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# Oxidation of Nitrate Ions at a Platinum Anode

**Bayramov RK**

LLC "Olympia", Transportnaya Street 26, 301650 Novomoskovsk, Tula region, Russia

**ABSTRACT**

The analysis of available works in the literature, including our own, was carried out, on the basis of which this review article was prepared. The interest shown in the processes of oxidative synthesis at high anodic potentials is associated with the production of various types of organic and inorganic, including mixtures of organo-inorganic compounds. The problem of electrochemical introduction of the $NO_3$ group into the molecules of organic and inorganic compounds, which are valuable products used in various fields of technology, is relevant. The electrochemical route to the synthesis of such compounds is complicated by the fact that, unlike perchloric and sulfuric acids, the anodic behavior of $NO_3$- has not been sufficiently studied. One of the reasons for this is the impossibility of obtaining reliable experimental data when using electrochemical cells in which the interelectrode spaces are separated by a glass porous diaphragm. The products of cathodic reduction, penetrating through the diaphragm into the anolyte, are oxidized by oxygen formed at the anode and significantly affect the reliability of the data obtained, in particular, the current yield (CO) of oxygen. Electrochemical cells in which the interelectrode spaces are separated by cation-exchange membranes have been developed and manufactured for the first time. In this case, the possibility of reduction products getting into the anolyte is excluded, which leads to reliable results. Only electrochemical cells of a new design, allowing reliable data to be obtained, were used in the studies. The direct (radiochemical) method proved the participation of nitrate ions in the anodic process - the oxygen evolution reaction (OER). It is shown that $NO_3$ ions participate in the OER in two ways. The analysis of the complex of the obtained data made it possible to propose a mechanism for the oxidation of nitrate ions.

***Corresponding author**
Bayramov RK, LLC "Olympia", Transportnaya Street 26, 301650 Novomoskovsk, Tula region, Russia.

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## Introduction

It is known that there are complex equilibria in the $HNO_3 – H_2O$ system, therefore it was advisable to analyze the literature data related to these equilibria in order to clarify the nature of the particles existing in the solution and data on their electrochemical behavior. A detailed analysis of the existing equilibria, the structure of aqueous solutions of nitric acid, its salts and their thermodynamics are given in the monograph and in the works [1-7]. In the range of acid concentration of interest to us (1-18N), along with the NO3- ion and hydrated $HNO_3$•$H_2O$, $NO_2$-, NO, $N_2O_3$, $N_2O_4$ are present in small quantities. Electrochemical oxidation of lower oxygen compounds on platinum to the $NO_3$-ion in nitric acid solutions is described in [8]. It has been shown that in solutions of nitric acid of low concentration (below 5.5N) compounds of two trivalent and tetravalent nitrogen are oxidized to nitrate ion only after their conversion to NO, with which they are in mobile equilibrium. In concentrated nitric acid, compounds of divalent and trivalent nitrogen are converted to $NO_2$, which is then oxidized at the anode to $NO_3$-. Analysis of literature data shows that at sufficiently high potentials in nitric acid solutions, all lower oxygen compounds of nitrogen are practically oxidized to $NO_3$-ion. Therefore, during anodic oxidation of $HNO_3$, the oxidized component can be both $NO_3$- ions and nitric acid molecules. The situation is somewhat simpler in salt solutions. These strong electrolytes are almost completely dissociated. We will not dwell in detail on the thermodynamics and structure of nitrate solutions, a generalized analysis of which is described in [1]. Comparison of the anodic behavior of the nitrate ion with the anions of sulfuric and perchloric acids indicates the specificity of its behavior. The nitrate ion is more weakly hydrated and has the greatest destructive effect on the structure of water of all the anions studied. Such behavior may be due to the flat structure of the nitrate ion [9].

A large number of works available in the literature are devoted to the reduction of the $NO_3$- ion [10-16]. Moreover, the process of anion reduction was studied on cathodes made of different metals. Perhaps this is due to the production of different products ($HNO_2$, $NO_2$, NO, etc.), as well as the determination and selection of stable materials used in the production of nitric acid. Of interest are the results described in works, which report on the reduction of nitrates to ammonia [15,16]. According to the authors, ammonia can become a source of renewable energy. In the future, the reduction of nitrate ions will be of little interest to us, the main attention will be paid to the anodic oxidation of the $NO_3$ - ion.

Electrochemical oxidation of nitrate ion in non-aqueous solutions (acetonitrile, acetic acid, etc.) is described in a number of works [17-19]. In works it is shown that oxidation of nitrate ion with formation of nitrogen pentoxide and oxygen occurs on the surface of platinum anode [17,18]. In the presence of additives, nitrate radical enters into intermediate reactions, and the process becomes more complicated. Attempts of these authors to record nitrate radical by electromagnetic resonance (EPR) during electrolysis of nitrate solutions were unsuccessful. Apparently, $NO_3$ radical was first recorded by EPR during photolysis of nitric acid at a temperature of 77K, and even under these conditions NO radical was detected [20]. As is known, with decreasing electrolysis temperature, stabilization of anion-radical particles obtained in the process occurs, which interact with each other with formation of dimeric products. During the electrolysis of aqueous solutions of sulfuric and perchloric acids at low temperatures, persulfuric acid, chloric anhydride, and sulfur peroxide are formed [21-23].

Compared to perchloric, sulfuric, and other acids, the anodic oxidation of nitrate ions in aqueous solutions has been studied to a much lesser extent.

According to available literature data, the formation of dimeric products during the electrolysis of solutions of nitric acid and its salts in the entire studied range of concentrations and temperatures was not observed. As far as could be determined, an analysis of the electrolysis products in these systems was not carried out. The anodic oxidation of nitrate ions that we carried out will be discussed in more detail later in Chapter 3.

In this review paper, we analyze the articles available in the literature, including ours, and also present in some detail the experimental results and their discussions obtained in studying the oxidation of nitric acid and its salts on a platinum anode in aqueous solutions using electrochemical cells whose interelectrode spaces are separated by a cation-exchange membrane.

## Experimental Part

Nitric acid, as noted above, is easily reduced at the cathode to nitrous acid, $NO_2$, NO [14]. In this regard, considerable attention was paid to the study of the complete separation of the interelectrode space. It is impossible to use the electrochemical cells described in when conducting experiments [22,24]. In it, the electrode spaces (anodic and cathodic) are separated by a glass porous diaphragm, through which the products of cathodic reduction enter the anolyte. The latter are oxidized by oxygen formed at the anode and significantly affect the reliability of the data obtained, in particular, the current yield (CO) of oxygen. To prevent the penetration of cathodic reduction products into the anolyte, a method for separating the anodic and cathodic spaces was developed, consisting of separating the interelectrode space with a cation-exchange membrane. Several designs of electrochemical cells were developed and manufactured (Figure 1, 2, 4), in which the cathodic and anodic spaces were separated by cation-exchange membranes [25,26]. It was shown that complete separation is achieved using the MK-100 cation-exchange membrane [27]. It showed good selectivity for cations, which was tested using labeled carbon in a sodium propionate solution and a sensitive analytical reaction for nitrite ion [28]. The developed electrochemical cells were used in balance, polarization, impedance and radiochemical experiments.

### Electrochemical Cells

Balance experiments were carried out in a cell with a cooled platinum anode (Figure 1) [25].

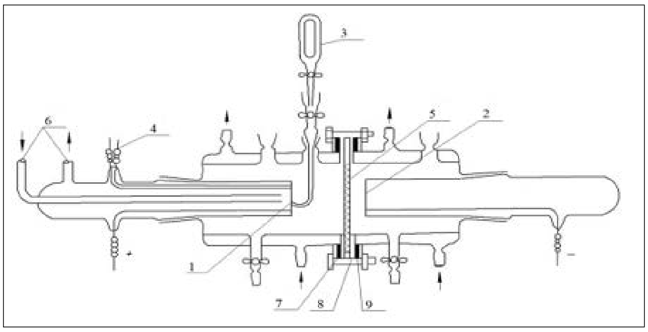

**Figure 1:** Electrochemical Cell with a Cation Exchange Membrane for Carrying out Balance Experiments
1 – Pt Anode; 2 – Pt Cathode; 3 – Reference Electrode; 4 – Thermocouple for Determining the Anode Temperature; 5 – Cation Exchange Membrane; 6 – Supply of Refrigerant to the Anode; 7 – Metal Half-Ring; 8 – Glass Flange; 9 – Rubber Gasket.

The anode and cathode sections of the cell end with thick-walled flanges, between which the membrane is fixed with metal half rings. The anode was cooled with a cooling liquid from a refrigeration machine. Electrolysis was carried out at a controlled potential, which was maintained by a P-10A potentiostat (output voltage 25 V, maximum possible current 10 A). The temperature of the anode, anolyte and catholyte was measured by chromel-copel thermocouples and controlled by a KSP-4 potentiometer. The amount of electricity passed was recorded using a coulometer. Electrolyte solutions were prepared on bidistillate water nitric acide of special purity and its twice recrystallized salts. To determine the balance of electrolysis products, the released anode gases (first passed through a trap with a neutral buffer solution of potassium iodide to isolate and quantitatively determine ozone) and then collected in a calibrated gas burette. Gas samples were taken from the latter and analyzed chromatographically using a chromatograph TSVET-1. It was found that the main oxidation product of acidic solutions is oxygen and a small amount of ozone (~0.5%). The potential was measured using a digital voltmeter EC-1 against a normal hydrogen or saturated calomel electrode. The potential values are given relative to a reversible hydrogen electrode in the same solution (φr).

### Polarization and Impedance Measurements

Polarization and impedance measurements were carried out in a cooled cell (Figure 2) [26].

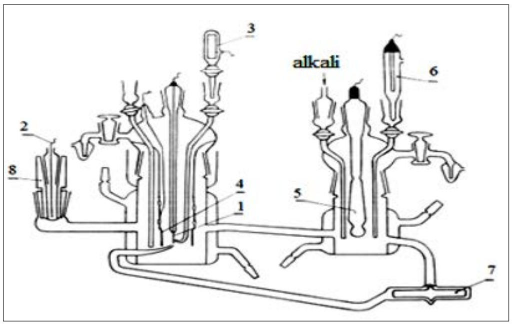

**Figure 2:** Electrochemical Cell for Measuring Polarization and Impedance with pH Clamping
1 - Platinum Anode; 2 – Platinum Cathode; 3 – Reference Electrode; 4 – Platinum Electrode; 5 – Glass Electrode; 6 – Silver Chloride Electrode; 7 – Magnetic Pump; 8 – Cathode Cartridge.

The experiments were carried out in acidic and weakly alkaline electrolytes. Since some of the experiments were carried out in weakly alkaline solutions, in which the pH of the medium changed during electrolysis, a cell with pH-stating in the volume of the solution and circulation of the latter was developed and manufactured. The cell consists of three main parts: the working part, used for polarization of the electrode, the auxiliary part for monitoring the pH of the solution and a magnetic pump for circulation of the electrolyte. To maintain a constant pH of the medium, a pH-stating system was used, consisting of a set of devices for potentiometric titration (pH meter, titograph, and autoburette), sensor electrodes (glass, silver chloride). Polarization of the electrode was carried out from a P-5827 potentiostat. A platinum wire with an area of 0.1 $cm^2$, sealed into glass, was used as a working electrode. Before the experiment, the working electrode was treated for 5 minutes in a mixture of hydrogen peroxide and sulfuric acid (in a ratio of 3:1), washed with bidistillate water and subjected to cathode-anodic activation in 1 N sulfuric acid. Activation was carried out using a preprogrammed device that allowed the required potential change program to be set. The device was equipped with a mechanical polarization cycle counter. In this case, activation was carried out in the potential range of 0.2 V (2 s) - 1.2 V (2 s) for 200 cycles.

Since the kinetics and impedance measurements were carried out with complete separation of the anodic and cathodic spaces, which is especially important in the case of nitric acid and its salts, due to the reduction of nitrate ions on the cathode. For this purpose, a detachable cylindrical Teflon cathode chamber with an MK-100 cation-exchange membrane was designed, which was inserted into the cathode space of the cell (Figure 3) [26].

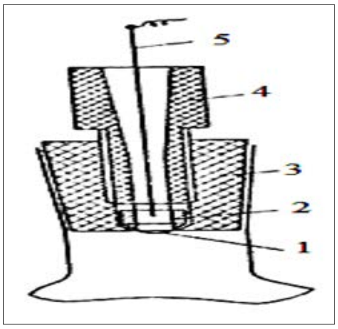

**Figure 3:** Cathode Cartridge
1 – Cation Exchange Membrane; 2 – Pressure Washer 3 – Membrane Holder; 4 – Bushing-Screw; 5 – Electrode.

The capacity and resistance of the system at a given potential were measured on two AC bridges: with series and parallel equivalent circuits. At high potentials, due to the large values of the measured capacity in the series circuit (hundreds of µF), the data obtained become unreliable, and it is not possible to expand the range of measured potentials. The use of a parallel circuit with a resistance equivalent to the resistance of the solution connected in series allows these difficulties to be eliminated in a number of cases. The data obtained on both bridges after the appropriate transformation from a series circuit to a parallel one are in good agreement with each other.

Determination of Anion Participation by the Labeled Atom Method
The technique for studying anion participation in the process of oxygen evolution using O18 was developed in detail and described in [29]. The setup in which the experiments were carried out consisted of an electrochemical cell (Figure 4) for polarization in a solution of labeled sodium nitrate, in potentiostatic and galvanostatic modes, a gas purification system, a sampling system, and a mass spectrometer for gas analysis MI-1309 [26].

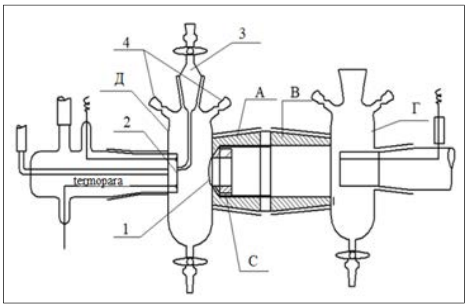

**Figure 4:** Electrochemical Cell for Radiochemical Measurements
A – Membrane Holder; b – Bushing-Screw; c – Conical Sealing Washer; d – Anode Compartment of the Cell; d – Cathode Compartment of the Cell;
1 – Membrane; 2 – Working Electrode; 3 – Electrolytic Key; 4 – Inlets for Sampling and Purging Gases.

The volume of the solution in the cell was 20 cm3, the volume of the gas above it was 5 cm3. To collect a gas sample, a flow-through ampoule with taps (volume ~ 1 $cm^3$) was connected to the cell on the ground section, between which a sample of the analyzed gas was collected. The working electrodes were a platinum wire with an area of 0.1 $cm^2$ or a platinum sheet with an area of 8 cm2. The electrode treatment was described earlier. Before the experiment, the cell and the ampoule for sampling were purged with purified nitrogen for 1 hour, and the first nitrogen sample was analyzed on a mass spectrometer for oxygen content. Nitrogen was considered pure if the peak of 32 mass did not exceed the peak of 32 mass of the mass spectrometer background. Then, the Pt anode was polarized at a given potential for a time required to form a sufficient amount of oxygen for analysis (0.1-0.5 ml), determined by the electrode area and current density. After completion of electrolysis, the oxygen collected in the cell was blown out with nitrogen into the ampoule, which was then analyzed for O18 content. The pressure at the sample inlet was 10-6 Torr. The mass spectra were recorded cyclically with a mass sweep from 35 to 27 and recorded on a KSP-4 recorder. Based on the peak values, taking into account the sensitivity of this scale, the concentration ratios O18O16/O16O16 (mass 34/32, R1) and O17O16/O16O16 (mass 32/32, R2) were found. The proportion of O18 in the total number of oxygen atoms was calculated using the formula:

$$\alpha = \frac{R1}{2+R1+R2} \qquad (1)$$

For each sample, the average (over 5-6 cycles) value of α was determined and the mean square error of the experiment was found. Usually, it fluctuated between 0.01 and 0.05%. The number of samples at each potential was at least 5-6. The solutions were prepared from twice recrystallized and calcined sodium and cesium nitrate salts of the "SP" brand in water enriched with H2O18. The heavy oxygen water was purified by boiling for many hours with the addition of alkali metal permanganate in a flask with a reflux condenser, after which the water was distilled. Water enriched with O18 to 2.34 and 8.5% was used. To verify the data on the participation of the anion in the anodic process, $NaNO_3$ salt labeled with O18 was prepared using the method described in [30]. Isotopic analysis of the water was carried out using the method in [31]. When analyzing the labeled NaNO3 for the O18 content, 10 mg of the suspension was introduced into the ampoule, which was evacuated (2-3•10-8 Torr) and sealed. Then the salt was thermally decomposed on the flame of a gas burner, and the released oxygen was analyzed on a mass spectrometer. The O18 content in water and salt was calculated using formula (1).

## Results and Their Discussion

As noted above, there are no data in the literature on the balance of the products of electrolysis of nitric acid solutions and its salts, which is very important for understanding the mechanism of the process. In this regard, experiments were conducted at a controlled potential (in the region of high anodic potentials) in a wide range of nitric acid concentrations (from 1 to 18 N) and its salts (1-5 N), temperatures (from +20 to -300C) and pH of the medium. There are also no direct data on the participation of $NO_3$- ions in the anodic process.

## Polarization and Impedance Measurements

Stationary polarization curves, changes in the capacity of the double electric layer and polarization resistance of the platinum electrode with potential (10 kHz, parallel circuit) for nitric acid solutions in 1 N and 10 N nitric acid solutions at room temperature (curve 1, 2) and the corresponding changes in capacity (curves

1′, 2′) and polarization resistance (curve 2″) are shown in Figure 5 [32].

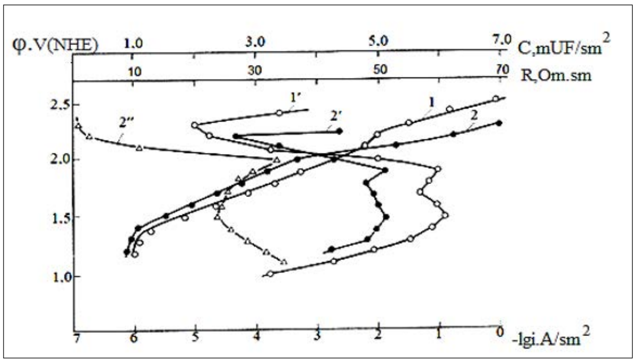

**Figure 5:** Polarization Curves (1,2) and Changes in Capacitance (1′, 2′) and Resistance (2″) Depending on the Potential at a Temperature of +200C. 1.1′- 1N $HNO_3$ Solution, 2.2′,2″- 10N HNO3 Solution

It is evident that at low potentials the C – φ curves do not differ from those for perchloric and sulfuric acids either in character or in absolute values of capacity [33]. Two small capacity maxima associated with the adsorption of oxygen dipoles and anions and a sharp drop in capacity above 1.9 V, caused by a change in the character of oxygen coatings on platinum and the onset of adsorption of anion discharge products, are clearly visible. In the upper section of the φ – lgi curve, the total rate of the anodic process increases with an increase in the acid concentration, and the beginning of the section shifts toward lower anodic potentials. The change in capacity at potentials of active participation of NO3 anions in the anodic process has a different character. The capacity here (curves 1′ and 2′) increases sharply and the earlier the concentrated acid was introduced, the earlier. In addition, the minimum value of capacity at φr (2.2–2.3 V) is somewhat higher than in perchloric and sulfuric acids. With increasing acid concentration, productivity increases, unlike the previously studied systems - perchloric and sulfuric acids. The appearance of a maximum polarization resistance at potentials of the transition region reflects a change in the state of the electrode surface and the inhibition of the process of oxygen release from water due to the adsorption of anions and strengthening of the bond of oxygen with the surface.

In what follows, the region of low potentials (up to 2 V) will be of little interest to us. The main attention will be focused on the analysis of the regularities of the process at high anodic potentials. Figure 6 shows polarization curves, capacity curves and resistance curves with potential for weakly alkaline solutions [34].

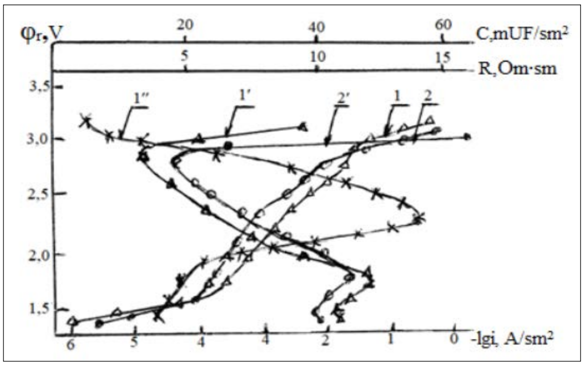

**Figure 6:** Polarization Curves (curves 1,2), Capacity Curves (curves 11,21) and Resistance Curves (111) with Potential for Weakly Alkaline Solutions (pH = 11)

$1, 1^1.1^{11}$ – 1 N $NaNO_3$; $2, 2^1$ - 5 N $NaNO_3$.

Unlike acidic solutions, where the polarization curve has two kinetic branches, weakly alkaline solutions are characterized by the presence of three kinetic sections and a small but clearly reproducible transition region between the second and third sections. With increasing sodium nitrate concentration, the third branch shifts to the region of high current densities. The transition region between the first and second sections of the polarization curve, the nature of which changes with increasing nitrate concentration, attracts attention: its length increases, and if in 0.1 N $NaNO_3$ it is outlined, then in 1 N and 5 N sodium nitrate solutions the state of the system becomes more stable. Due to the appearance of large transition regions, the beginning of the third kinetic region in weakly alkaline solutions shifts toward more positive potentials relative to the reversible hydrogen electrode than in acidic solutions. For example, for 5N nitric acid, the beginning of the upper kinetic section is at 2.1 V, then in sodium nitrate (pH ~ 11) the beginning of the upper section is at a potential of 2.7V. However, if the curves in acidic and slightly alkaline solutions are attributed to the same reference electrode, for example, to a normal hydrogen electrode, then the beginning of these sections coincide and begins at a potential of 2.1 V. From our point of view, the use of the φr scale is due to the fact that water is more or less involved in the process over the entire potential range. A similar picture is observed for other mineral acids (sulfuric and perchloric). It is important to note here that regardless of the pH of the solution, the discharge of nitrate ions begins earlier in potential than perchlorate and sulfate ions, which, as noted, is associated with the specific behavior of $NO_3$ ions.

The most interesting data were obtained when studying the nature of the impedance change in concentrated nitric acid (above 12N) at low temperatures. Figure 7 shows data on the change in capacity with potential of 18N $HNO_3$ at temperatures of +200C (curve 2′) and -260C (curve 1′).

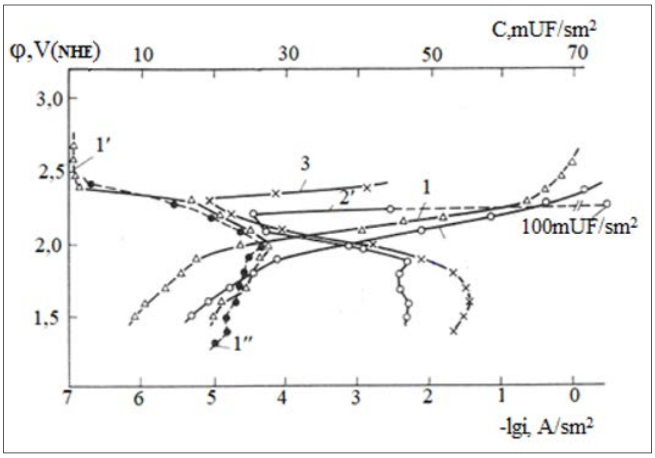

**Figure 7:** Polarization Curves in a Solution of 18N $HNO_3$ at -260C and +200C (curves 1 and 2) and Changes in Capacity in a Solution of 18N $HNO_3$ at Room (+200C, curve 2′) and Low (-260C, curve 1′) Temperatures, C-φ in a Solution of 18N $HNO_3$ at -260C (curve 1″, Recalculation According to a Sequential Scheme). 3 – Capacity in a 10N $HNO_3$ Solution at +200 C

In the region of low potentials, the nature of the change in capacity is similar to that described earlier for a platinum electrode in acidic solutions. At potentials of the upper kinetic branch, when the $NO_3$ ion begins to participate in the anodic process, the capacity, as in acidic solutions, increases, which is due to the equivalent electric diagram of the adsorption capacity, reflecting the presence of active labile anion-radical complexes on the surface of the oxidized electrode, through which the process of oxygen evolution occurs. Note that this type of change in capacity at high potentials for acidic and alkaline solutions (for all concentrations) is observed at positive temperatures, i.e., under conditions when the reaction of oxygen evolution with the consumption of four electrons is mainly realized. It also follows from the figure that if at room temperature the capacity begins to grow at high potentials, then at low temperature in this potential region the capacity decreases sharply, which most likely characterizes the appearance of chemisorbed anion-radical complexes on the electrode surface, possibly dimeric, similar to those formed during the electrolysis of sulfuric and perchloric acids at low temperatures. It is characteristic that a sharp decrease in capacity occurs under conditions of an "apparent" excess of CO oxygen over 100%, which is associated with the formation of an intermediate peroxide compound of the N2O6 ads type. For comparison, this figure also shows the nature of the change in capacity with potential for 10N HNO3 at a temperature of +200C (curve 3). Under these conditions, only one mechanism of oxygen release occurs, and in accordance with this, the capacity increases at high potentials.

### Determination of the Balance of the Electrolysis Products of Nitric Acid Solutions and Its Salts

As noted earlier, there are no data in the literature on the balance of the electrolysis products of nitric acid and its salts. To eliminate this drawback, balance experiments were conducted on the electrolysis of solutions of nitric acid and its salts. In all cases, the values of the oxygen (CO) current output were calculated based on the volumetric analysis data, taking into account that 4 faradays are spent on the formation of 1 mole of oxygen. The results of the experiments on the electrolysis of nitric acid solutions of different concentrations at different temperatures are given in Table 1 [25].

**Table 1: Results of Experiments to Determine the Balance of Products Obtained during the Electrolysis of Nitric Acid Solutions**

| 1 N $HNO_3$<br>φ = 2,35v,<br>t = +20 °C | | 10N $HNO_3$<br>φ = 2,35v,<br>t = +20 °C | | 12N $HNO_3$<br>φ = 2,35v,<br>t = +20 °C | | 15N $HNO_3$<br>φ = 2,35v,<br>t = +20 °C | | 18N $HNO_3$<br>φ = 2,35v,<br>t = +20 °C | |
|---|---|---|---|---|---|---|---|---|---|
| Q, cul. | CO $O_2$, % | Q, cul. | CO $O_2$, % | Q, cul. | CO $O_2$, % | Q, cul | CO $O_2$, % | Q,cul | CO. % |
| $3\cdot10^3$ | 99,0 | $3\cdot10^3$ | 99,0 | $3\cdot10^3$ | 99 | $3\cdot10^3$ | 100 | $3\cdot10^3$ | 99,0 |
| $6\cdot10^3$ | 99,0 | $6\cdot10^3$ | 100,0 | $6\cdot10^3$ | 100 | $6\cdot10^3$ | 99 | $6\cdot10^3$ | 100 |
| $9\cdot10^3$ | 100 | $9\cdot10^3$ | 99 | $9\cdot10^3$ | 99 | $9\cdot10^3$ | 100 | 9·10+ | 100 |
| φ = 2,4v,<br>t = - 5 °C | | φ = 2,35v,<br>t = - 20 °C | | φ = 2,35v,<br>t = -20 °C | | φ = 2,35v,<br>t = -20 °C | | φ = 2,35v,<br>t = -26 °C | |
| $3\cdot10^3$ | 100 | $3\cdot10^3$ | 101 | $3\cdot10^3$ | 105 | $3\cdot10^3$ | 107 | $3\cdot10^3$ | 117 |
| $6\cdot10^3$ | 100 | $6\cdot10^3$ | 101 | $6\cdot10^3$ | 106 | $6\cdot10^3$ | 108 | $6\cdot10^3$ | 118 |
| $9\cdot10^3$ | 100 | $9\cdot10^3$ | 100 | $9\cdot10^3$ | 106 | $9\cdot10^3$ | 108 | $9\cdot10^3$ | 118 |

It is evident from the table that during electrolysis of nitric acid solutions in the entire concentration range at temperatures above 00C, the current efficiency (CO) of oxygen calculated for a four-electron reaction is close to 100%. At the same time, the anolyte remained colorless throughout the experiment. On the contrary, new phenomena were observed during electrolysis of concentrated acid (12N and higher) at temperatures below 0°C. Firstly, as can be seen from the table, the CO of oxygen calculated for a four-electron reaction becomes greater than 100%. Secondly, passing a small amount of electric power already leads to yellowing of the anolyte, which is due to the presence of dissolved nitrogen dioxide. Both of these effects are enhanced by decreasing temperature and increasing acid concentration. Further, when the temperature increases after electrolysis at low temperatures, brown $NO_2$ vapors appear above the solution in concentrated acid solutions, which indicates the decomposition of electrolysis products in the anolyte with the release of nitrogen dioxide. An analysis of these data, taking into account the possible equilibria in nitric acid known from the literature, showed that these phenomena can be explained if we assume the decomposition of a nitrogen compound richer in oxygen, for example, nitrogen peroxide, formed during the electrolysis of concentrated acid at low temperatures with the release of oxygen and nitric oxide ($N_2O_4$) [2-7]. The "apparent" excess of CO oxygen (~20%) observed in concentrated acid solutions at low temperatures indicates the inclusion of another mechanism for the release of oxygen in the process with the consumption of a smaller number of electrons per 1 mole of $O_2$, and the magnitude of this imbalance served in the experiments as a measure of the inclusion of the new mechanism. The data obtained at low temperatures in concentrated solutions indicate that, along with the main mechanism of oxygen release with the consumption of 4 faraday per 1 mole, there is a second path, when oxygen is formed as a result of the reaction:

$$2NO_3^- - 2e \rightarrow 2NO_{3ads.};\ 2NO_{3\,ads.} \rightarrow N_2O_{6ads.} \qquad (1)$$

$$N_2O_{6ads.} \rightarrow N_2O_4 + O_2;\ N_2O_4 \rightarrow 2NO_2. \qquad (2)$$

The contribution of this mechanism increases with decreasing temperature and increasing acid concentration and can reach ~20% at $-26^0$C.

Unfortunately, further lowering of the electrolysis temperature becomes impossible due to freezing of the aqueous electrolyte solution. Studying and selecting a non-aqueous (organic) solvent for preparing a concentrated nitric acid solution will allow to sharply lower the temperature of the electrolysis process. When carrying out the process in such a system, the formation of $NO_3$ radical can occur. During the dimerization of radicals, it is possible to obtain a dimeric product - nitrogen peroxide ($N_2O_6$). Similar studies of the current efficiency (CO) of oxygen were carried out during the electrolysis of weakly alkaline nitric acid solutions at potentials corresponding to the participation of nitrate ion in the anodic process. Unlike acidic solutions, nitrite ions ($NO_2$-) are detected in the anolyte under these conditions. The experimental results for 5N $NaNO_3$ for pH = ~ 11 are given in Table 2.

**Table 2: Experimental Results for 5N NaNO3 for pH ~ 11**

| φ r, V | t, °C | Q,·$10^{-3}$, cul. | Concentr. of NO3 -, gr- egv./ l | CO P, % | |
|---|---|---|---|---|---|
| | | | | $NO_3$- | $O_2$ |
| 2,9 | 20 | 1,9 | 5,9 ·$10^{-5}$ | 0,05± ,02 | 100±1 |
| 3,1 | 20 | 1,9 | 1,13 ·$10^{-4}$ | 0,11± ,02 | 100±1 |
| 2,8 | -8 | 1,9 | 2,0 ·$10^{-5}$ | 0,02± ,02 | 100±1 |
| 3,1 | -8 | 1,9 | 8,5 ·$10^{-3}$ | 7,2± ,02 | 107±1 |
| 3,1 | -8 | 3,8 | 1,7 ·$10^{-2}$ | 7,2± ,02 | 107±1 |

As can be seen from the table, at room temperature the oxygen current output (per 4-electron reaction) is close to 100% and the nitrite ion concentration is low (~ 10-4 ÷ 10-5 g.eq/l). The accuracy of the volumetric method (1÷2%) under these conditions does not allow one to sense the oxygen imbalance. When the temperature decreases to -80C, the oxygen CO increases, but not as sharply as in acidic solutions and at φr= 3.1V is 107%. The current output (CO) of the nitrite ion is in good agreement with these data (about 7%). An increase in the amount of electricity passed leads to an increase in the nitrite ion concentration in the solution; however, the current output remains virtually unchanged. As can be seen from the data obtained, at room temperature the $NO_2$- ion is formed in very small quantities. When the temperature decreases under our conditions (the pH of the solution is constant at ~11), the nitrite ion accumulates in the solution and its current yield reaches ~7% (the last two lines of Table 2) and corresponds to the "apparent" excess of CO of oxygen, more than 100% (~7%). These data allow us to assume that in this case, as in acidic environments, when the temperature of the reaction zone decreases, the process can also proceed along the second path (reactions 1 and 2).

The anodic behavior of nitrate ion in aqueous solutions is covered most fully in [35]. It studies the kinetics of anodic processes occurring in nitrate solutions on a Pt electrode. It is shown that, as in solutions of sulfuric and perchloric acids, the polarization curves of platinum in nitric acid solutions consist of two linear sections delimited by a transition region. The first section of the polarization curve corresponds to the process of oxygen formation from water. Inhibition of the anodic process, expressed in the appearance of a transition region, is caused by the adsorption of nitrate ion and the beginning of its discharge. In the second section of the φ-lgi curve, as the authors assume, nitrate ions participate in the process of oxygen evolution at high anodic potentials. At the beginning of the second section of the φ-lgi curve, $NO_2$- anions were detected in the anolyte, but with prolonged electrolysis and an increase in current density, this anion could not be detected. The nature of the accumulation of nitrite ions (curve with a maximum) gave the authors grounds to assume an autocatalytic mechanism of oxidation of nitrites to nitrates. In this work, correct assumptions were made about the participation of $NO_3$- anions in reactions occurring at high anodic potentials. The mechanism of oxidation of nitrate ion through the formation of nitrogen dioxide and nitric acid proposed by him cannot be considered fully proven. The authors of another work, in which, based on a study of the anodic oxidation of hydrochloric acid in a nitric acid mixture, an assumption was made that at low temperatures (below 5 °C) the discharge of nitrate ion is followed by the formation of nitrogen pentoxide [36]. In, the authors showed that, in contrast to the chemical nitration of lignin in a concentrated nitric acid solution at high temperature, electrochemical nitration at room temperature in dilute acid solutions prevents emissions of nitrogen oxides into the atmosphere, thereby being more environmentally friendly [37]. In this case, the authors refer to the mechanism of oxidation of nitrate ions, described earlier in [34].

### Determination of the Participation of Anion in the Anodic Process by the Method of Labeled Atoms

For direct proof of the participation of NO3 ions in the anodic process, the stable isotope O18 was used, which was introduced into water or anion, and then its appearance in the anode gas was recorded using a mass spectrometer. Since in acidic solutions a very rapid exchange between the oxygen of water and the anion occurs, weakly alkaline solutions of sodium nitrate were used in these experiments [38]. Measurements were carried out in the potential range (from 1.6 V to 3.1 V) in 1 N and 5 N sodium nitrate solutions. The results of the experiments (from 5 to 6 measurements taking into account the mean square error), obtained during the electrolysis of 5N NaNO3 in water labeled with O18, are presented in Table 3 [34].

**Table 3: The Result of the Electrolysis of Solutions $NaNO_3$**

| Series of experiments | The content O18 in $H_2O$ or $NaNO_3$ | φr, V | I, A/sm² | Content O18 in the sample, % | The share participation A, % | |
|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| 1 | 2,36 ± 0,04% | 1,6 | 2,15· $10^{-5}$ | 2,3 ± 0,04 | 97 ±3,0 | 3 ± 3,0 |
| 2 | | 2,7 | 3,2 · $10^{-3}$ | 2,14 ± 0,15 | 89,8 ± 6,9 | 10,2 ± 6,9 |
| 3 | | 2,8 | 5,4 · $10^{-3}$ | 2,08 ± 0,03 | 87,0 ± 1,4 | 13,0 ± 1,4 |
| 4 | | 2,9 | 3,2 · $10^{-2}$ | 1,31 ± 0,06 | 51,4 ± 2,8 | 48,6 ± 2,8 |
| 5 | | 3,0 | 1,6 · $10^{-1}$ | 0,66 ± 0,21 | 21,3 ± 9,7 | 78,7 ± 9,7 |
| 6 | | 3,1 | 4,3 · $10^{-1}$ | 0,27 ± 0,02 | 3,65 ± 0,6 | 96,4 ± 0,6 |
| 7 | 6,8 ± 0,05% | 3,1 | 4,0 · $10^{-1}$ | 6,34 ± 0,02 | 6,9 ± 0,3 | 93,03 ±0,3 |

The data presented in the first through sixth rows of the table correspond to the experiments conducted in water enriched with O18; the seventh row contains the results obtained with labeled O18 in the $NO_3$ anion for comparison. The second column of the table contains the data on the O18 content in water or in the anion, which were 2.36 ± 0.04% and 6.8 ± 0.05%, respectively. The O18 content in the anode gas (sample) is given in column 5. It follows from the table that the data on the participation of the $NO_3$ ion in the anode process, obtained in the experiments with labeled water and the labeled $NO_3$ anion, are in good agreement with each other. Thus, for a potential of 3.1 V, these shares are 96.4% and 93%, respectively. As can be seen from the table, up to a potential of 2.5 V, the anion practically does not participate in the anode process (its share of participation is within the limits of experimental error). Its noticeable participation in the process of oxygen release begins at the potentials of the second kinetic branch (φr = 2.6-2.8 V), but this share is still insignificant - up to 13%. A sharp bend occurs at the potentials of the third kinetic section (above 2.8 V). The share of anion participation here quickly increases with potential and reaches almost 100% at φr = 3.1 V. Based on polarization measurements and data on the degree of anion participation at different potentials, partial polarization curves of the rates of oxygen release from water and the $NO_3$- anion were calculated (Figure 8).

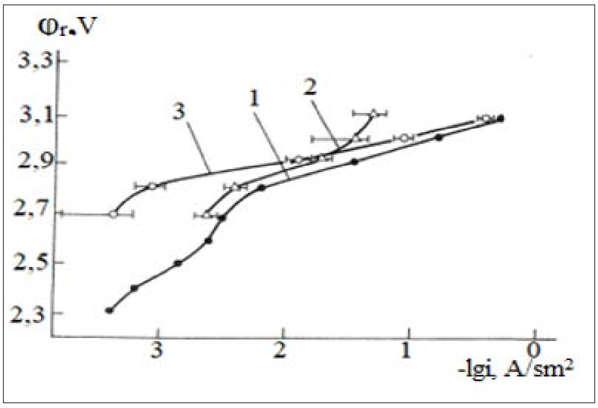

**Figure 8:** General (1) and Partial Polarization Curves (2; 3) for 5N NANO3 Solutions,
2 – for $H_2O$, 3 – for $NO_3$- ion.

The slope of the partial polarization curve of oxygen formation from the anion is 120 mV, and for water it increases from 200 mV to 500 mV in the region φr = 2.9-3.1 V.

Based on the analysis of the complex of data obtained, the possible ways of participation of the nitrate ion in the process of oxygen release can be presented as follows (Figure 9)

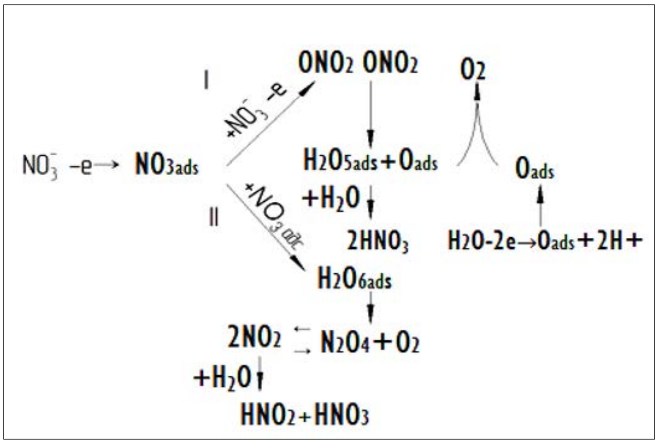

**Figure 9:** Possible Ways of Participation of Nitrate Ion in the Process of Oxygen Release

Firstly, the participation of the $NO_3$- anion in the anodic process has been proven; its share at high potentials and positive temperatures of electrolysis reaches almost 100%. This means that the oxygen molecule is formed from active oxygen atoms formed during the dimerization of $NO_3$ complex particles. This path is possible with some filling of the electrode surface with anion-radical complexes, which is expressed in the appearance of a small adsorption capacity (~ 50 μF/cm2) in impedance measurements. At positive potentials, when the share of the anion participation is less than 100%, both the oxygen of the anion and the oxygen formed during the discharge of water molecules participate in the formation of the oxygen molecule. This mechanism of oxygen formation is shown in the figure by the sequence of reactions I. In fact, this path assumes the intermediate formation of nitrogen pentoxide in the reaction layer with its subsequent interaction with water. Secondly, when the temperature in concentrated solutions of acid and its salts decreases, the second mechanism of oxygen formation is realized along with the main mechanism (with a maximum share of up to 20% under extreme conditions). As noted above, the decrease in temperature leads to partial stabilization of $NO_3$ radicals and, probably, to the formation of an intermediate complex ($ONO_2$ $ONO_2$ads. ) with its subsequent decomposition. This path is shown in the figure by the sequence of reactions II. The release of oxygen by this mechanism consumes 2 electrons, which leads to an "apparent" excess of CO oxygen by more than 100%. This reaction path is in good agreement with all the observed experimental data: the appearance of nitrogen dioxide in the solution of concentrated acid during electrolysis at low temperatures, a sharp decrease in capacity under these conditions, the formation of an equivalent amount of nitrite ion in the anolyte in weakly alkaline solutions.

## Conclusion

Based on the literature analysis, including our own works, a review article has been prepared, which also presents the experimental results obtained in studying the oxidation of nitrate ions on a platinum anode. The study used for the first time the developed electrochemical cells of a new design, in which the interelectrode spaces are separated by a cation-exchange membrane, which made it possible to obtain reliable experimental results. The participation of nitrate ion in the anodic process - the oxygen evolution reaction (OER) - was proven by the radiochemical method. It was shown that with a further decrease in the electrolysis temperature (below 300C), it is possible to obtain a strong oxidizer - nitrogen peroxide (N2O6). A mechanism for the oxidation of nitrate ions is proposed.

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