

CYCLIC VOLTAMMETRY STUDY ON THE REDUCTION OF NITRATE AND NITRITE ON A COPPER ELECTRODE

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SUMMARY

The cathodic reduction of nitrate and nitrite ions on a copper electrode in aqueous potassium chloride solutions was studied using cyclic voltammetry technique. The cyclic voltammograms showed that nitrate and nitrite ion reduction occurred in the 0.14 M KCl solution with peak potentials of -1.25 to -1.30 V and -1.20 to -1.25 V (Ag/AgCl) respectively. It was suggested from the data analysis that in the potassium chloride solution the reduction of nitrate and nitrite ions is irreversible. A minimal effect of pH on the reduction rate of nitrate and nitrite ions was found for the acidic and neutral solutions, but it increased in the alkaline solutions.

I - INTRODUCTION

The nitrate contamination is one of the major water quality problems today. The uptake of nitrate in the human body causes oxygen-deficiency such as cyanosis and breathing problems. Such toxicity is not due to nitrate itself but to nitrite formed from it. Nitrate is converted to nitrite by microorganisms present in the upper gastrointestinal tract and then nitrite adsorbed into the bloodstream reacts with hemoglobin to form methemoglobin. Methemoglobin formation prevents blood from carrying oxygen [1]. Furthermore, nitrite impacts negatively on the body involve its reaction with secondary amines and amides to form N-nitroso amines and N-nitroso amides. These products are well-known precursors to cancer causing agents [2].

In 1985, the World Health Organization reported that nitrate concentrations in surface waters had increased extensively over the

previous 30 - 40 years in many countries due to increasing use of artificial fertilizers [3]. As an agricultural country, Vietnam faced a big health risk due to the large nitrate concentration in ground and surface waters.

Electrochemical reduction of nitrate and nitrite ions is one of the methods used to remove nitrate compounds from water. Several studies on the reduction of nitrates and nitrites have been carried out on various noble metal and noble metal-modified electrodes in acidic solutions [4 - 10] or in alkaline [10 - 16]. However, few studies have been done in neutral solutions [17 - 20]. The catalytic influence of Cu ions was shown in some papers [9, 10, 17].

The aim of our work is to use inexpensive metals as electrode materials for the electrochemical reduction of nitrate and nitrite ions in neutral solutions. In this paper the reduction of nitrate and nitrite ions on a copper electrode in neutral potassium chloride solutions was studied by cyclic voltammetry (CV).

II - EXPERIMENTAL

Electrochemical measurements were performed in a three-electrode electrochemical cell using an Eco Chemie Autolab 30 potentiostat/galvanostat.

Working electrode was prepared by a copper rod mounted in epoxy with an exposed area of 0.07 cm^2 . Before measurements the working electrode surface was polished with 1200 grit emery paper, rinsed with distilled water and degreased with ethanol. The reference electrode was Ag/AgCl. All potential values in this paper are reported with respect to saturated Ag/AgCl electrode. The counter electrode was a platinum wire.

For all experiments, except the ones on effect of the potential scan rate, the cyclic voltammetry was run with the scan rate of 100 mV/s .

The CV experiments were conducted using the 0.14 M potassium chloride (KCl) solution as a supporting electrolyte. Sodium nitrate

(NaNO_3) and sodium nitrite (NaNO_2) were used as analyses for the experiments. All solutions were prepared just prior to use from analytical-reagent grade chemicals with twice distilled water. The pH of solutions was measured before and after experiments.

III - RESULTS AND DISCUSSION

From the cyclic voltammograms (CVs) with scan rate 100 mV/s in the 0.14 M KCl solution showed in the Fig. 1 no reduction current density was observed until cathodic potential of -1.20 V . In the presence of 0.01 M NaNO_3 (Fig. 1, a), nitrate reduction started at about -0.80 V but was not significant until the cathodic potential reached -1.00 V . It was observed a cathodic current peak (i_{peak}) of about $1.3 \mu\text{A}/\text{cm}^2$ at the peak potential (E_{peak}) of -1.29 V . Meanwhile the nitrite reduction (Fig. 1, b) is initiated at the potential of -1.00 V and reaches a maximum value of $1.0 \mu\text{A}/\text{cm}^2$ at E_{peak} of -1.24 V with the same potential scan rate as in the case of 0.01 M NaNO_3 .

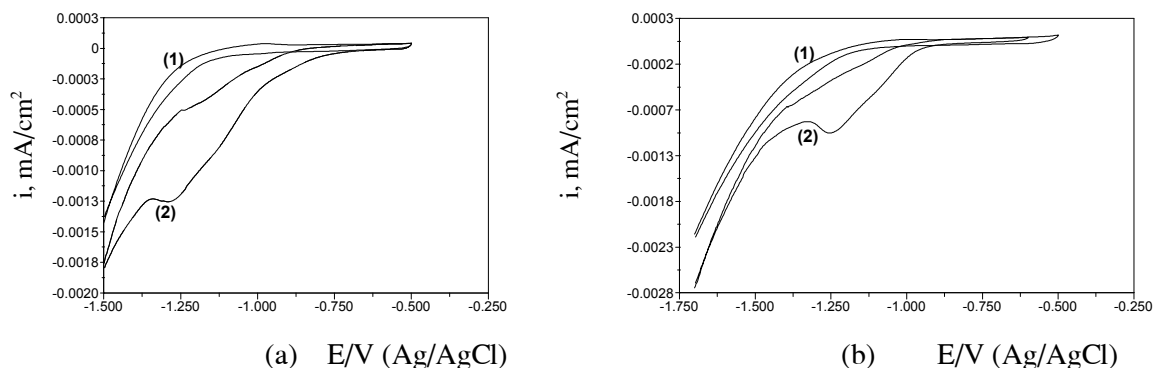
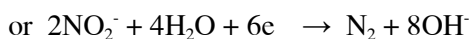
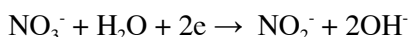
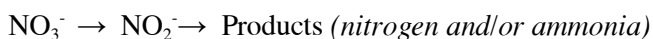


Figure 1: (a) CVs in 0.14 M KCl + $x \text{ NaNO}_3$: (1) $x = 0.0 \text{ M}$; (2) $x = 0.01 \text{ M}$
 (b) CVs in 0.14 M KCl + $y \text{ NaNO}_2$: (1) $y = 0.0 \text{ M}$; (2) $y = 0.01 \text{ M}$

The CVs in Fig. 1 and Fig. 3b lead to the suggestion that nitrite is an intermediate formed from nitrate reduction in the KCl solution. So the mechanism of nitrate reduction has at least two steps. A two-step mechanism of nitrate reduction was also observed by De *et al.* [19, 20] in NaClO_4 solutions at iridium-modified carbon fiber electrodes as the following:



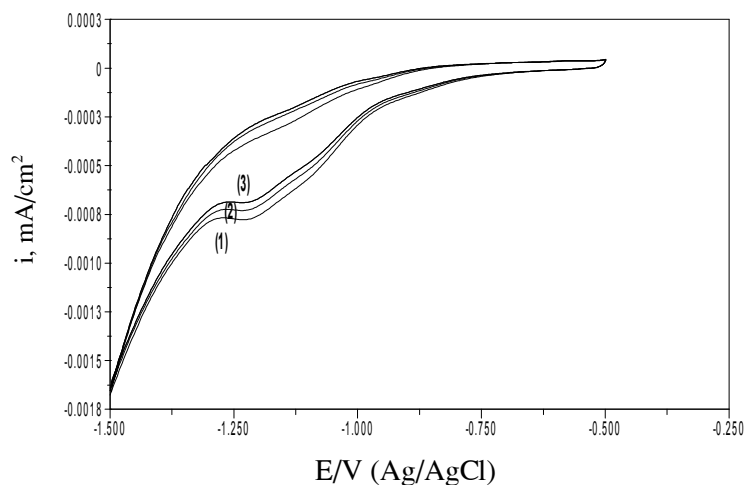


Figure 2: Multi-cyclic voltammograms in 0.14 M KCl + 0.005 M NaNO₃
(1) 1st cycle; (2) 2nd cycle; (3) 3rd cycle.

Table 1: Effect of multiple scan on cyclic voltammograms of nitrate ion reduction

Figure	Solutions	E_{peak}, V	$-i_{\text{peak}} \cdot 10^3, \text{mA/cm}^2$
1	0.14 M KCl (solution A)		
1(a)	A + 0.01 M NaNO ₃	-1.29	1.26
2	A + 0.005 M NaNO ₃ , 1 st cycle	-1.25	0.78
2	A + 0.005 M NaNO ₃ , 2 nd cycle	-1.24	0.73
2	A + 0.005 M NaNO ₃ , 3 rd cycle	-1.23	0.69

It was showed from the Fig. 2 and table 1 that with the increase of scan cycles the reduction peak potential slightly shifted toward the positive values and the cathodic current density decreased.

Fig. 3 and Fig. 4 show the effect of the nitrite and nitrate ion concentration on the reduction rate. As the concentration increases, the reduction peak for nitrite ions shifts toward the more negative potentials and the cathodic current density increases (Fig. 3a). The same phenomena were observed for the nitrate reduction (Fig. 3b and Fig. 4).

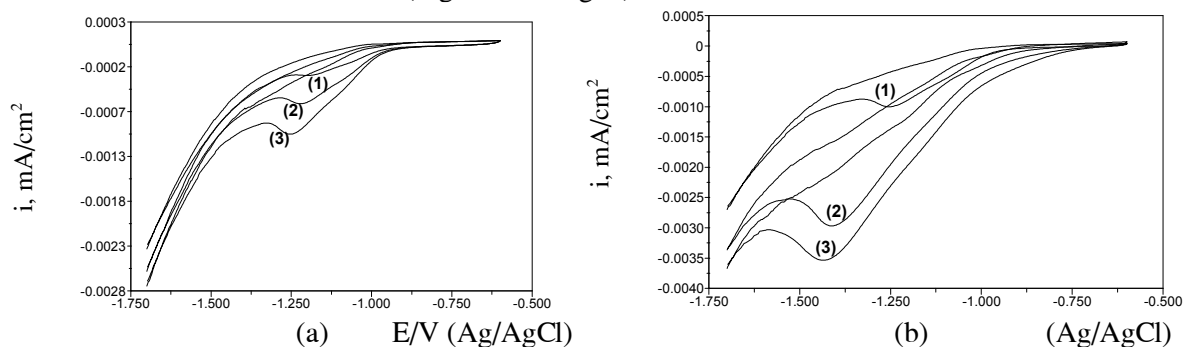


Figure 3: CVs in 0.14 M KCl

(a): + x NaNO₂; (1) x = 0.002 M; (2) x = 0.005 M; (3) x = 0.01 M

(b): + 0.01 M NaNO₂ + y NaNO₃; (1) y = 0.0 M; (2) y = 0.02 M; (3) y = 0.05 M

Table 2: Electrochemical parameters of nitrate and nitrite reduction in 0.14 M KCl solution

$C_{NO_2^-}$, M	$C_{NO_3^-}$, M	$-E_{peak}$, V	$-i_{peak} \cdot 10^3$, mA/cm ²
0.002	0	1.20	0.357
0.005	0	1.21	0.669
0.010	0	1.27	1.249
0	0.005	1.25	0.780
0	0.010	1.29	1.260
0.010	0.020	1.39	2.959
0.010	0.050	1.41	3.534

Fig. 3b shows the voltammograms obtained in a mixed nitrate and nitrite ions solutions. The CVs are similar to those obtained with either nitrate or nitrite ions only. The cathodic peak shifted toward the negative potentials and its current density values increased as nitrate ion concentration increased (table 2).

The variation of peak current density with nitrate concentration is plotted in Fig. 4. The fact that peak current density linearly increases with increasing nitrate concentration suggests that the reduction of NO_3^- ions should be the first-order with respect to nitrate.

Fig. 5 shows the effect of scan rates on nitrate and nitrite ion reduction. In both cases

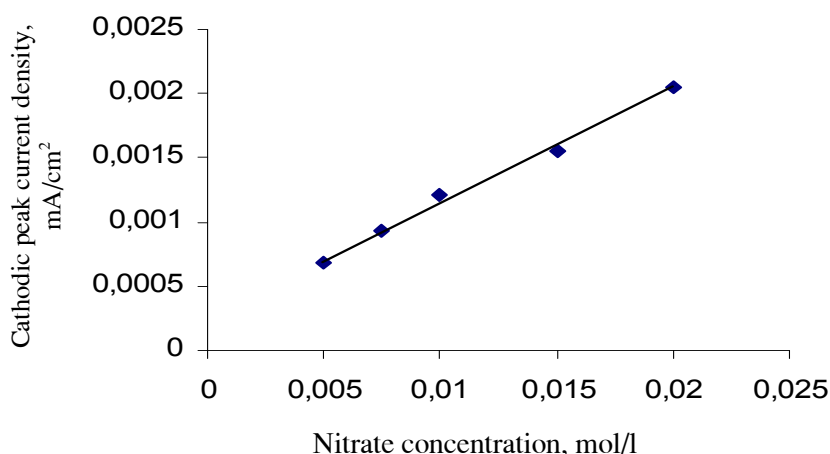


Figure 4: Effect of nitrate concentration on the cathodic peak current density

the E_{peak} shifts toward more negative values with increasing sweep rate (ν). This implies that the reaction is irreversible, because of the reversible reactions the peak potentials are independent with sweep rate according to Eq. (3) [21] for room temperature.

$$E_{peak} = 28.5/n \quad (3)$$

In addition, no anode peaks were observed in the cyclic voltammograms, which means the studied reaction is neither reversible nor quasi-reversible.

So the nitrate reduction in the KCl solution might be an irreversible reaction and the relationship between E_{peak} and potential scan rate may be describe by the Eq. (4) [21].

$$E_{peak} = E^{0'} - \frac{RT}{\alpha F} \left[0.780 + \ln \frac{D_0^{1/2}}{k^0} + \frac{1}{2} \ln \frac{\alpha F \nu}{RT} \right] \quad (4)$$

The effect of pH on the CVs obtained in 0.14 M KCl solution in the presence of 0.004 M $NaNO_3$ and 0.002 M $NaNO_2$ at scan rate 100 mV/s was showed in Fig. 6. The pH was adjusted using either hydrochloride acid or sodium hydroxide. In the pH range from 2 to 12 it was observed a minimal influence of pH on nitrate and nitrite ion reduction rate at the copper electrode in acidic and neutral solutions. However the effect of pH increased in alkaline media.

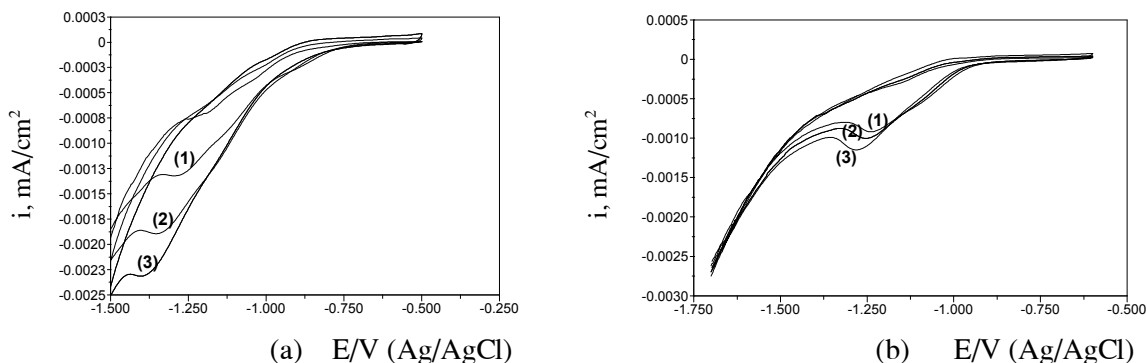


Figure 5: Effect of scan rate on the CVs
 (a) in 0.14 M KCl + 0.02 M NaNO₃: (1) 25 mV/s; (2) 100 mV/s; (3) 200 mV/s;
 (b) in 0.14 M KCl + 0.01 M NaNO₂: (1) 50 mV/s; (2) 100 mV/s; (3) 200 mV/s.

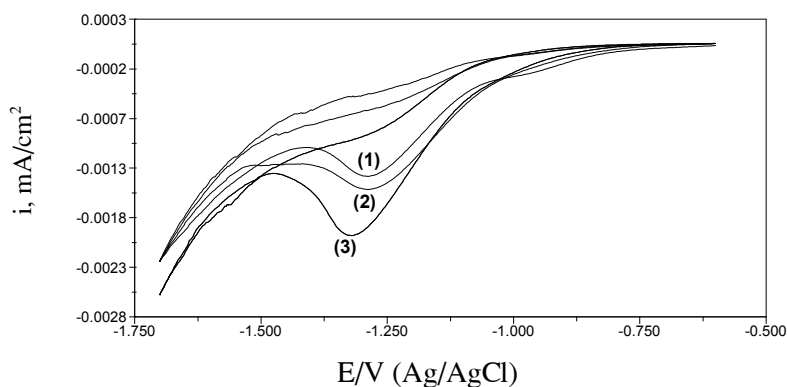


Figure 6: Effect of pH on the CVs in 0.14 M KCl + 0.004 M NaNO₃ + 0.002 M NaNO₂:
 (1) pH 2; (2) pH 7; (3) pH 12

IV - CONCLUSIONS

In neutral potassium chloride solutions, nitrate and nitrite ions are electrochemically reduced at the copper electrode. The reduction of nitrate and nitrite ions starts at potentials of - 0.75 and - 0.95 V, current peaks are observed at -1.25 to - 1.30 V and -1.20 to -1.25 V respectively. The reduction current density increases linearly with increasing ion concentration, while current peaks shift toward more negative potentials. From the dependence of the cyclic voltammogram parameters on the sweep rate it may be concluded that both nitrate and nitrite reduction reactions are irreversible.

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