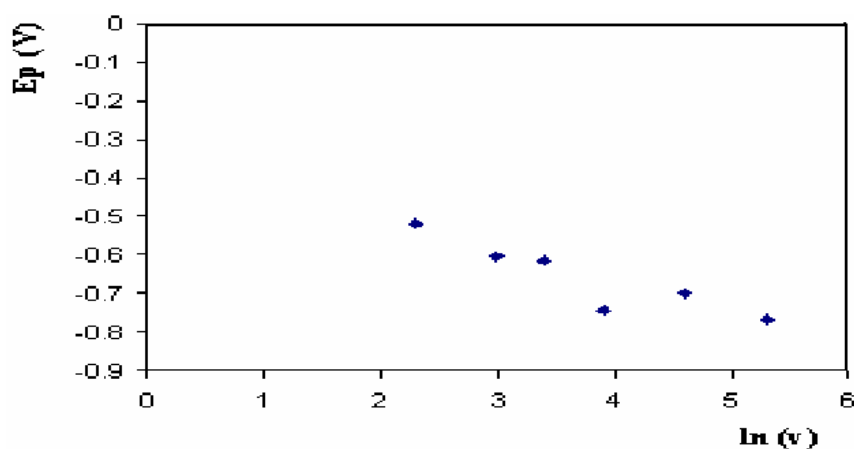
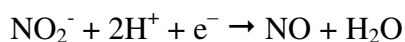


Figure 6. Plot of the peak potential function, $\ln v$ (scan rate).

Fig. 7 shows the dependence of peak (C2) current density, j_p , as a function of the square root of the scan rate $v^{1/2}$. A plot of the C2 peak current density, j_p , as a function of the square root of the scan rate $V^{1/2}$ is shown in Fig. 7. The number of electrons (n) involved in the reaction associated with the C2 peak was found to be 1, what corresponds to the following reaction:



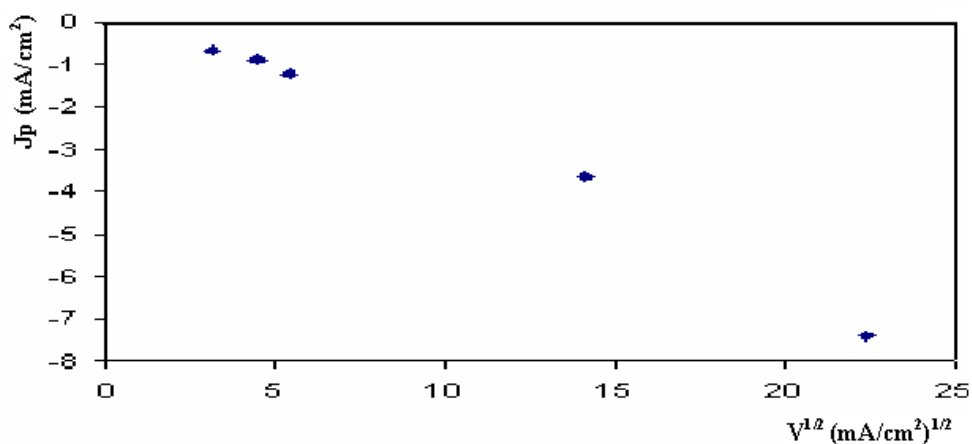


Figure 7. Variation of the peak current density (from LSV for system: Cu/ in 0.1 M HClO₄ in presence of 0.235M NaNO₃) as a function of the square root of the scan rate $v^{1/2}$.

The controlled potential electrolysis performed at -0.6 V. This potential value corresponds to the peak C1. During the electrolysis the conductivity of solution-time curves were recorded. The conductivity-time curves recorded have presented steps of constant conductivity for 250 minutes. Then the conductivity undergoes a significant decrease after 250 min of electrolysis from 25 to 5 S.cm², what corresponds probably to the disappearance of the ions loaded, confirming the second reaction characterized by the formation of a neutral molecule NO (Fig. 8).

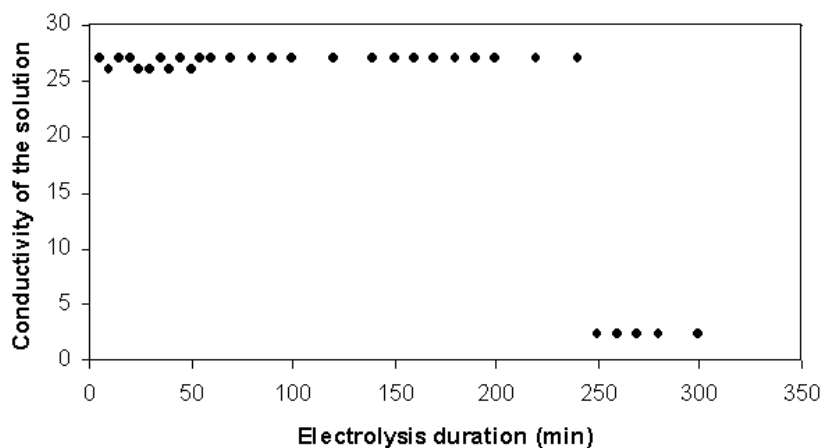


Figure 8. Dependence of the solution conductivity as a function of duration of NO₃⁻ electrolysis.

Other linear sweep voltammograms were recorded as a function of nitrate concentration. The results are summarized in Fig. 9.

According to Fig. 9, the peak potential shifts to the negative direction with an increase in nitrate concentration, which is in accordance with the behaviour of the irreversible charge transfer reactions. The peak current density increases with nitrate concentration, confirming the participation of nitrate or intermediates at charge transfer steps (Fig. 10).

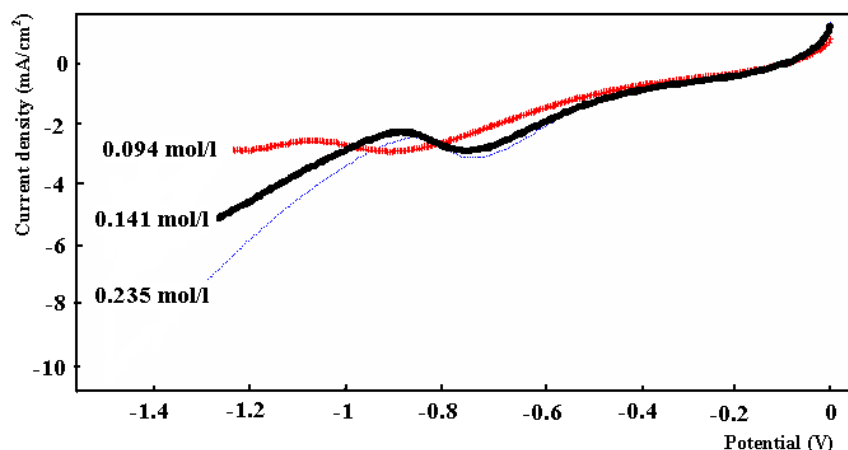


Figure 9. Linear sweep voltammograms at a Cu electrode recorded in 0.1 M HClO₄ containing different nitrate concentrations. Scan rate 50 mV.s⁻¹.

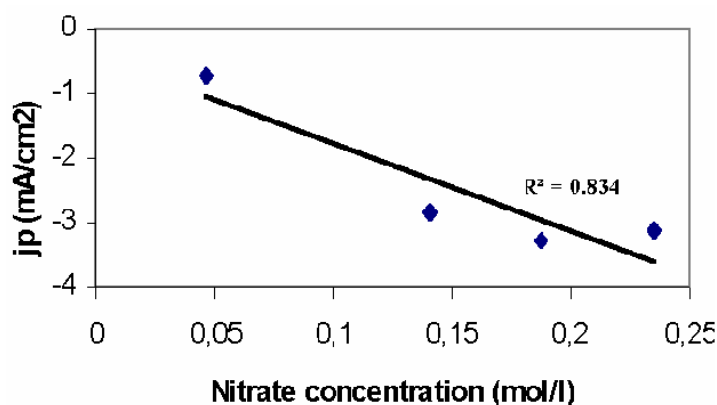


Figure 10. Effect of nitrate concentration on the peak current density (from LSV for system: Cu/ in 0.1 M HClO₄ in the presence of different concentrations of NaNO₃).

Fig. 11 shows the dependence of nitrate and formed nitrite concentrations during the electrolysis of 0.1 M HClO₄ solution containing 0.235 M NO₃⁻. In the course of the electrolysis the disappearing of nitrate and appearance of nitrite take place at the same rate.

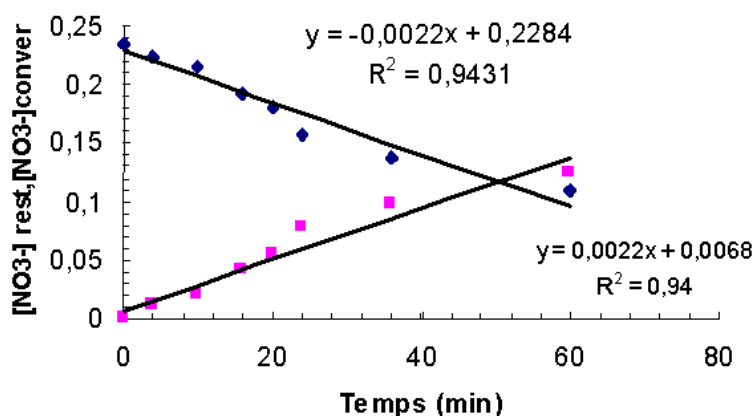


Figure 11. Evolution of consummate nitrate and formed nitrite according to the electrolysis duration.

Conclusion

The electrocatalytical reduction of nitrate at the copper electrode in 0.1 M HClO₄ has been investigated by the linear sweep voltammetry method. The reaction proceeds in two charge transfer steps. Nitrate is reduced to nitrite at -0.6 V, and nitrite (NO₂⁻) is reduced to NO at -0.7 V.

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