

## Electrochemical Chelation and Reduction of Nitrate Ion on EDTA Modified Carbon Paste Electrode

El Mastour J, El Qouatli SE, Zaroual A and Chtaini A\*

Molecular Electrochemistry and Inorganic Materials Team, Beni Mellal Faculty of Science and Technology, Sultan Moulay Slimane University, Morocco

### Abstract

The aim of this work is to combine two methods for removing nitrate ions from concentrated aqueous solutions. This involves chelating and then reducing  $\text{NO}_3^-$  by EDTA modified carbon paste electrode (EDTA-CPE). We find that in the absence of EDTA on the carbon paste electrode surface, the nitrate reduction is almost impossible. The reduction of nitrate ions was investigated on the surface of the EDTA-CPE, the cyclic voltammograms recorded in electrolytic medium 0.1 M KCl, shows two reduction peaks, the first at -0.2 V, attributed to the reduction of nitrite ions ( $\text{NO}_2^-$ ) and the second one at 0.8 V which corresponds to the reduction of nitrate to nitrite ions.

**Keywords:** Nitrate; Electrochemical reduction; EDTA; Chelating; Modified electrode

### Introduction

The nitrate contamination is a wide spread and serious problems. Heavy utilization of artificial fertilizers has been known to cause penetration of large quantities of nitrates into ground and surface waters [1]. Nitrate ( $\text{NO}_3^-$ ) is the principal form that can be utilized by plants. The World Health Organization (WHO) has fixed a tolerable nitrate concentration at 50 ppm in drinking water [2]. Nitrate must be removed because high concentrations can cause adverse environmental effects and also limit water use in the industry. This contamination mainly due to industrial waste, or chemical fertilizers represents a risk not only on aquatic ecosystems [3] but also for the human health [4,5]. Several processes including biological [6] and physico-chemical methods [7-10] are known for reduce nitrate ions from contaminated water. However, these techniques have considerable disadvantages, such as the low reaction rate, the continuous monitoring of physical parameters, such as pH, temperature, the addition of a large amount of by-products, the consumption of expensive  $\text{H}_2$  or catalyst preparation, which are difficult to accept for large-scale applications. In contrast, the electrochemical reduction of  $\text{NO}_3^-$  becomes an alternative 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. The nitrate reduction method proposed in this work consists first of all in chelating the nitrate ions with EDTA (Ethylene Diamine Tetra-Acetic) and then reducing them. The originality of this work lies in the combination of these two processes in an EDTA modified carbon paste electrode.

### Experimental Section

#### Apparatus

Electrochemical experiments were performed using a Voltalab Potentiostat (model PGSTAT100, 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 EDTA modified carbon paste working, platinum counter an Ag-AgCl reference electrodes was used.

The pH-meter (Radiometer Copenhagen, PHM210, Tacussel, and French) was used for adjusting pH values.

#### Reagents

Merk p.a. KCl and  $\text{NaNO}_3$  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 measurement the working electrode was cycled between -1.5 V and 1.5 V at 0.1 v/s until the typical cyclic voltammetry for a clean electrode was obtained.

#### Electrodes preparation

Modified electrodes were prepared by mixing a carbon powder and the desired weight of EDTA. The body of the working electrode for voltammetric experiments was a PTFE cylinder that was tightly packed with carbon paste. The geometric area of this electrode was 0.1256  $\text{cm}^2$ . Electrical contact was made at the back by means of a bare carbon.

#### Procedure

The initial working procedure consisted of measuring the electrochemical response at EDTA-CPE at a fixed concentration of nitrate ion. Standard solution of nitrate was added into the electrochemical cell containing 100 mL of supporting electrolyte.

#### Results

Figure 1 shows the cyclic voltammograms obtained respectively for carbon paste electrode (CPE) and EDTA modified carbon paste electrode (EDTA-CPE), in 0.1 M KCl solution. The comparison of the two recorded voltammograms, respectively for CPE (curve a) and EDTA-CPE (curve b), shows that they have different gaits, which confirms the modification of the carbon paste electrode [19].

\*Corresponding author: Chtaini Abdellah, Molecular Electrochemistry and Inorganic Materials Team, Beni Mellal Faculty of Science and Technology, Sultan Moulay Slimane University, Morocco, Tel: +212523485112; E-mail: [a.chtaini@usms.ma](mailto:a.chtaini@usms.ma)

Received December 28, 2017; Accepted February 21, 2018; Published March 01, 2018

Citation: El Mastour J, El Qouatli SE, Zaroual A, Chtaini A (2018) Electrochemical Chelation and Reduction of Nitrate Ion on EDTA Modified Carbon Paste Electrode. J Material Sci Eng 7: 433. doi: [10.4172/2169-0022.1000433](https://doi.org/10.4172/2169-0022.1000433)

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Examination of the voltammogram recorded for the EDTA-CPE electrode shows two redox peaks, the first in the direction of the anodic scanning, at about 0.1 V, which corresponds to the oxidation of EDTA

and the second one at -0.5 V attributed to the reduction of EDTA. These two peaks are symmetrical which shows that the oxidation and reduction reactions of EDTA are reversible.

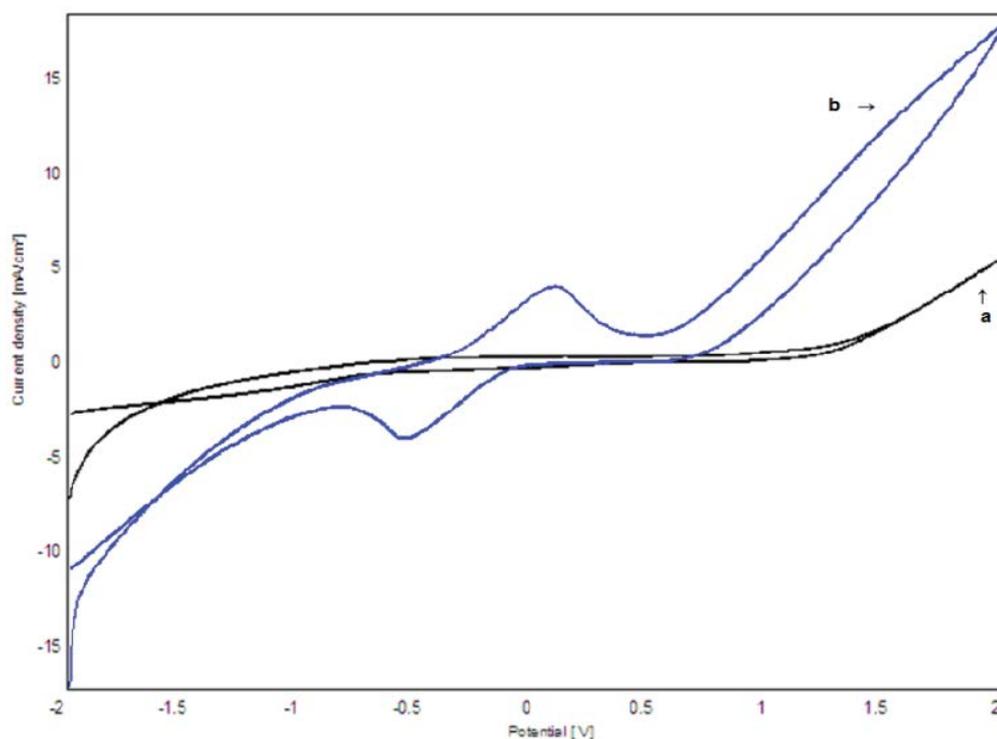


Figure 1: Cyclic voltammograms recorder in 0.1 M KCL, at 100 mV/s at a- CPE and b- EDTA-CPE.

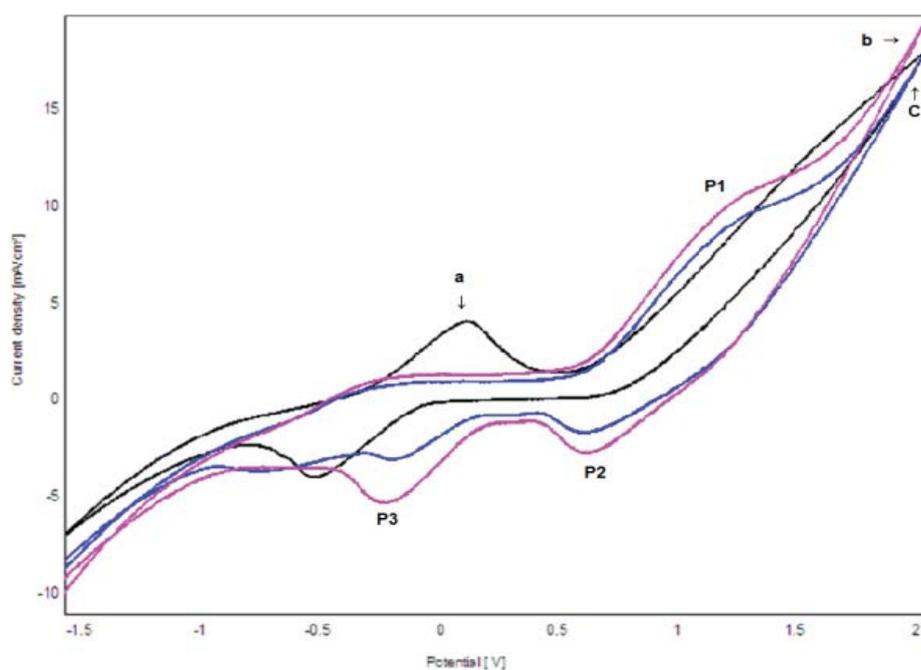


Figure 2: Cyclic voltammetric curves for the EDTA-CPE recorded in 0.1 M KCL at 100 mV/s, a) in absence of  $\text{NaNO}_3$ , b) in presence of 0.01 mol/L of  $\text{NaNO}_3$  and c- in presence of 0.027 mol/L of  $\text{NaNO}_3$ .

In the presence of nitrate ions in the electrolytic medium, the two redox peaks of EDTA are replaced by three peaks, P1, P2 and P3 (Figure 2 curves b and c).

### Conclusion

The peaks P1 and P2 could be attributed to the oxidation and reduction reactions of the nitrate-EDTA complex, these two peaks

are symmetrical, suggesting that the corresponding reactions are reversible. The peak P3 corresponds to the reduction of the nitrate in the nitrate EDTA complex [20].

On the potential sweep in the cathodic direction the current density peaks (P2 and P3) increases considerably with the nitrate concentration (Figure 3). The current density depends on the concentration of Nitrate.

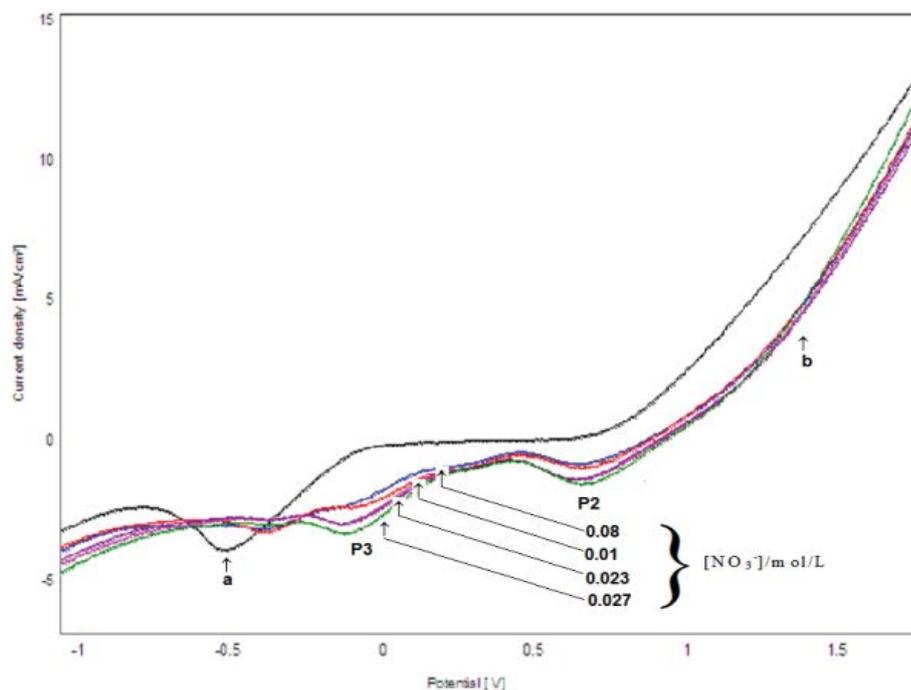


Figure 3: Linear voltammograms recorded at EDTA-CPE, in a) 0.1 M KCL solution, b) 0.1 M KCl + different concentrations of  $\text{NaNO}_3$ .

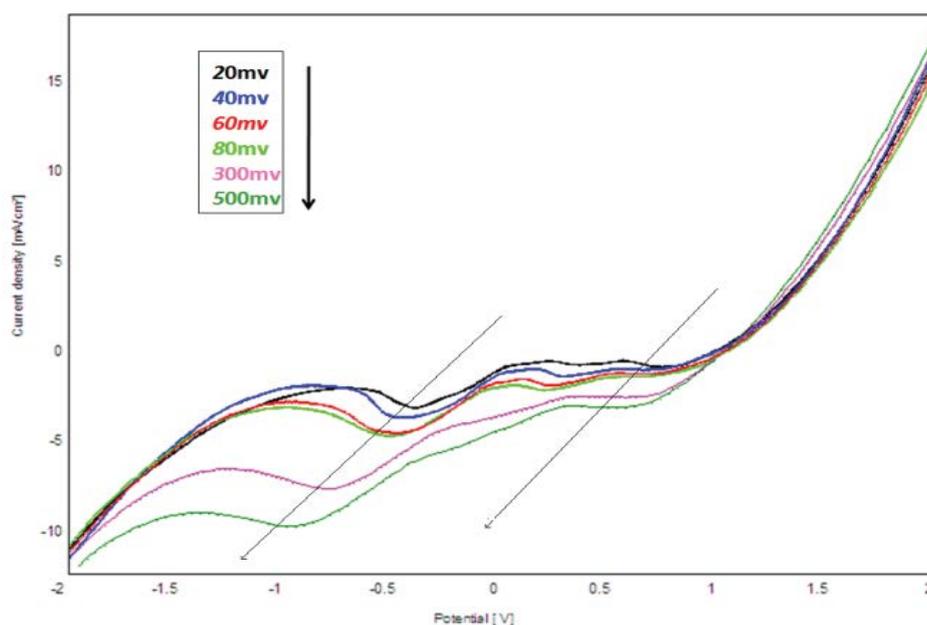


Figure 4: Cyclic voltammetric curves for the EDTA-CPE recorded in 0.1 M KCL containing  $\text{NaNO}_3$  at different scan rates.

The effect of sweeping speed on reducing current densities has been studied. In Figure 4 we present the linear voltammograms recorded on the surface of the elaborated electrode EDTA-CPE, in electrolytic medium containing the nitrate ions, at different scanning speed. A reduction peak was observed in cathodic potential and there was no corresponding oxidation peak under anodic scan.

The reduction current densities of the nitrate ions increase linearly with the square root of the speed of the scanning rate ( $V^{1/2}$ ) (Figure 5). This shows that the reduction current can be expressed by Randles-Sevcik equation:

$$I_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} C_i v^{1/2}$$

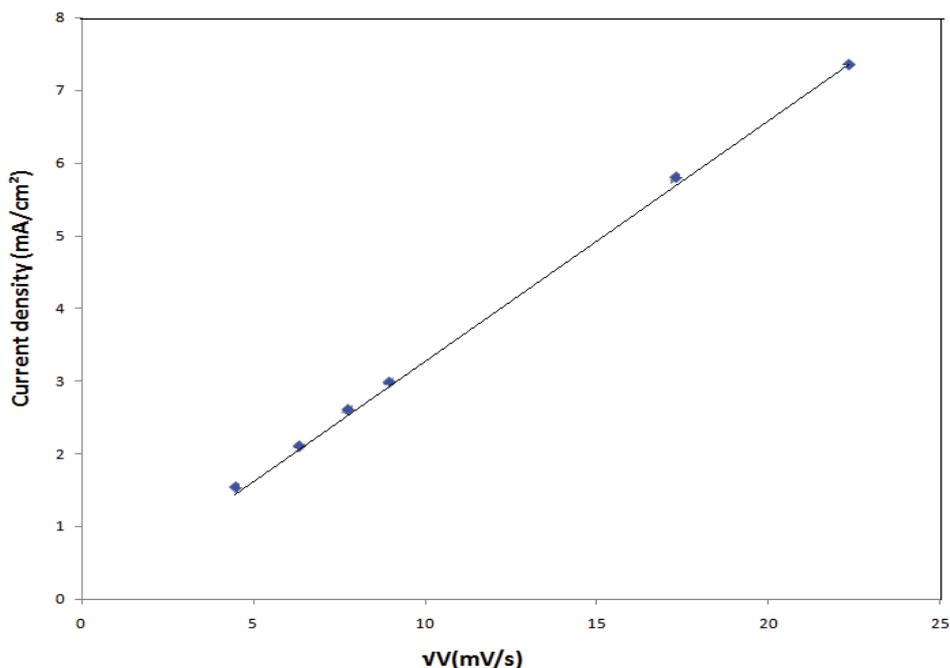


Figure 5: The reduction peak currents (P3) vs. the square root of the scan rate extracted from cyclic voltammetric curves.

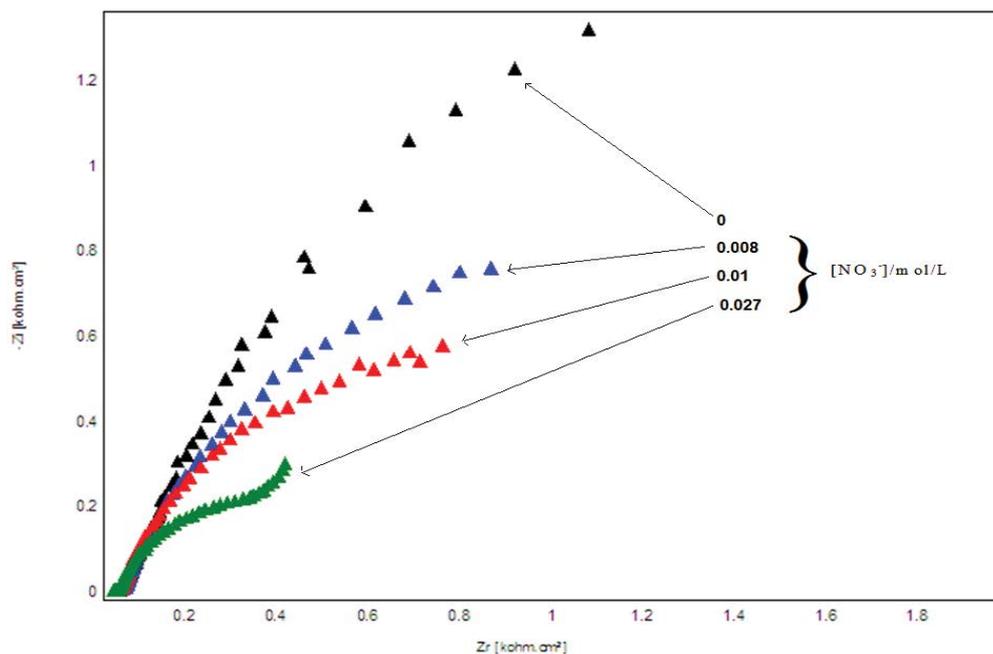


Figure 6: Electrochemical impedance recorded at EDTA-CPE in 0.1M KCl containing  $\text{NaNO}_3$ .

Where  $I_p$ : is the cathodic peak current;  
 $n$ : is the number of electron involved in the reaction;  
 $D$ : is the diffusion coefficient of nitrate;  
 $A$ : is the electrode surface area;  
 $C$ : is the nitrate concentration;  
 $V$ : is the scan rate.

Figure 6 shows the electrochemical impedance curves recorded for EDTA-CPE in 0.1 M KCl solution containing different concentrations of nitrate. It can be seen that in all the cases the impedance curves are in the form of one semi-circle, indicating one time constant attributed to an electron transfer step. We find that the diameter of the semi-circle decreases as the nitrate concentration increases, suggesting that the nitrate-ion redistribution reaction is highly dependent on the electron transfer resistance.

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