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**New insight into the electroreduction of nitrate ions at a copper electrode,
in neutral solution**

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The electroreduction of nitrate ions was investigated at a copper electrode in an unbuffered neutral aqueous solution. In the presence of nitrates, cyclic voltammetry revealed three cathodic waves. Rotating disk electrode measurements and the effect of potential scan rate were combined to further explore the reaction mechanism. Taking into account water reduction and using Koutecky-Levich analyses of the data obtained with linear sweep voltammetry at various electrode rotation rates, the number of electrons involved in the global reaction was found to be 2, 7 and 8, in accordance with nitrate reduction into nitrite, hydrazine and ammonia, respectively. Finally, we suggest that nitrogen oxides due to ammonia oxidation at the Pt counter electrode adsorb on copper electrode and block the nitrate reduction.

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Introduction

Among nitrate removal methods, the electrochemical reduction allows to convert nitrate into industrially useful compounds such as hydrazine, hydroxylamine and nitrous oxides and, also to produce nitrogen during water treatment. Therefore, the electroreduction of nitrate has received renewed attention over the last decade. A large number of metal cathodes were investigated and the highest catalytic activity was observed on copper electrode^{1,2}.

With a few exceptions^{1,3,4} the electrochemical reduction of NO_3^- at copper was studied either in acidic or in strongly alkaline solutions^{2,5,6,7,8,9,10,11,12}. It has been established, basically using colorimetric methods, that nitrate reduction proceeds through the formation of nitrite until ammonia^{1,3,5,8,9,11}. Other possible intermediates and side products are yet to be defined. It is the aim of the present work to specify the nitrate reduction mechanism that takes place at a copper electrode in neutral solutions.

Experimental

Stationary and rotating disc electrode voltammograms were recorded using a one compartment and a two compartment cell, respectively. A polycrystalline copper disk (0.2 cm^2) was polished to a mirror finish with $0.3 \text{ }\mu\text{m}$ diamond paste then cleaned with water in an ultrasonic bath for 5 min prior to being used as the cathode material. A platinum grid acted as the counter electrode. A saturated calomel electrode (SCE) was used and all potentials refer to this electrode. The potentiostat (Autolab PGSTAT100) and the rotating disk electrode system were from Eco Chemie.

Ultrapure water and pure reagents (*p.a.* grade) were used in the preparation of all the solutions. The electrochemical cell was purged with argon gas for 30 min before commencement. A stream of argon was then kept over the solution during the measurements. The experiments were performed either at 20°C or at 25°C .

Results and discussion

Cyclic voltammetry

Nitrate addition into the solution gives rise to three cathodic peaks named P1, P2 and P3 in Fig. 1. No anodic peak has appeared showing that the reduction of nitrate is irreversible. A comparison of voltammetric curves obtained in nitrate and nitrite containing solutions (Fig. 1), clearly indicates that peak P1, is associated with nitrate reduction into nitrite, *i.e.* NO_3^- undergoes a two electron reduction process.

In order to confirm this finding and to shed some light on reactions associated with P2 and P3 peaks, the effect of varying the potential scan rate on the peak current (j_p) was explored.

From Fig. 2, one can notice that the variations of P1 and P3 peak reduction currents as a function of the square root of the potential scan rate are linear suggesting that the corresponding reactions are limited by the diffusion of nitrates from the solution bulk. For an irreversible electrochemical process, the number of electrons n involved in the reaction can be determined through the use of the following equation¹³:

$$j_p = (2.99 \times 10^5) n \alpha^{1/2} C_0 D^{1/2} \nu^{1/2} \quad (\text{in A cm}^{-2}) \quad [1]$$

where α is the transfer coefficient, n is the number of electrons transferred, C_0 is the bulk nitrate concentration (in mol cm^{-3}), ν is the potential scan rate (in V s^{-1}) and D is redox species diffusion coefficient (in $\text{cm}^2 \cdot \text{s}^{-1}$). For the nitrate ions, at 25°C , D equals $1.8 \cdot 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ ¹¹, the value at 20°C has been calculated according to the expression given in Ref. 14. D equals $1.65 \cdot 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ at 20°C .

Besides α is given by:

$$\Delta E_p = | E_p - E_{p/2} | = \frac{1.857 R T}{\alpha F} \quad [2]$$

where E_p is the peak potential and $E_{p/2}$ is the potential for which $j = j_p/2$, R is the gas constant, T is the solution temperature (293 K) and F is the Faraday constant.

P2 peak is partly concealed by P3 peak making a simple determination of P2 peak position impossible. Therefore, only α associated with P1 and P3 peaks were calculated. ΔE_p was estimated at 0.17V and 0.22V for P1 and P3, respectively, leading to α equals 0.27 and 0.21, respectively, at 273K. Thus using equation [1], the number of electrons involved in the reaction associated with P1 peak was found to be 1.7 confirming that nitrate reduction into nitrite is taking place at this potential (Fig. 1). For P3 peak, n was found to be equal to 7.6 suggesting nitrate reduction into ammonia.

Rotating disk electrode (RDE)

In order to confirm the previous results and to estimate the electron number involved in the reduction step associated with P2 peak, electrochemical measurements were performed using RDE voltammetry.

RDE experiments were firstly carried out in a conventional one compartment cell. It was observed for the higher electrode rotation rates used, all the peak currents decrease instead of increase as observed for the lower rotation rates used and as expected for a process limited by diffusion. Furthermore, stopping the electrode spin did not allow to recover the copper activity. Obviously, the copper surface was inhibited by nitrate reduction products.

In the literature, it is pointed out that the decrease in nitrate reduction current at a copper electrode could be vanished by adding Cu(II) ions into a basic solution¹ or by using a strong acid medium⁹. Moreover Reyter *et al.* observed only very low blocking effect by separating the counter electrode compartment from the working electrode one by a Nafion membrane¹¹.

We can explain all these findings by the fact that ammonia ($pK_a=9.2$), which is the main product obtained at the lowest potentials (see previous section), can be oxidized at the platinum counter electrode when the electrolyte pH overreaches 9 (ammonium ions are not oxidized at a Pt electrode⁸). Therefore, we can propose that ammonia oxidation products

poison the copper surface blocking the nitrate reduction. Indeed, Cu(II) ion addition allows one to deposit a new Cu(0) layer but also to ‘neutralize’ NH₃, the adding of protons into the solution prevents the presence of ammonia, and finally the use of a two compartment cell allows to separate ammonia which is produced at the cathode from the platinum anode.

Actually, it was shown that ammonia oxidation at a platinum electrode leads to nitrogen oxides formation¹⁵. Thus, we can propose that nitrous oxides are responsible for copper poisoning. Some experiments are in progress in order to verify this assumption.

Then, a two compartment cell was used. Figs. 3 and 4 show the RDE linear sweep voltammetry recorded in the presence of nitrates and nitrites, respectively. From these figures, one can notice that the limiting current increases with the electrode rotation speed.

In totally mass-transfer-limited condition at the RDE, the mass transfer limiting current (j_L) depends on the angular rotational velocity of the electrode and the bulk concentration of redox ions according to the Levich equation:

$$j_L = 0.62nFD^{2/3}\Omega^{1/2} \nu^{-1/6} C_0 \quad (\text{in A cm}^{-2}) \quad [3]$$

where Ω stands for the electrode rotation speed and ν is the kinematic viscosity. If the process is only diffusion-limited, Levich plot should be linear and pass through the origin. Here, for the highest rotation rates a deviation of the j_L vs. $\Omega^{1/2}$ plot from a straight line is observed (not shown).

Moreover, since the water reduction begins to take place (see Fig. 1), the total cathodic current is the sum of two partial currents:

$$j_{\text{tot}} = j_{\text{H}_2\text{O}} + j_{\text{NO}_3^-} \quad [4]$$

For nitrate reduction, the Koutecky-Levich relation reads:

$$\frac{1}{j_{\text{NO}_3^-}} = \frac{1}{j_{\text{KIN}}} + \frac{1}{j_L} \quad [5]$$

leading to

$$j_{\text{tot}} = A + \frac{1}{B + C\Omega^{-1/2}} \quad [6]$$

where $A=j_{\text{H}_2\text{O}}$ $B=1/j_{\text{KIN}}$ and $C=\Omega^{1/2}/j_{\text{L}}$.

The experimental data reported in Figs. 3 and 4 were fitted using equation [6]. The fits are shown in the insert of these figures. The determined parameters, A, B and C, are given in Table 1. According to equation [3], C allows one to estimate the number of electrons exchanged, found to be 2 for P1, 7 for P2 and 8 for P3 in a nitrate containing solution. When substituting nitrate by nitrite, n was estimated at 5 for P2 and 6 for P3. These findings relate P1 to nitrate reduction into nitrite, P2 to nitrate reduction into hydrazine and P3 to nitrate reduction into ammonia in good agreement with the results obtained in varying the potential scan rate.

Moreover, if our model is correct, A parameter should increase along the series $P3>P2>P1$ owing to the water reduction current increase. B parameter, however, should decrease along the same series as the electron transfer rate increases. B and C values displayed in table 1 are fully consistent with this scenario. Moreover, these findings were validated by colorimetric determination of the products after a long electrolysis at a fixed potential. Nitrite, hydrazine and ammonia were found to be the nitrate reduction main product at -1V, -1.2V and -1.3V/SCE, respectively.

Conclusion

The mechanism of electroreduction of nitrate ions at a copper electrode in neutral media was studied by combining voltammetry and RDE experiments. Both techniques reveal three reduction features with 2, 7 and 8 transferred electrons, respectively. These findings were found to be in agreement with colorimetric titrations with the subsequent formation of nitrite, hydrazine and ammonia. If a one compartment electrochemical cell is used, when the cathodic

currents are high (due to electrode rotation, for example), the copper electrode begin to be blocked toward nitrate reduction. This finding is ascribe to the oxidation products of ammonia formed at the Pt anode that poison the copper cathode.

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FIGURE CAPTIONS

Figure 1: Cyclic voltammograms at a copper electrode in 0.5 M NaClO₄ (dotted line) + 10⁻² M NaNO₃ (full lines) or + 10⁻² M NaNO₂ (dashed lines), at 20°C. Potential scan rate: 20 mV s⁻¹.

Figure 2: Linear sweep voltammograms at a copper electrode recorded at different potential scan rates in 10⁻² M NaNO₃ + 0.5 M NaClO₄ aqueous solution, at 20°C. Inset: variation of the peak current for P1 and P3 features with the square root of the potential scan rate.

Figure 3: Linear sweep voltammograms at a copper electrode recorded at different electrode rotation speeds in 10⁻³ M NaNO₃ + 0.5 M NaClO₄ aqueous solution, at 25°C. Potential scan rate: 10 mV/s. Ω : 100, 125, 175, 225, 300, 400, 600, 900, 1200 rpm. Inset: Scatters: experimental data at -0.9V (■), -1.1V (▲) and -1.2V (●). Full lines: fitted data using eq. 6, the values of the parameters are reported in table 1.

Figure 4: Linear sweep voltammograms at a copper electrode recorded at different electrode rotation speeds in 10⁻³ M NaNO₂ + 0.5 M NaClO₄ aqueous solution, at 25°C. Potential scan rate: 10 mV/s. Ω : 100, 125, 175, 225, 300, 400, 600, 900, 1200 rpm. Inset: Scatters: experimental data at -1.1V (▲) and -1.2V (●). Full lines: fitted data using eq. 6, the values of the parameters are reported in table 1.

Table 1: A, B and C parameters determined by simulation using eq. [6], for nitrate and nitrite containing solutions (Figs. 3 and 4) and n calculated using C parameter and eq. [3].

Feature	Nitrate containing solution			Nitrite containing solution	
	P1	P2	P3	P2	P3
A (j_{H_2O})	0.560	0.562	0.623	0.368	0.594
B ($1/j_{KIN}$)	0.067	0.020	0.007	0.018	0.004
C ($\Omega^{1/2}/j_L$)	5.53	1.58	1.35	2.21	1.84
Chi ²	0.0003	0.0010	0.0002	0.0007	0.0015
n	2.2	7.1	8.2	4.8	6.3

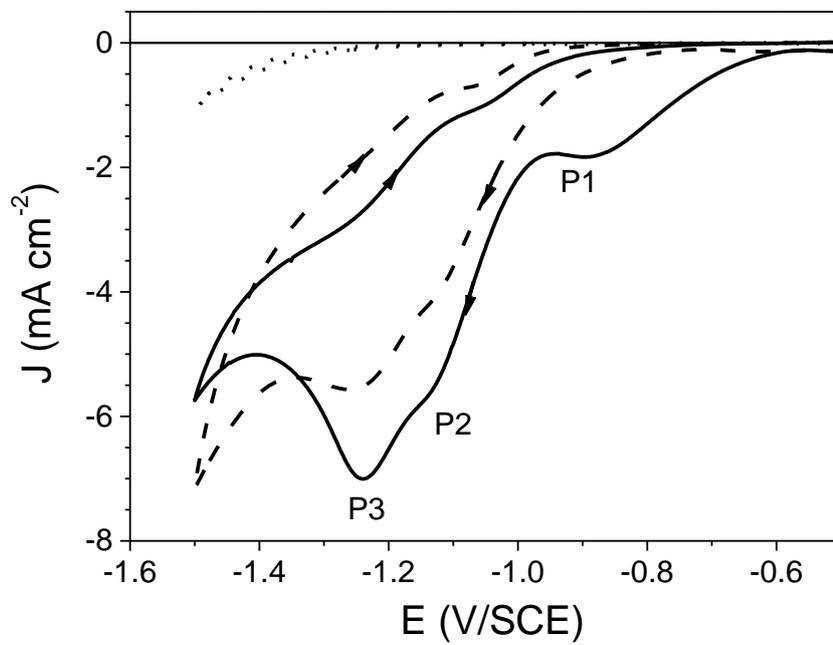


Figure 1

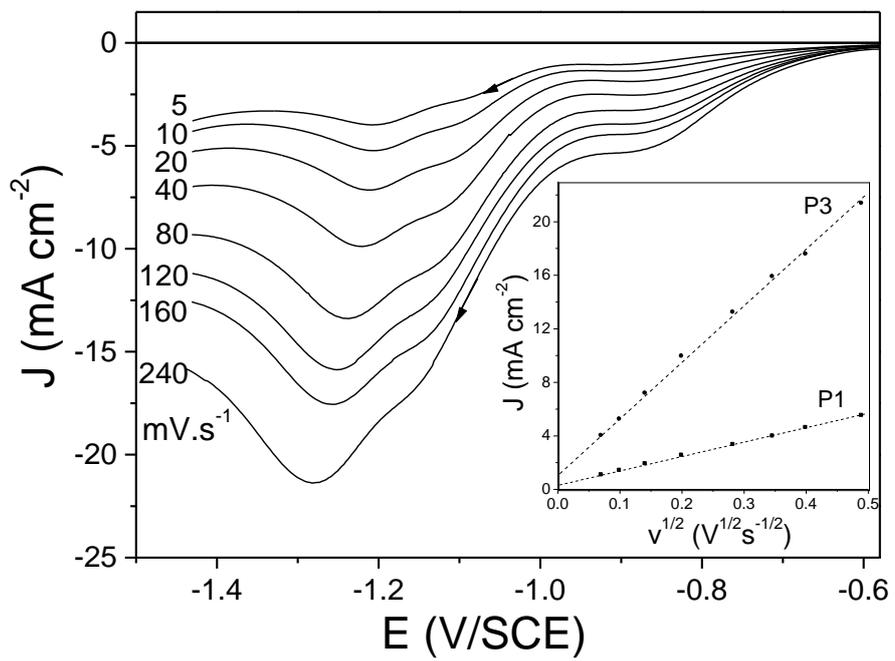


Figure 2

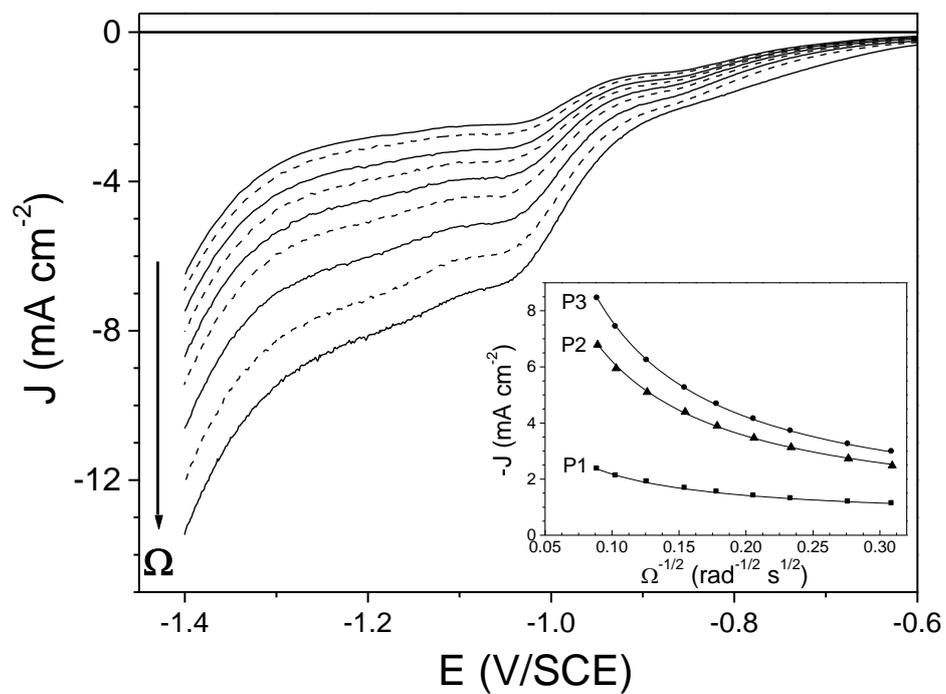


Figure 3

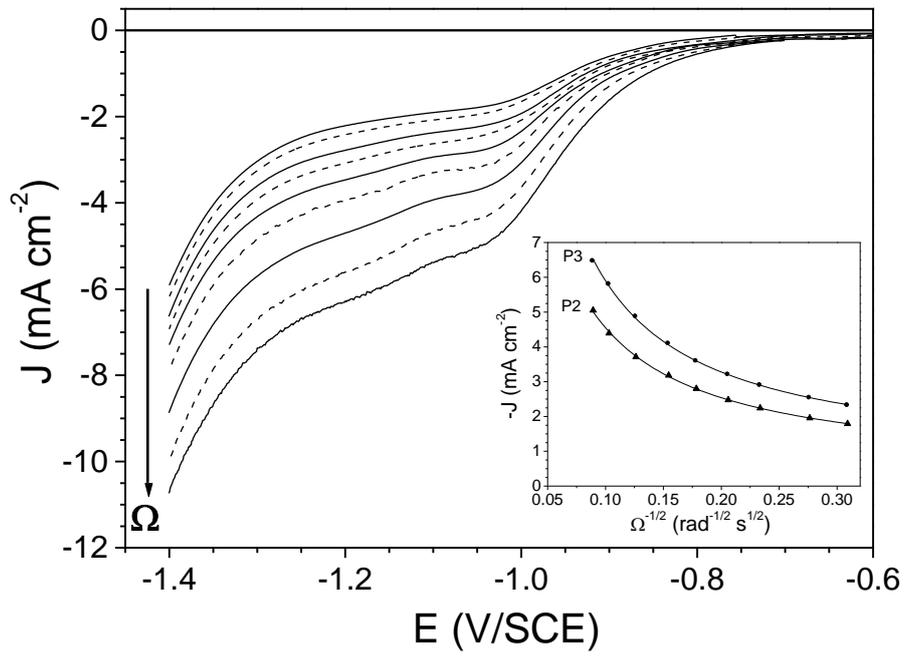


Figure 4