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ИССЛЕДОВАНИЕ ЭЛЕКТРОХИМИЧЕСКОГО ИНТЕРКАЛИРОВАНИЯ ГРАФИТА В РАСТВОРАХ HNO_3 МЕТОДОМ ХРОНОВОЛЬТАМПЕРОМЕТРИИ

Исследованы физико-химические свойства суспензий графит-азотная кислота, подобраны соотношения компонентов в суспензии, обеспечивающие возможность их анодного окисления с образованием соединений внедрения графита. Определены значения электропороводности суспензий графит – азотная кислота с различным соотношением твердой и жидкой фаз. Максимальные значения электропроводности суспензий достигаются при массовом соотношении графит : HNO_3 ≈ 1:0,66. Разработана конструкция электрохимической ячейки для проведения хроновольтамперометрических измерений на суспензионном графитовом электроде. Исследованы природа и кинетика электродных процессов на дисперсных графитовых электродах в 60% азотной кислоте. Показано, что

при анодной поляризации дисперсного графитового электрода протекает комплекс анодных процессов: окисление поверхностных функциональных групп, образование соединений внедрения и выделение кислорода. Наибольшая электрохимическая обратимость анодных процессов на суспензиях графит-HNO_3 отмечается при $E_{рев} < 1,2$ В, скорости реакций образования соединений внедрения графита и реакций с участием поверхностных функциональных групп на суспензионном электроде возрастают в диапазоне потенциалов 1,2-1,7 В, причем увеличение тока, главным образом, вызвано электрохимически обратимым процессом интеркалирования, так как на обратном цикле в катодной области также регистрируется рост тока, обусловленный реакцией деинтеркалирования. Электрохимическое окисление дисперсного графитового электрода в HNO_3 следует вести в интервале потенциалов от 1,2 В до 2,1 В, что обеспечит образование соединений внедрения графита с максимальной скоростью и наименьшими энергозатратами.

Ключевые слова: соединения внедрения графита, хроновольтамперометрия, нитрат графита, электрохимическое интеркалирование, суспензионный электрод

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STUDY OF ELECTROCHEMICAL INTERCALATION OF GRAPHITE IN SOLUTIONS OF HNO_3 WITH METHOD OF CHRONOVOLTAMPEROMETRY

The physico-chemical properties of suspensions of graphite-nitric acid were studied. The ratios of the components in suspension providing the possibility of their anodic oxidation with the formation of compounds of the implementation of graphite were determined. The values of electrical conductivity of suspensions of graphite-nitric acid with different ratio of the solid and liquid phases were determined .The maximum value of the electrical conductivity of suspensions is achieved at the mass ratio of graphite to $HNO_3 \approx 1:0.66$. The design of the electrochemical cell for carrying out chronovoltamperometric measurements on a suspension graphite electrode was developed. The nature and kinetics of electrode processes on dispersed graphite electrodes in 60% nitric acid were studied. It is shown that under anodic polarization of dispersion graphite electrode the

complex of anodic processes occurs: the oxidation of surface of functional groups, the formation of compounds of implementation and evolution of oxygen. Maximum electrochemical reversibility of the anodic processes on the suspensions of graphite-HNO_3 observed at E_{rev}< 1.2 V, the rate of reactions of formation of compounds of the introduction of graphite and reactions involving surface functional groups on the electrode slurry increases in the range of potentials of 1.2-1.7 V. At that, the current is increase mainly causes by electrochemically reversible process of intercalation, since at the reverse cycle in the cathode area also recorded the growth of the current due to the reaction of deintercalation. An electrochemical oxidation of dispersed graphite electrode in HNO_3 should be in the range of potentials from 1.2 V to 2.1 V, which will provide formation of compounds of introduction of graphite with the maximum rate and minimum power input.

Key words: graphite implementation compound, chronovoltamperometry, graphite nitrate, electrochemical intercacclation, suspension electrode

INTRODUCTION

Identifying of the nature of the cathodic and anodic reactions in solutions of HNO_3 is a necessary step in the development of electrochemical technologies of the synthesis of compounds of implementing of graphite (CIG). The threshold concentration of the nitric acid with sufficient potential for spontaneous intercalation in graphite oxidation (0.995 V) is ~75% [1,2]. It is known that the formation of nitrate graphite of the highest levels is possible during anodic intercalation of graphite in 60% or more concentrated HNO_3 [1-3]. During the electrochemical oxidation, CIG are formed in solutions of HNO_3 and with smaller concentration to 20% [2]. However, the mechanism of electrochemical intercalation of graphite and the nature of anode processes at disperse carbon materials are not fully understood untill the present. The electrochemical behavior of graphite electrodes in concentrated nitric acid solutions described only sporadically in the literature [4-8], and the bulk of information obtained by using of pyrolytic graphite. To obtain preliminary data with the aim of developing methods of electrochemical synthesis of protecting thermal expanding graphite compounds in nitrate electrolytes the potentiometric and chronovoltammetric measurements on dispersed graphite electrodes were carried out. The physico-chemical properties of suspensions of graphite-HNO_3 were studied, the ratio of the components in suspension providing the possibility of their anodic oxidation with the formation of compounds of the implementation of graphite was selected.

THE METHOD OF THE EXPERIMENT

The studies performed with dispersed graphite powders of Chinese origin (standard GB/T 3518-95), ash content is 0.2%, particle size – 250÷300 μm. The study of graphite electrodes was carried out without prior surface preparation. To obtain suspensions of graphite-HNO_3, particulate graphite powder with a certain mass placed into a glass container and mixed with the necessary amount of acid of appropriate concentration. The obtained suspension was mixed for a uniform distribution of components and aged under static conditions. The 60% nitric acid solution of brand KHCH (TU 701-89E) was used as the electrolyte. All electrochemical studies were carried out using a potentiostat P-5848, the registration of potential in time was carried out with a digital DC voltmeter SCH-1413 with a limit of permissible error of ±0.05+0.02·(10/x-1)%, where x – is the reading, V. Concurrently with the potential in time recorded self-recording potentiometer KSP-4 with the basic reduced error of reading of 0.5%. Under chronovoltamperometria measurements the sweep rate of potential was 10÷20 mV/s. The reference electrode served as silver chloride electrode brand EWLa-1. The electrical conductivity of graphite powders and suspensions were measured in a glass cell with two flat vertical platinum electrodes with a working area of 1 cm^2 and interelectrode distance of 1.5 cm.

After the graphite powder or graphite-HNO_3 suspension was load into the cell, a constant current from 2.2 to 15 mA with the registration of the ohmic voltage drop in the cell was passed. The voltage drop in the cell did not reach settings that allow the flow of the faraday reactions. This was confirmed by a rectilinear course of the dependency of voltage variation on the cell under the current. The injection of acid into suspension was carried out by microdonation with a precision of 0.02 ml.

In the current range, where the Ohm law for a site of a circuit was remain, a specific conductivity were calculated using the formula:

$$\chi = \frac{I \cdot l}{U \cdot S}, \qquad (1)$$

where χ – specific conductivity, Ohm$^{-1\cdot}$ cm^{-1}; I – DC current, A; *U* – voltage, V; *S* – area of electrode, cm^2; *l* – the distance between the electrodes, cm.

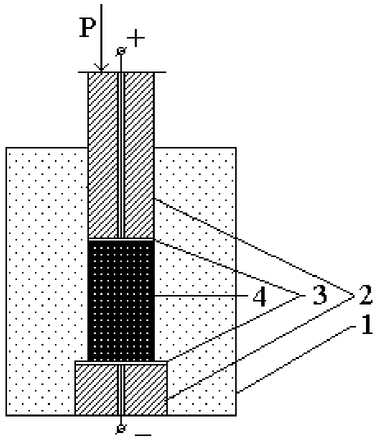


Fig. 1. Scheme of the cell for measuring conductivity and volume of the graphite powders. 1 – glass body; 2 – steel punches; 3 – platinum electrodes; 4 – graphite powder
Рис. 1. Схема ячейки для измерения электропроводности и объема порошков графита. 1 – корпус из стекла; 2 – стальные пуансоны; 3 – платиновые токоотводы; 4 – порошок графита

Electrochemical measurements were carried out in a small electrochemical cell made of glass with two flat vertical platinum electrodes (Fig. 2), the cathode was sealed in separator material (polypropylene filtrate(CN 5636)).

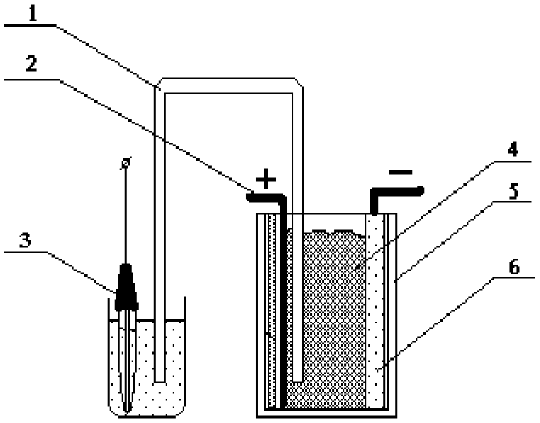


Fig. 2. Electrochemical cell for the synthesis of graphite nitrate suspensions: 1 – electrolyte; 2 - platinum current collector of the anode; 3-silver-chloride reference electrode; 4 - suspension of graphite-HNO_3; 5 - the body of the cell from organic glass; 6 – titanium cathode for a diaphragm case
Рис. 2. Электрохимическая ячейка для синтеза нитрата графита из суспензий: 1- электролитический ключ; 2- платиновый токоотвод анода; 3-хлорсеребряный электрод сравнения; 4- суспензия графит-HNO_3; 5- корпус ячейки из оргстекла; 6- титановый катод в диафрагменном чехле

The study of the electrochemical behavior of dispersed graphite is associated with the solution of the question of the formation of the electrode having electronic conductivity and uniform distribution of the electrolyte in their volume. In comparison with compact graphite electrodes, the use of carbon powders requires a study of the properties of the graphite-acid suspension, as the ratio of the components in suspension and the degree of pressing to tocollection will determine the kinetics of electrode processes.

For the process of anodic intercalation all particles of the dispersed graphite needs to be in contact with each other providing the electronic conductivity. It is obvious that only pasty mixtures with a predominant solid phase will have electronic conductivity. At the same time, during anodic oxidation of graphite-acid suspensions with the aim of obtaining compounds of introduction of graphite according to the reaction:

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

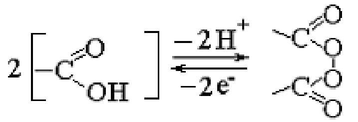
(n – the number of stages of CIG), it is necessary enough acid in the mixture for maximally possible filling of the graphite matrix with intercalation.

As the electrochemical oxidation of graphite in solutions with water content of more than 20% produces nitrate graphite of the 2nd and higher level [7], the mass ratio of graphite and HNO_3 in the suspension, calculated according to reaction (2) must be not less than 1:0.33. The excess of liquid phase will lead to the stratification of the suspension and loss of electronic contact between the graphite grains, and the lack of it will lead to uneven distribution of components and the formation of electrolytically unbound particles of graphite, which will lead to the exclusion of such sites from the electrochemical process. Under the wetting of graphite powder by acid regardless of its concentration, the volume of suspension is almost constant until the achieving the mass ratio of graphite : HNO_3 = 1:0.5. Then, under the increasing of the volume of liquid phase the volume of suspension decreases accompanied by a sharp increase in its density. This is due to the filling the voids with acid in the volume of graphite powder, which promotes the agglomeration of the graphite grains and the formation of quasi-crystalline structures [9]. In terms of the dispersion stability at the maximum content of the liquid phase, the electrical conductivity of every studied suspension ($\chi_{\text{сус}}$) increases in 3.2 times in comparison with the corresponding acid solution ($\chi_{\text{к}}$), which indicates the presence of the electronic component of conductivity. The measurement of electrical conductivity of suspensions of graphite – HNO_3, confirmed the improving of contact between the particles of the dispersed graphite under wetting them with solutions of HNO_3. The maximum value of the electrical conductivity of suspensions is achieved when the mass ratio of graphite: $HNO_3 \approx 1:0.66$. Further dilution of the suspension with nitric acid leads to decreasing of conductivity due to the stratification of suspension and increasing of the proportion of the ionic component in the process of charge transfer.

The study of reversibility of the anodic process using the method of cyclic chronovoltamperometria on suspension graphite electrode is associated with certain difficulties, due to the poor reproducibility because of the instability of the dispersed electrodes structure. It is difficult to interpret the results obtained from the reverse potential in excess of 1.65 V, as a result of intensive gassing of the graphite particles in the suspension electrode structure is exposed to fluctuations leading to the disruption of the contact between them, as a consequence of it there is partial or complete shutdown of a suspension of the electrochemical process. This is due to the decrease of the cathodic and anodic current densities with cycling of the electrodes (curve 5, Fig. 3). Maximum electrochemical reversibility of the anodic processes on the suspensions of graphite-HNO_3 observed in $E_{rev} < 1.2$ V (Fig. 4), the speed of reactions of formation of CIG (2) and reactions with surface functional groups [10]:

$$\geq C\text{-}OH \rightleftarrows \;>C{=}O + H^+ + e^- \qquad (3)$$

$$\geq C\text{-}OH + H_2O \rightleftarrows -C(=O)OH + 2H^+ + 2e^- \qquad (4)$$



$$2\left[-C(=O)OH\right] \underset{-2e^-}{\overset{-2H^+}{\rightleftarrows}} -C(=O)-O-O-C(=O)- \qquad (5)$$

on the suspension electrode increase in the range of potentials of 1.2÷1.7 V, the current increases by electrochemically reversible process of intercalation, since the reverse cycle, the cathode range also registered the growth of the current caused by the reaction of deintercalation. A further decrease of $Q_к/Q_a$ due to the irreversible reactions with the involvement of oxygen [4]:

$$2H_2O \leftrightarrows O_2 + 4H^+ + 4e^- \qquad (6)$$

$$C + H_2O \leftrightarrows CO + 2H^+ + 2e^- \qquad (7)$$

$$C + 2H_2O \leftrightarrows CO_2 + 4H^+ + 4e^- \qquad (8)$$

and peroxidation of nitrate graphite:

$$C_{24}{}^+NO_3{}^-\cdot 2HNO_3 + 3HNO_3 \rightarrow$$
$$\rightarrow 2C_{12}{}^+NO_3{}^-\cdot 2HNO_3 + H^+ + e^- \qquad (9)$$

In this range of potentials the anodic currents in the suspension electrode is much higher on the first cycles of potentiometric curves, however, there is a tendency to equalize the speeds of anodic reactions on a subsequent cycle.

The more definite conclusion about the influence of the mode of anodic oxidation of dispersed graphite electrode on electrochemical processes of implementation can be done on the basis of research of properties of some samples of CIG. The obtained information provided a focused development of the methodology of electrochemical synthesis of CIG samples with nitric acid based on the dispersed graphite.

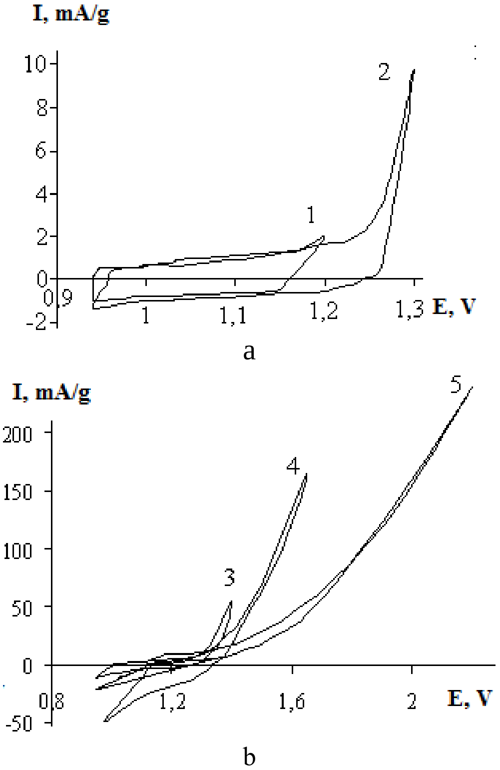


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Fig. 3. Cyclic potentiometric curves (10th cycle) for suspension graphite electrode in 60% HNO_3 at different voltages of reverse: 1-1.20; 2-1.30; 3-1.40; 4-1.65; 5-2.2 V

Рис. 3. Циклические потенциодинамические кривые (10-цикл) для суспензионного графитового электрода в 60%-й HNO_3 при различных потенциалах реверса: 1-1,20; 2-1,30; 3-1,40; 4-1,65; 5-2,2 В

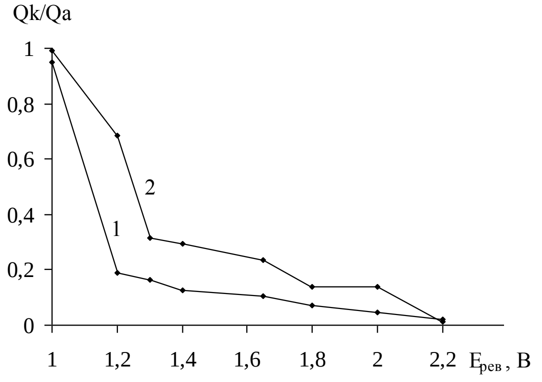

Fig. 4. The reversibility of the anodic processes at different voltages of reverse of cyclic potentiometric curves for suspensions of graphite - 60% HNO_3. Q_k – quantity of cathode electrons, Q_a – quantity of anodic electrons

Рис. 4. Обратимость анодных процессов при различных потенциалах реверса циклических потенциодинамических кривых на суспензии графит - 60%-й HNO_3. Q_k-количество электронов катода, Q_a –количество электронов анода

CONCLUSION

The compositions of the graphite – HNO_3 suspensions with the electron component of conductivity, which make them anodic oxidation without forced pressing were installed.

It is established that electrochemical oxidation of dispersed graphite electrode in HNO_3 should be in the range of potentials from 1.2 V to 2.1 V, that will ensure the formation of a CIG with maximum speed and minimum power input.

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