ISSN 0036-0244, Russian Journal of Physical Chemistry A, 2018, Vol. 92, No. 11, pp. 2348–2350. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © G.K. Aibolova, E.Zh. Tuleshova, 2018, published in Zhurnal Fizicheskoi Khimii, 2018, Vol. 92, No. 11, pp. 1817–1819.

SHORT COMMUNICATIONS

Kinetics and Mechanism of Cathodic Reduction of Nitrate Ions in a Sulfuric Acid Solution

G. K. Aibolova[a] **and E. Zh. Tuleshova**[a],*

[a]Akhmed Yassawi International Kazakh-Turkish University, Turkestan, 161200 Kazakhstan

*e-mail: elmira.tuleshova@ayu.edu.kz, t.elmira@mail.ru

Received March 1, 2018

Abstract—The cathodic reduction of nitrate ions in aqueous solutions of sulfuric acid in the presence of chromium(III) ions is studied via potentiometry. It is shown for the first time that nitrate ions are reduced to nitrogen in nitrate-containing solutions in the presence of chromium(III) ions.

Keywords: potentiodynamic polarization curves, electrochemical behavior, nitric oxide, sulfuric acid, electrode

DOI: 10.1134/S003602441811002X

INTRODUCTION

Electrochemical processes are of great importance in developing technologies for neutralizing gases containing nitrogen(II) oxide, and in the production of elemental nitrogen and nitrogen compounds. Reduction of nitrogen oxide and dioxide to N_2 is the effective means of their removal [1].

However, there is virtually no data in the literature on the electrochemical reduction of nitrate ions on a titanium electrode in the presence of Cr(III) ions catalyst in acidic solutions. In order to fully understand the electrode processes in the reduction of nitrate ions in a solution of sulfuric acid, we measured the cathodic potentiodynamic polarization curves in these solutions.

EXPERIMENTAL

To clarify the mechanism behind the reduction reactions, we studied the cathodic reduction of nitrate ions via potentiometry on an IPC Pro potentiostat. The voltammetric curves were registered at a potential sweep rate of 10 mV/s using an H 301/1 flatbed two-coordinate potentiometer. Bulk titanium electrodes 1/5 mm in diameter and 3.0 mm long were used as the cathode, and graphite plates were used as the anode.

A YaSE-2 special electrochemical cell mounted in an ITZh-0-03 thermostat was used to conduct our studies at a constant temperature.

Electrolysis was performed in galvanostatistic conditions in a 100 mL cell. In all experiments, the duration of electrolysis was 0.5 h.

RESULTS AND DISCUSSION

It is known from the literature [2] that the electrochemical reduction of nitrate ions proceeds according to the reaction

$$\begin{gathered} 2NO_3^- + 10\overline{e} + 12H^+ = N_2 + 6H_2O, \\ E^0 = +1.25 \text{ V}. \end{gathered} \tag{1}$$

However, our electrolysis results showed that nitrate ions were reduced to nitrogen(II) oxide in a solution of sulfuric acid:

$$\begin{gathered} NO_3^- + 3\overline{e} + 4H^+ \rightarrow NO + 2H_2O, \\ E^0 = +0.96 \text{ V}. \end{gathered} \tag{2}$$

The cathodic reduction of nitrate ions was studied in a 0.5 M solution of sulfuric acid. The hydrogen reduction currents can be seen on the cathodic polarization curve in the potential range of −1.25 V... −1.5 V (Fig. 1, curve *1*). No other reduction currents were observed on the polarogram.

When nitrate ions were added to a sulfuric acid solution, the maximum reduction current of nitrate ions was observed in the potential range of −0.50 V...−0.75 V (Fig. 1, curve *2*). When we performed electrolysis under galvanostatic conditions, the final product was nitrogen oxide(II) according to reaction (2). From the viewpoint of thermodynamics, nitrate ions are reduced to nitrogen by reaction (1), but this process in fact proceeds with high overpotential and does not occur.

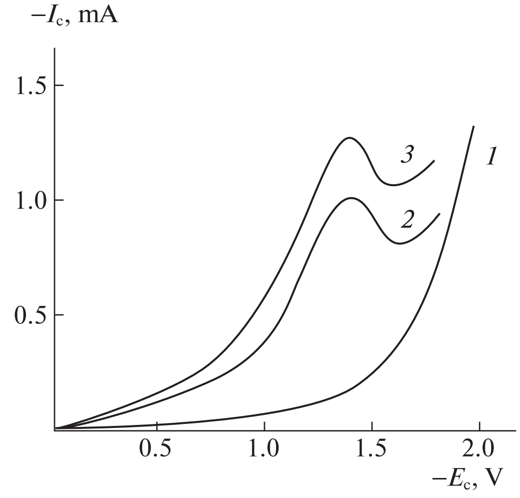


Fig. 1. Cathodic polarization curves of the nitrate ions reduction in solution of sulfuric acid: (*1*) background, 0.5 M H_2SO_4; (*2*) 1.0 M KNO_3 + 0.5 M H_2SO_4; (*3*) 1.0 M KNO_3 + 0.5 M H_2SO_4 + 4 g/L Cr(III).

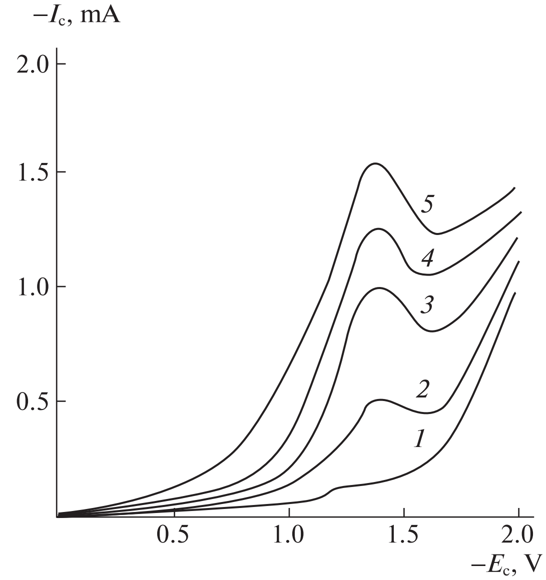


Fig. 2. Effect of NO_3^- ions concentration on the reduction of nitrate ions in solution of sulfuric acid: 0.5 M H_2SO_4 + 4 g/L Cr(III); KNO_3 (M): (*1*) 0.25, (*2*) 0.5, (*3*) 0.75, (*4*) 1.0, (*5*) 1.5.

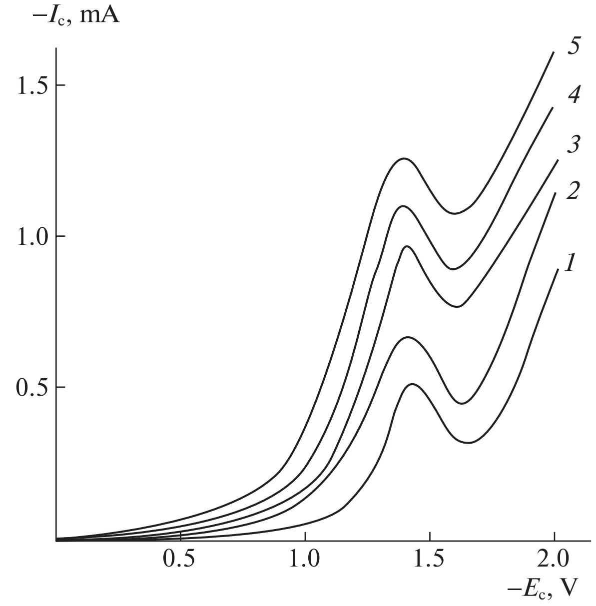


Fig. 3. Cathodic polarization curves at different concentrations of chromium(III) ions 0.5 M H_2SO_4 + 1 M KNO_3, Cr(III), g/L: (*1*) 0.5, (*2*) 1.0, (*3*) 2.0, (*4*) 3.0, (*5*) 4.0.

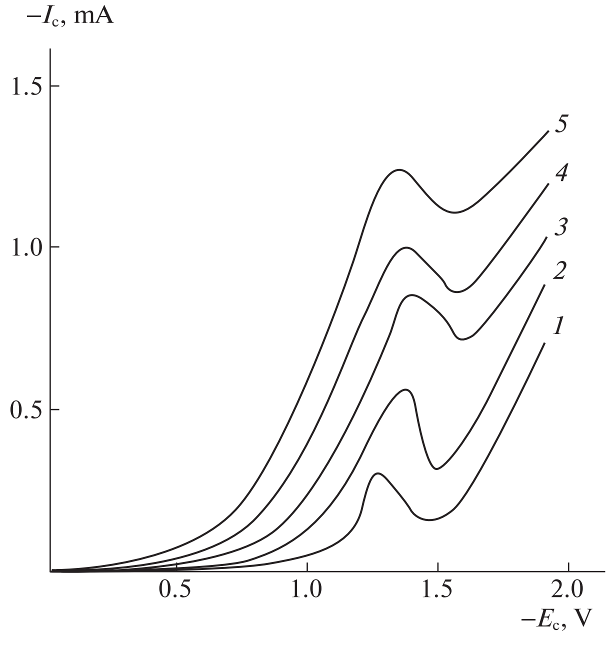


Fig. 4. Cathodic polarization curves at different concentrations of sulfuric acid: 1 M KNO_3 + 4 g/L Cr(III); H_2SO_4, mol/L: (*1*) 0.1, (*2*) 0.2, (*3*) 0.3, (*4*) 0.4, (*5*) 0.5.

The maxima of nitrate ions reduction currents on the polarogram increased when trivalent chromium ions were added to the solution of sulfuric acid containing nitrate ions (Fig. 1, curve *3*).

The electroreduction of nitrate ions is greatly affected by the concentration. We measured the cathodic potentiodynamic polarization curves for different concentrations of nitrate ions and chromium(III) ions.

It can be seen from Fig. 2 that the values of the reduction maxima on the curve grow in proportionally to the increase in the concentration of nitrate ions. The maxima on the polarogram are directly related to the reduction of nitrate ions. The reaction order of 1.09, which is typical of complex electrochemical

Table 1. Effect of the catalyst (chromium(III) ions) on the current efficiency of the reduction of nitrate ions in the solution of sulfuric acid

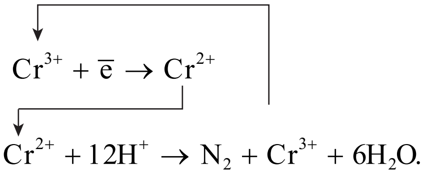
Cr(III), g/L	0.5	1.0	1.5	2.0	3.0	4.0
Current efficiency, %	38.7	45.2	54.8	61.3	74.2	80.6

reactions that proceed through intermediate stages, was determined using linear dependence log *i*—log *C*.

The effect of the concentration of chromium(III) ions was considered for the reduction of nitrate ions (Figs. 3 and 4). The current maxima grow in proportionally to the concentration of chromium(III) ions in the solution of sulfuric acid.

As a result of the redox reaction, a new active electrochemical pair forms on the electrode's surface. This process can be considered catalytic. At high cathodic current densities, the cation in the highest oxidation state is reduced on the cathode to the lowest oxidation state according to the scheme $Cr^{3+} + e^- \to Cr^{2+}$. Nitrate ions are then reduced in sulfuric acid solutions to nitrogen with Cr^{2+} ions in the near-cathode space with formation of Cr^{3+}.

As was shown above, the metal ions that form on the cathode's surface in the lowest oxidation state immediately interact with the nitrate ions in the near-electrode space. At the same time, metal ions in the highest oxidation state are regenerated, which are again reduced on the cathode and participate in the next act of nitrogen formation. In other words, the Cr^{3+} ions act as a catalyst in this process, and this will be repeated in cycles, according to the scheme



$$Cr^{3+} + \bar{e} \to Cr^{2+} \tag{3}$$

$$2NO_3^- + Cr^{2+} + 12H^+ \to N_2 + Cr^{3+} + 6H_2O.$$

To characterize the electroreduction of nitrate ions, the following kinetic parameters were calculated using the Galus technique [3]: the number of ion transport (α_n), the diffusion coefficient (D), and the heterogeneous rate constant of the electrode process (k_s), which are, respectively: $\alpha_n = 2.32 \times 10^{-1}$, $D = 8.4 \times 10^{-5}$ cm^2/s, $k_s = 2.6 \times 10^{-1}$ s^{-1}.

The experimental data showed that nitrate ions are reduced to nitrogen upon the cathodic polarization under galvanostatistical conditions in the cathode space (Table 1).

CONCLUSIONS

The kinetics of the electrochemical reduction of nitrate ions was studied via potentiometry. It was shown that rather complex electrochemical reactions occur in aqueous solutions of sulfuric acid. It was established for the first time that chromium(III) ions accelerate this electrochemical process.

REFERENCES

1. S. N. Orlik, Theor. Exp. Chem. **37**, 135 (2001).
2. *The Chemist's Handbook* (Khimiya, Moscow, 1964), Vol. 3 [in Russian].
3. Z. Galus, *Theoretical Foundations of Electrochemical Analysis* (Panstw. Wyd. Naukowe, Warszawa, 1971).

Translated by L. Mosina