DOI: 10.6060/ivkkt.20186107.5776

УДК: 546.26-162:628.16:541.183.12

ЭЛЕКТРОХИМИЧЕСКИЕ ПРОЦЕССЫ НА ДИСПЕРСНЫХ ГРАФИТОВЫХ ЭЛЕКТРОДАХ В РАСТВОРАХ HNO_3

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Потенциодинамическим методом исследованы механизм и кинетика анодных процессов на дисперсном графитовом электроде. Варьирование потенциала реверса в анодной области на потенциодинамических кривых позволило оценить соотношение анодной и катодной емкостей и определить коэффициент обратимости электрохимических реакций. По степени обратимости электрохимических реакций выделены 3 области потенциалов I - Ест... 1,15В; II- 1,15...1,4В; III- > 1,4В, соответствующих последовательному протеканию процессов интеркалирования графита нитрат ионами, окисления поверхностных функциональных групп, образования окись подобных соединений графита. В области потенциалов I отмечается максимальная обратимость анодного процесса, обусловленная протеканием процесса интеркалирования-деинтеркалирования, с образованием соединений внедрения графита. Затем отмечено закономерное снижение коэффициента обратимости, связанное с протеканием реакций с участием поверхностных кислородсодержащих групп и реакциями с участием кислорода. Данный комплекс электрохимических процессов сопровождается образованием соединений внедрения графита нестехиометрического состава и, вероятно, окись подобных структур. Переход в III область потенциалов характеризуется скачкообразным снижением коэффициента обратимости и ростом анодных токов, которые с циклированием снижаются. В данных условиях, вероятно, протекают реакции окисления графитовой матрицы с образованием CO и CO_2. Выявлено увеличение скорости необратимых реакций при снижении концентрации HNO_3. В 45% HNO_3 значительно ускоряются реакции переокисления СВГ и образования окисных соединений графита. В 30% HNO_3 на дисперсном графитовом электроде регистрируются наиболее высокие анодные токи первого цикла из исследованных растворов, при этом обратимость анодных процессов ниже, чем в 60% HNO_3. Показано, что в HNO_3 с концентрацией менее 15% процесс интеркалирования графита протекает с незначительной скоростью и сопровождается поверхностными реакциями с участием кислорода.

Ключевые слова: соединения внедрения графита, нитрат графита, электрохимическое интеркалирование

ELECTROCHEMICAL PROCESSES ON DISPERSE GRAPHITE ELECTRODES IN HNO_3 SOLUTIONS

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The mechanism and kinetics of anodic processes on a dispersed graphite electrode are investigated by a potentiodynamic method. Variation of the reversal potential in the anode zone on potentiodynamic curves PDC allow to estimate the ratio of the anode and cathode capacities and to determine the coefficient of reversibility of electrochemical reactions. By the degree of reversibility of electrochemical reactions, three potential zones are distinguished: Ist - E ... 1.15 V; II-1.15 ... 1.4V; III -> 1.4B corresponding to the sequential course of the intercalation of graphite with nitrate ions, oxidation of the surface functional groups, the formation of oxide-like graphite compounds. In the zone of potentials I, the maximum reversibility of the anodic process is noted, due to the intercalation-deintercalation process, with the formation of graphite intercalation compounds. Then, a regular decrease in the coefficient of reversibility associated with the occurrence of reactions involving surface oxygen-containing groups and reactions involving oxygen is noticed. This complex of electrochemical processes is accompanied by the formation of graphite intercalation compounds of non-stoichiometric composition and, probably, the oxide of similar structures. The transition to the potential of zone III is characterized by an abrupt decrease in the coefficient of reversibility and the growth of anode currents, which decrease with cycling. Under these conditions, oxidation reactions of the graphite matrix are likely to occur with the formation of CO and CO_2***. An increase in the rate of irreversible reactions is revealed with a decrease in the concentration of*** HNO_3***. In 45%*** HNO_3***, the re-oxidation reactions of graphite intercalation compound and the formation of oxide compounds of graphite are significantly accelerated. In 30%*** HNO_3***, the highest anode currents of the first cycle from the solutions studied are recorded on a dispersed graphite electrode, and the reversibility of the anode processes is lower than in 60%*** HNO_3***. It has been shown that in*** HNO_3*** with a concentration of less than 15%, the intercalation of graphite proceeds at a low rate and is accompanied by the surface reactions involving oxygen.***

Keywords: graphite intercalation compounds, graphite nitrate, electrochemistry

Для цитирования:

Яковлев А.В., Яковлева Е.В., Рахметулина Л.А., Соловьева Н.Д., Лопухова М.И. Электрохимические процессы на дисперсных графитовых электродах в растворах HNO_3. *Изв. вузов. Химия и хим. технология*. 2018. Т. 61. Вып. 7. С. 122–129

For citation:

Yakovlev A.V., Yakovleva E.V., Rakhmetulina L.A., Solovyova N.D., Lopukhova M.I. Electrochemical processes on disperse graphite electrodes in HNO_3 solutions. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* 2018. V. 61. N 7. P. 122–129

INTRODUCTION

Previous studies [1-3] have revealed the complex effect of the concentration of the HNO_3 solution on the kinetics of conjugated surface and bulk anodic reactions on graphite electrodes. As it was shown in [3], that the diluting of the electrolyte shifts the threshold potential in the positive direction, whereas the potential of the re-oxidation of graphite intercalation compounds (GICs) and oxygen reaction moves in the negative direction. A sufficient amount of water in the electrolyte leads to the formation of graphite oxide of the general formula: Cx + (OH) y (H_2O) z with C-O covalent bonds between the atoms of carbon networks and oxygen in the intercalate [4-6] when GICs is re-oxidized. The amount of covalently bounded oxygen depends on the composition and the conditions for the production of graphite oxide and increases when GICs is highly oxidized [5]. According to the same source, a significant portion of oxygen in graphite oxide is in the composition of PVG and not in the form of an intercalate. It should also be noted that the electrochemical reversibility of graphite oxide decreases with the increase in the acid concentration in the electrolyte [5]. In work [7], the attention is paid to the decrease in the ability of the graphite nitrate for cathodic reduction during its re-oxidation and the formation of more stable bonds between graphite and intercalate. There is an opinion [8] on the possibility of the chemical formation of graphite oxide in the anodic synthesis of GICs in dilute solutions. Simultaneously, in less concentrated solutions, parallel to the processes of electrochemical intercalation, the reactions of carbon oxidation and release of oxygen are possible [3]. The presence of active forms of oxygen, as a necessary component of the production of graphite oxide, is noted in a number of works [5,9]. A number of authors assume the participation of water in the processes of electrochemical intercalation. Even in concentrated solutions, the presence of up to 4% (by weight) of water is observed in the composition of GICs [10]:

$$C_x + xyA^- + 2xyHA + \nu xyH_2O \rightarrow$$
$$\rightarrow [C_y + yA^-{\cdot}2yHA{\cdot}\nu yH_2O]\ x + xye. \qquad (1)$$

Graphite nitrate, obtained in concentrated solutions of HNO_3, also contains water: $C_{(8+2x)n}N_2O_5{\cdot}xH_2O$ ($n = 1,2,3...,0 \leq X \leq 3$) [11]. In less concentrated solutions, the intercalation process is also carried out with the participation of water, the latter acts as a supplier of protons for compatible acid anions [8]:

$$C_x + (y+z)A^- + zH_2O \rightarrow C_x^{y+}{\cdot}yA^-{\cdot}zHA + zOH^- + ye^-. \qquad (2)$$

Comparing the conditions for conducting our experimental studies with the foregoing concepts, it can be stated that in the solutions under study, it is inevitable that the part of carbon is deeply oxidized by the defects and edges of the polyarene grids that occurs parallel to the reaction of electrochemical intercalation. In this case, it is necessary to take into account the high probability of formation of graphite oxide. Taking into account the fact that GICs of an acceptor-type obtained by the anodic oxidation of the carbon material have a high electrochemical reversibility [7, 12, 13], and the processes of the formation of CO, CO_2 and O_2 are practically irreversible, it is advisable to trace the change in the ratio of the amounts of electricity consumed for the oxidation and reduction of the compounds obtained. In order to identify the areas of potentials in which intercalation reactions and irreversible surface processes take place with the formation of gaseous products, cyclic PDCs at various reversal potentials in the anode range and increased sensitivity of the current recorder were taken on the graphite electrode in HNO_3 solutions of various concentrations.

EXPERIMENTAL PROCEDURE

Dispersed graphite powders of the Chinese production (standard GB/T 3518-95), ash content 0.2%, particles size 250-300 μm were used in the studies. As an electrolyte, a 60% nitric acid solution of KhCH (TU701-89E) brand was used. Less concentrated solutions were prepared by diluting 60% HNO_3 with bi-distilled water, and the concentration was determined by the titration with 0.1 M KOH. Electrochemical measurements on the disperse graphite electrodes were carried out in three-electrode cells [3], using platinum cathodes and anode current lead. To form the working electrode, the graphite powder was poured into the cylindrical body of the cell [3], made of fluoroplastic and pushed by the cathode piston to the platinum collector. The electrolyte enters the reaction zone through the perforation of the piston sewn into the diaphragm of polypropylene (TU54411-78). Through the hole in the piston a capillary of the electrolytic key was fed to the graphite layer. All electrochemical studies were carried out using the potentiostat IPC-ProMF (manufacturer OOO Techoborudovanie St. Petersburg). The range of regulated potentials was ± 5 V. Scanning speed ranged from 0 to ± 100 V/s. Current ranges were ± 1μA, ± 10 μA, ± 100 μA, ± 1 mA, ± 10 mA, ± 100 mA, ± 1 A. Built-in memory (up to 16,000 points) connected to a personal computer.

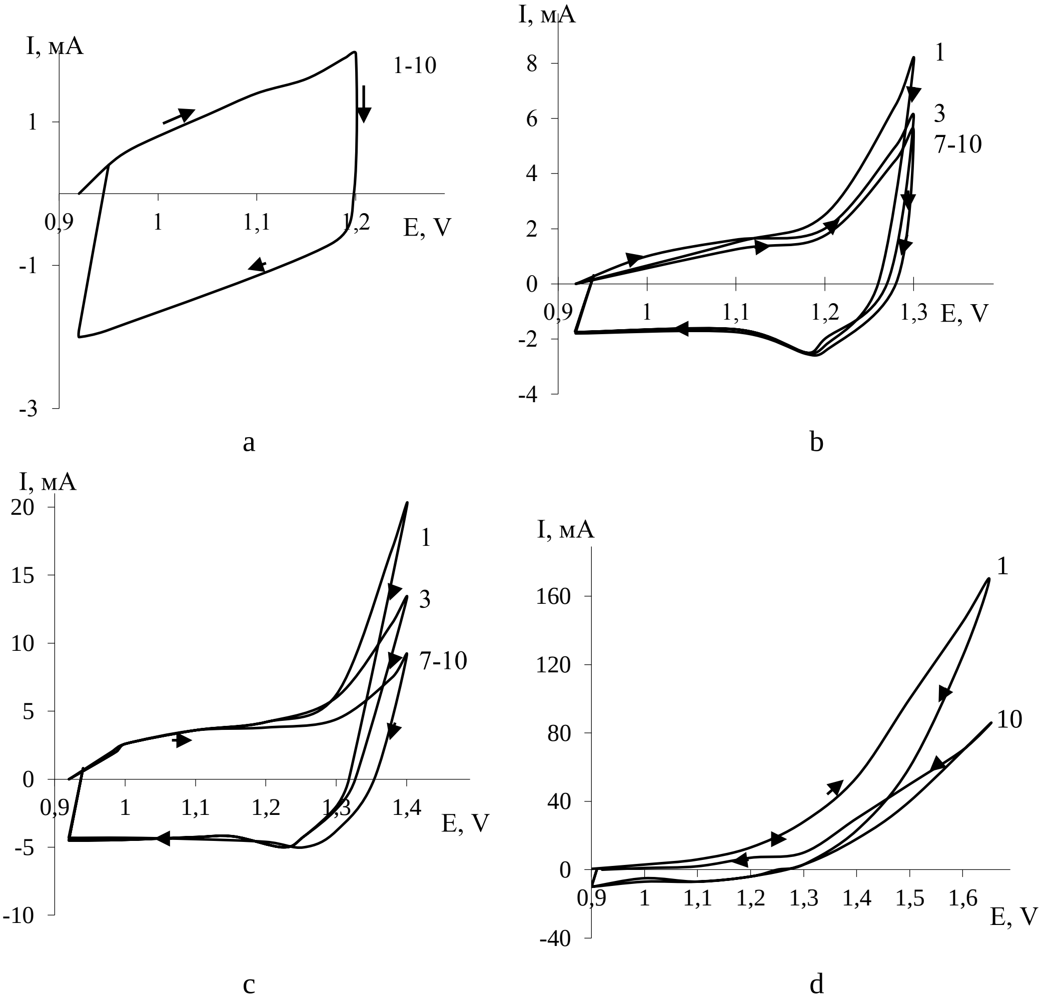
RESULTS AND THEIR DISCUSSION

The direct and reverse traverse of the potential sweep in the range E_{st} - 1.2 V (Fig. 1a) shows high electrochemical reversibility of the processes on the dispersed graphite electrode in 60% HNO_3 ($K_{rev} = Q_k/Q_a$ = 0.96-0.95) , which does not change during cycling. On the anode branch of PDC, there is a constant current increase with a potential sweep and an inflection in the from1.14 to 1.16 V range is observed, indicating a superposition of a new process on the ongoing reactions.

Taking into account the large true surface of the slurry electrode the process rate is very slow. The currents in the studied potential area can be caused both by the oxidation of PVG [14-18] and by the intercalation processes [7, 19]. According to the data [14, 20, 21], the oxidation of PVG under insignificant polarizations proceeds reversibly. Therefore, it is impossible to separate the two indicated processes under the conditions of our experiment. Moreover, clear current peaks reflecting the formation of individual GIC stages are unlikely to appear on the slurry electrode, and the reactions involving PVG should also be characterized by a wide response of currents due to the variety of surface group composition. When the sweep potential is shifted to the anode range up to 1.3 V (Fig. 1b), the current increase is observed, caused by the process, the beginning of which was observed earlier (1.15 V). It is this process that results in the current peak on the cathode part of the cyclogram.

At a given reverse potential, as the electrode is cycled, the amount of electricity of the anode reactions decreases and a certain increase in the area of the cathode half-cycle is observed. The coefficient of reversibility in this case increases (Table 1) from 0.5 (1 cycle) to 0.79 (7-15 cycles). In general, this trend continues with the growth of the reversal potential (Fig. 1 c, d); however, as the cycling proceeds, the anode capacity decreases sharply, simultaneously with the increase in the amount of electricity in the cathode area (Table 1). At the same time, the potential of the cathodic peak remains practically unchanged (1.1-1.2 V) and becomes blurred by the anode polarization to higher potentials, resulting in a current delay (Fig. 1 d). The value of K_{rev} in the range of potentials of 1.4-1.5 V decreases in a stepwise manner (Table 1). A similar change in the ratio Q_k/Q_a was observed in [10] during the re-oxidation of the GICs.

The conducted experiment makes it possible to distinguish three potential ranges in the anode area: I-E_{st}... 1.15 V; II-1.15 ... 1.4 V; III-> 1.4 V (Table 1). Range I was previously observed in the data in Fig. 2 a, b; the second range is fixed in the form of bends at the first-cycle PDC and is identified as a fuzzy current pad by long cycling (Fig. 1d).



a b

c d

Fig. Cyclic potentiodynamic curves for graphite in 60% HNO_3 at the reversal potentials 1.2 V (a); 1.3 V (б); 1.4V (в); 1.65 V (г) (t = 24 °C, V = 20 mV/s)

Рис. Циклические ПДК для графита в 60% HNO_3 при потенциалах реверса 1,2В (а); 1,3В (б); 1,4В (в); 1,65В (г) (t= 24 °C, V = 20 мВ/с)

Table 1

The dependence of anode (Q_a) and cathode (Q_k) amounts of electricity on cyclic potentiodynamic curves on the interval of potential scanning (E_{rev}) and the number of the cycle in 60% HNO_3

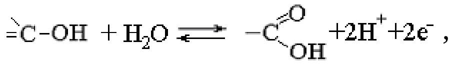
Таблица 1. **Зависимость анодного (Q_a) и катодного (Q_k) количеств электричества на циклических ПДК от интервала сканирования потенциала ($E_{рев}$) и номера цикла в 60% HNO_3**

E_{rev}, V	1.20	1.30		1.40		1.55		1.65		2.20	
cycle	1-10	1	7-10	1	7-10	1	7-10	1	7-10	1	7-10
Q_a, Kl	0.0130	0.050	0.034	0.150	0.113	0.800	0.477	6.600	1.630	14.57	7.280
$Q_к$, Kl	0.0125	0.025	0.027	0.075	0.082	0.088	0.105	0.198	0.326	0.583	1.166
K_{rev}	0.96	0.5	0.79	0.5	0.73	0.11	0.22	0.03	0.2	0.04	0.16

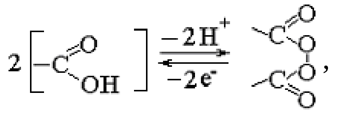
Taking into consideration the literature data and the results of the evaluation of the electrochemical reversibility of the products of the anodic oxidation of graphite (Table 1), the following processes are likely to proceed in the identified ranges: I-formation of GICs (reaction 1,2,5):

$$24nC + 3HNO_3 = C_{24n}^{+}\cdot NO_3^{-}\cdot 2HNO_3 + H^{+} + e^{-}; \quad (3)$$

II- oxidation of PFG [3]:



$$=\!C-OH + H_2O \rightleftarrows -C(=O)OH + 2H^{+} + 2e^{-}, \quad (4)$$



(5)

reoxidation of GICs:

$$C_{24}^{+}NO_3^{-}\cdot 2HNO_3 + 3HNO_3 \rightarrow 2C_{12}^{+}NO_3^{-}\cdot 2HNO_3 + H^{+} + e^{-} (6)$$

and a partial transfer of GICs into graphite oxide:

$$C_{24}^{+}NO_3^{-}\cdot 2HNO_3 + H_2O \rightarrow C_{24}^{+}\cdot OH^{-}\cdot 2H_2O + 3HNO_3, (7)$$

in addition, CO and CO_2 can be separated [3];

III - formation of oxide-like graphite compounds of non-stoichiometric composition:

$$C_{24}^{+}OH^{-}\cdot 2H_2O + 3H_2O \rightarrow 2C_{12}^{+}\,OH^{-}\cdot 2H_2O + H^{+} + e^{-} \quad (8)$$

with the superposition of reactions that release oxygen in the form of CO, CO_2 and O_2 [3]. The above-mentioned assumptions are in good agreement with the results of [7] by the values of the potentials, as well as with the general concept outlined in [5]. Indeed, in the range of potentials I, high electrochemical reversibility of the processes is due to the absence of the reactions with gas evolution. The decrease of K_{rev} (Table 1) in the range of potentials II is possible both as a result of the re-oxidation of GICs, that is, the formation of covalent bonds [7], and because of the formation of CO and CO_2. According to the published data [22, 23], the threshold potential for the formation of the NG of stage II for the solutions under studies should be within the range 1.2-1.3 V, which is confirmed by the shift of the potential in the positive direction, when passing from the anode area to the cathode one. When the reverse potential is shifted to 1.3 V, the irreversibility of the anodic processes increases due to the reactions (4, 5), which results in the increase in the oxygen content in the PVG composition, which can be restored at potentials <0.3 V [14, 15]. Taking into account the fact that the area of the pressed graphite electrode is practically unchanged, higher anode currents in the first cycles are caused by the possibility of intercalation of all interlayer spaces, with more positive $E_{rev.}$ the oxidation of the edge carbon atoms and the defects of the graphite matrix is not excluded. The transition of potentials to area III is characterized by an abrupt decrease in K_{ob} and the growth of anode currents, which decrease by cycling (Fig. 1, Table 1). At the same time, the capacitance in the cathode area of the PDC grows, increasing its value by increasing the number of cycles. By cycles 5-7 chronovoltamperograms cease to change and then they are recorded without changes. The growth of Qa, especially when reaching a potential of 1.65 V, is obviously associated with the possibility of the oxidation of H_2O to oxygen. In the first cycles, when the formed oxygen atoms are actively captured by the graphite surface, the anode currents have maximum values, by cycling they decrease, and oxygen is released already in the form of CO, CO_2 and O_2.

Table 2

Change in average cathode currents (I_k^{avr}) with potentiodynamic curves vs reverse potential (E_{rev}) on the pressed disperse graphite electrode in 60% HNO_3

Таблица 2. **Изменение средних катодных токов ($I_k^{ср}$) на ПДК от потенциала реверса ($E_{рев}$) на подпрессованном дисперсном графитовом электроде в 60% HNO_3**

E_{rev}, V		1.20	1.30	1.65	2.20
I_k^{avr}, мА	1 cycle	0.80	1.50	6.32	8.85
	10 cycle	0.82	1.72	20.10	35.60

Chemisorbed oxygen has a catalyzing effect on the processes of electrochemical intercalation [5] with the formation of nitrate and graphite oxide. The amount of electricity on the reverse cycles in the cathode area will be determined by the recovery currents of PVG, GICs, graphite oxide and adsorbed oxygen. The increase in Q_k, as the cycling proceeds with simultaneous decrease in anode currents, can be caused only by the bulk intercalation reactions, since in this case the structure of the graphite electrode is arranged and the intercalation processes are facilitated. From this point of view, the dynamics of the variation of the average cathode currents (Table 2) (calculated from Q_k) shows that, with an increase in the anode potential, in spite of a clear decrease in the current yield, the rate of intercalation processes increases.

In literature sources, information is given on the possibility of obtaining intercalation compounds by anodic treatment of graphite in electrolytes with a low content of NO_3^- and other anions [8, 13]. By diluting HNO_3 solutions, when the rate of reactions involving H_2O increases, the partial currents of the anode process are redistributed. The share of currents associated with the oxidation of PVG, the formation of CO, CO_2 and the release of O_2, should increase. Electrochemical intercalation is inhibited because of a decrease in the concentration of NO_3^- ions and their increasing solvation [8]. It is possible to assume a faster transition of GICs into graphite oxide and an increase in the water content of the intercalated layer. The presented data are also confirmed by the experimental measurements [3]. As it was noted earlier, the increase in anode currents at the PDC with a decrease in nitric acid concentration up to 30% is caused by the growth of the rate of electrode reactions involving water. One cannot ignore the change in the structure and properties of HNO_3 solutions, in particular, a decrease in viscosity and density with diluted solutions will enhance the wettability of graphite particles, increase in the volume of working pores, that is, the true surface of the electrode.

The cycling of a compressed disperse graphite electrode in HNO_3 solutions of various concentrations from a stationary potential to E_{rev} = 1.4 V (boundary of areas II and III for 60% HNO_3) also confirms the increase in the rate of irreversible processes with the transition to less concentrated electrolytes (Table 3). If our assumptions are correct, then already in 45% HNO_3, the reactions of re-oxidation of GICs and the formation of oxide compounds of graphite are accelerated considerably. The highest anode currents of the first cycle [3] are recorded on the dispersed graphite electrode in 30% HNO_3, the reversibility of the anode processes being lower than in 60% HNO_3. According to the data (Table 3), a decrease in the concentration of HNO_3 simultaneously with a significant increase in Q_a slightly changes the cathode capacity (Q_k), which agrees with the literature [7] and with the described concept. High reversibility of the anode processes in 15% HNO_3 is unlikely to be associated with intercalation-deintercalation reactions, since according to [23] this concentration is close to the threshold one in which the formation of GICs is possible, and the rate of this process is slow. Low anode currents in 15% HNO_3 allow to suppose that the surface reactions of reversible chemisorption of oxygen are predominate, which is also confirmed by a slight decrease in Q_a as the cycling proceeds. A more definite conclusion about the effect of the concentration of the nitric acid electrolyte on the processes of electrochemical intercalation can be made on the basis of the study of the properties of the GIC samples synthesized in HNO_3 solutions.

Table 3

The dependence of anode (Q_a) and cathode (Q_k) amount of electricity on cyclic potentiodynamic curves in HNO_3 solutions at E_{rev} = 1.4V

Таблица 3. **Зависимость анодного (Q_a) и катодного (Q_k) количества электричества на циклических ПДК в растворах HNO_3 при $E_{рев}$= 1,4В**

C (HNO_3), %	60		45		30		15	
№ cycle	1	10	1	10	1	10	1	10
Q_a, Kl	0.150	0.113	0.217	0.103	0.219	0.118	0.120	0.105
Q_k, Kl	0.075	0.082	0.054	0.059	0.064	0.070	0.065	0.068
K_{rev}	0.50	0.73	0.25	0.57	0.29	0.59	0.54	0.65

CONCLUSIONS

On the basis of the conducted studies the following conclusions can be drawn: 1. Regularities in the variation of the kinetics of electrochemical processes on disperse graphite electrodes are determined, depending on the concentration of nitric acid. 2. It has been established that a complex of processes proceed on graphite anodes: oxidation of surface functional groups, electrochemical intercalation and oxidation of carbon material accompanied by the formation of O_2, CO, and CO_2. 3. It has been established that the formation of GICs proceeds most intensively in the potential range from 1.7 to 2.1 V.

ЛИТЕРАТУРА

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Поступила в редакцию 20.11.2017
Принята к опубликованию 28.05.2018

Received 20.11.2017
Accepted 28.05.2018