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Electroreduction of nitrate on natural phosphate modified copper electrode

R.Najih, H.Oulfajrite, A.Chtaini*

Equipe d'Electrochimie Moléculaire et Matériaux Inorganiques, Université Sultan Moulay Slimane,
Faculté des Sciences et Techniques de Beni Mellal, (MAROC)

E-mail : chtainia@yahoo.fr

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INTRODUCTION

Pollution of ground and surface waters by nitrates is a wide spread and serious problems. Heavy utilization of artificial fertilizers has been know to cause penetration of large quantities of nitrates into ground and surface waters^[1]. The nitrate has to be removed since high concentrations of nitrate have a detrimental effect on environment and also limit 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 NO_3^- 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 NO_3^- ions form contaminated water. However, these techniques present considerable drawbacks, such, low reaction rate, continuous monitoring, large amount of by-products, costly H_2 consumption or catalyst elaboration, which are hardly acceptable for large scale applications. In contrast, the electrochemical reduction of NO_3^- represents an attractive and promising solution due to its convenience, environmental freindliness, 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 stud-

ied. Even at a monometallic electrode nitrate electroreduction is very complex, and strongly depends on the experimental conditions. Thus, before any elaboration of bimetallic Cu-Metal electrodes, it appears essential to clearly understand the different processes taking place at a pure copper electrode during the nitrate electroreduction.

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

EXPERIMENTAL

Apparatus

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 conventional three-electrode system consisting of the HAP-modified carbon paste working, platinum counter and SCE reference electrodes was used. The pH-meter (Radiometer Copenhagen, PHM210, Tacussel, French) was used for adjusting pH values.

Fourier transformed infrared spectroscopy (FTIR) analysis (PERKIN-ELMER FTIR) was performed in order to determine phosphate stoichiometric deviations, in particular the PO_4^{3-} and/or OH^- groups. The X-ray diffraction analysis (XRD: $\text{CuK}\alpha$ radiation, XPERT) was carried out to evaluate the purity of the natural phosphate^[19].

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Reagents

Merk p.a. HClO_4 , H_2SO_4 and NaNO_3 were used. The water was deionized and twice distilled. Before each experiment the solutions were deaerated by nitrogen bubbling, and a nitrogen stream was maintained over the solution during the measurements.

Before each measurements the working electrode was cycled between -1 and 0.5 V at 0.1 V/s until the typical cyclic voltametry for a clean electrode was obtained.

Natural phosphate

Natural phosphate (NP) used in this work was obtained in the khouribga region (Morocco)^[19]. Prior to use this material requires initial treatments such as crushing and washing. For use in electrochemical study, the NP is treated by techniques involving attrition, sifting, calcinations (900°C), washing, and recalcination. These treatments lead to a fraction between 100 and 400 μm that is rich in phosphate.

Preparation of the copper modified NP electrode (CuNP)

The modified electrode (CuNP) were obtained by electrodeposition of natural phosphate into copper plate (1 cm^2). Prior to use, the copper plate was polished by smooth paper. Electrical contact was established by a wire of copper.

RESULTS AND DISCUSSION

Natural phosphate characteristics

The surface structure of natural phosphate was observed using scanning electron microscopy (Figure 1). The treated NP has following composition P_2O_5 (34,86%), CaO (53,50%), F (3,37%), SiO_2 (2,42%), SO_3 (2,21%), CO_2 (1,13%), Na_2O (0,92%), MgO (0,68%), Al_2O_3 (0,46%), Fe_2O_3 (0,36%), K_2O (0,04%) and several metals (Zn, Cu, Cd, V, U, Cr) in the range of ppm.

Electrochemical behavior of CuNP modified electrode

Figure 2 shows the cyclic voltammogram (CV) of the CuNP modified electrode in 0,1M HClO_4 solution at the potentiostat scan rate 50 mV/s. It is noteworthy

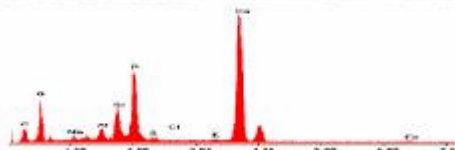
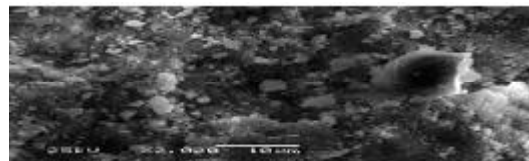


Figure 1 : Scanning electron micrograph of natural phosphate

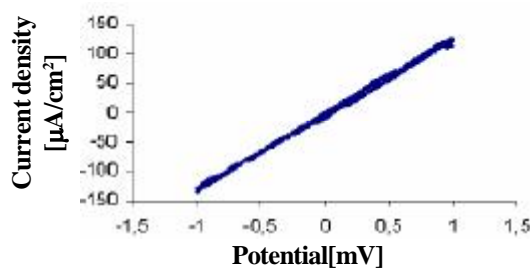


Figure 2 : Cyclic voltammogram of CuNP modified electrode in 0.1M HClO_4 solution at 50mV/s

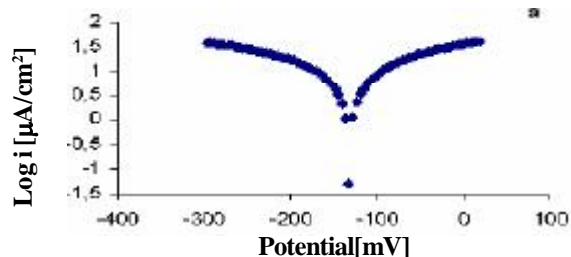


Figure 3 : Polarization curves for copper (a) and CuNP electrode (b) in 0.1M HClO_4 solution

TABLE 1: The electrochemical parameters for studied electrode

Sample	$E(i=0)/\text{mV}$	$R_p/\text{Kohm.cm}^2$	$J_{\text{corr}}/\text{mA.cm}^{-2}$	B_a/mV	B_c/mV
copper	-132.2	3.68	12.42	274.6	-322.9
CuNP	-49	7.04	6.53	280	-284.6

that in the entire potential range studied, there was no redox signal for copper.

The polarization curves of copper and CuNP modified electrodes are presented in figure 3, the presence of phosphate resulted in a shift of the corrosion potential (E_{corr}). The corrosion parameters j_{corr} (corrosion current density), E_{corr} (corrosion potential), B_a (anodic tafel slop), B_c (cathodic tafel slop) obtained for copper and CuNP modified electrode are given in TABLE 1. The decrease of j_{corr} demonstrate the effi-

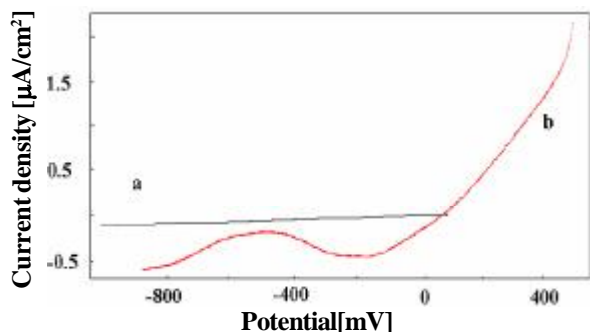


Figure 4 : Linear sweep voltammograms on CuNP modified electrode in 0.1M HClO₄ (curve a) in presence of 0.6M NaNO₃ (curve b) at 50 mV/s

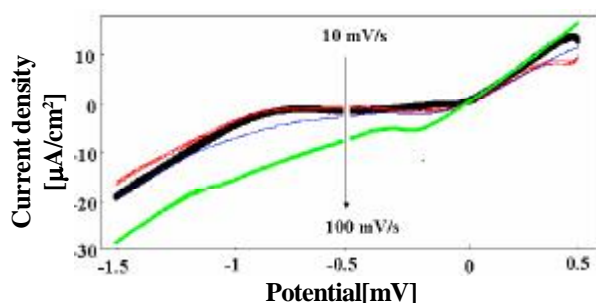


Figure 5 : Linear voltametric curves at CuNP modified electrode for different scan rates (from 10 to 100 mV/s) in 0.1M HClO₄ + 0.6M NO₃⁻

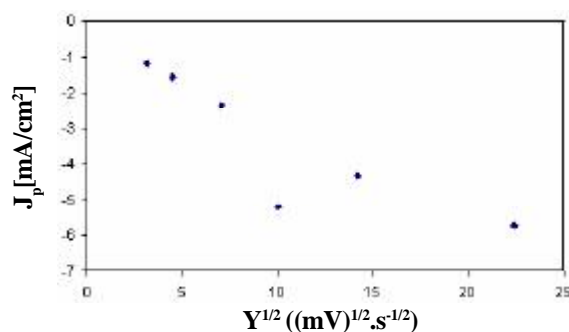


Figure 6 : Dependence of the peak currents on the square root of the scan rate $v^{1/2}$ extracted from linear voltammograms at a CuNP modified electrode in 0.1M HClO₄ + 0.6M NaNO₃

ciency of NP as corrosion inhibitor. The change in the value of cathodic (Bc) and anodic (Ba) tafel slopes, between copper and CuNP modified electrode, suggested that the presence of NP may change the mechanism of cathodic and anodic reactions.

Electroreduction of nitrate

Figure 4 (curve a) shows the linear sweep voltammogram (LSV) at a CuNP modified electrode in

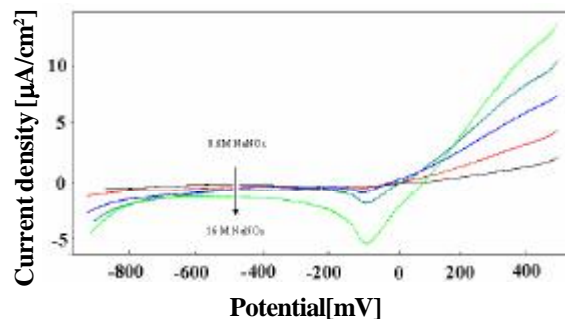


Figure 7 : Linear voltammograms curves at a CuNP modified electrode for different concentrations of nitrates in 0.1M HClO₄ solution at 50 mV/s

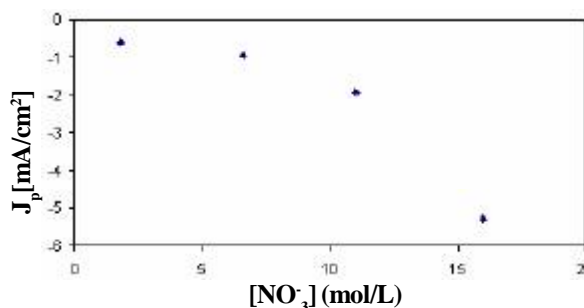


Figure 8 : Dependence of the peak currents on the nitrate concentration in 0.1M HClO₄ at 50 mV/s

0,1M HClO₄. No peak appears. The (LSV) of CuNP modified electrode in presence of 0,6M nitrate (NO₃⁻) in 0,1M HClO₄ (curve b) shows several peaks in the range of potential between 0 and -0,4V. These peaks are related to the reduction of nitrate to nitrite and the reduction of nitrite to hydroxylamine and ammonia^[20] according the following process:

$$\text{NO}_3^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{NO}_2^- + 2\text{OH}^-$$

$$\text{NO}_2^- + 4\text{H}_2\text{O} + 4\text{e}^- \rightarrow \text{NH}_2\text{OH} + 5\text{OH}^-$$

$$\text{NO}_2^- + 5\text{H}_2\text{O} + 6\text{e}^- \rightarrow \text{NH}_3 + 7\text{OH}^-$$

Figure 5 shows the LVSs of CuNP modified electrode in 0,1M HClO₄ in presence of 0,6M NaNO₃ as a function of scan rate. The cathodic peaks are shifted to more negative potentials as the scan rate increases, as expected for irreversible and quasi-reversible redox processes^[21].

A plot of the peak current density j_p as a function of the square root of the scan rate $v^{1/2}$ is shown in figure 6. The peak current exhibit a linear dependence on the potential scan rate in the range from 10 to 100 mV/s indicating that the CuNP modified electrode reaction is controlled by nondiffusion process.

Figure 7 shows some linear voltammetric curves

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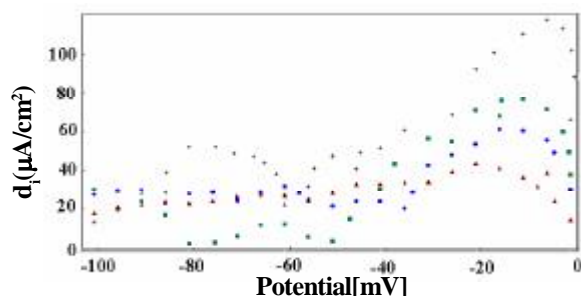


Figure 9 : Square wave voltammograms in 0.1M HClO₄ at CuNP modified electrode in presence of different concentrations of nitrate at 50mV/s. (+)16M, (■) 11M, (●) 6.6M, (■) 1.8M and (▲) 0.6M

recorded at CuNP modified electrode in 0.1M HClO₄ solution in presence of different nitrate concentrations at 50 mV/s. The reduction peaks are shifted to more negative potentials as the nitrate concentrations increases. The reduction current peaks increases with the nitrate concentrations and presents a linear dependence. (Figure 8)

Figure 9 shows some of typical square wave voltammetry curves recorded at CuNP electrode in 0.1M HClO₄ solution in presence of different nitrate concentrations. A calibration graph was then constructed from the observed peak currents. The square wave voltammetric response was linearly dependent on the concentration of nitrate. The linear regression analysis gave

$j_p = -0.2776[\text{NO}_3^-] + 0.1859$ with a correlation coefficient of 0.8182.

CONCLUSION

In this study, the electroreduction of nitrate was studied on a CuNP modified electrode in 0.1M HClO₄ solution.

The electroreduction of nitrate was evaluated using the linear cyclic voltammetry measurements (LCV). The LCV response showed several reduction peaks associated to the different stages of reduction of nitrate. The proposed electrode (CuNP) can also play the part of an electrochemical sensor for determination of nitrate containing in drinking water. The results obtained here show that the proposed square wave voltammetry method is fast, sensitive and better suited than conventional methods, like spectrophotometry or chroma-

tography, to characterizing fast variations in concentration of dilute nitrate aqueous solutions.

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