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ВЫБОР РЕЖИМА АНОДНОЙ ОБРАБОТКИ ГРАФИТА В ОТРАБОТАННОМ АЗОТНОКИСЛОМ РАСТВОРЕ ТРАВЛЕНИЯ ДЛЯ ПОЛУЧЕНИЯ ТЕРМОРАСШИРЯЮЩИХСЯ СОЕДИНЕНИЙ ГРАФИТА

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Показана возможность использования отходов гальванических производств для синтеза терморасширяющихся соединений графита. В качестве примера был взят электролит на основе отработанного азотнокислого раствора травления медных деталей, содержащий в своем составе катионы различных металлов, тем самым решен экологический вопрос, связанный с проблемой утилизации растворов, содержащих в своем составе анионы азотной или серной кислот. Методом потенциодинамических кривых исследованы процессы, протекающие при синтезе терморасширяющихся соединений графита на платиновом и графитовом электродах в исследуемом электролите. Токи на потенциодинамических кривых до достижения потенциала выделения кислорода обуславливаются процессом окисления поверхностно функциональных групп с последующим интеркалированием графитовой матрицы. Выявлено, что потенциал выделения кислорода в электролите на основе отработанного азотнокислого раствора травления медных деталей несколько ниже, чем в 58% HNO_3, из-за присутствия в составе катионов металлов. Свободные катионы металлов оттягивают на себя часть молекул воды, образуя гидратные оболочки, при этом катионы меди образуют комплексы, где молекулы H_2O является лигандами, что затрудняет выделение кислорода. При электрохимическом синтезе терморасширяющихся соединений графита были применены потенциостатический и гальваностатический режимы. Выбран интервал потенциалов 1,8 - 2,2 В для проведения синтеза в потенциостатическом режиме. Даны рекомендации по применению гальваностатического режима с током анодной обработки 60 - 140 мА (на 1 г графита) для синтеза терморасширяющихся соединений графита в промышленных объемах. Полученный таким образом терморасширенный графит характеризуется насыпной плотностью менее 2 г/дм^3.

Ключевые слова: углеродные материалы, терморасширяющиеся соединения графита, анодный синтез

SELECTION OF MODE OF ANODIC TREATMENT OF GRAPHITE IN A SPENT NITRIC ACID ETCHING SOLUTION FOR PRODUCING THERMALLY EXPANDING GRAPHITE COMPOUNDS

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The possibility of using galvanic waste for the synthesis of graphite thermo expanded compounds has been shown. An electrolyte on the basis of a spent nitrate solution of etching copper parts containing cations of various metals in its composition was taken as an example, thereby solving an environmental issue related to the problem of utilization of solutions containing nitric or sulfuric anions in its composition. The processes occurring in the synthesis of thermally expanding graphite compounds on platinum and graphite electrodes in the electrolyte under investigation were studied by the method of potentiodynamic curves. The currents on the potentiodynamic curves before reaching the oxygen evolution potential were due to the oxidation of the surface-functional groups followed by intercalation of the graphite matrix. It was revealed that the potential for oxygen evolution in the electrolyte based on the spent nitric acid solution of etching of copper parts is slightly lower than in 58% HNO_3 due to the presence of metal cations in the composition. Free metal cations attract a part of water molecules to form hydrate shells, while copper cations form complexes where H_2O molecules are ligands, which makes it difficult to release oxygen. In the electrochemical synthesis of thermally expanding graphite compounds, potentiostatic and galvanostatic modes were applied. A range of potentials of 1.8 - 2.2 V was chosen for performing the synthesis in the potentiostatic mode. Recommendations are given for the application of the galvanostatic mode with the current of anodic treatment of 60 - 140 mA (per 1 g of graphite) for the synthesis of graphite thermo expanding compounds in industrial volumes. The thermo expanded graphite obtained in this manner is characterized by a bulk density of less than 2 g/dm^3.

Key words: carbon materials, thermoexpanding graphite compounds, anodic synthesis

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INTRODUCTION

With the development of modern science, various carbon materials and compounds on their basis are becoming increasingly in demand. One of such materials is thermally expanded graphite (TEG), which is a foam-like carbon structure formed by the rapid heating of thermo expanding graphite compounds (TEGCs).

TEG has a number of unique properties: high porosity, low bulk density, high specific surface area, as well as chemo- and thermal stability. Due to these properties, TEG has acquired a wide range of applications: as an adsorbent for water purification and water treatment [1, 2], a component of numerous composites of various functional purposes [3, 4] and in electrodes of chemical current sources [5,6]. It is also used for the production of sealing, lining, gasket materials and products [7]. It can serve as a catalyst and a catalyst carrier [8].

Nowadays, there are two methods of obtaining TEGCs: chemical and electrochemical [9, 10]. The simplest and most common one is a chemical method of preparation, which consists in processing disperse graphite with concentrated solutions of acids (H_2SO_4, HNO_3), with the addition of strong oxidizing agents (CrO_3, $KMnO_4$) [11]. An electrochemical method is practically not used in industrial synthesis of TEGCs because of high energy costs, complex equipment design and high cost of components. However, the electrochemical method makes it possible to use less concentrated solutions of acids to produce TEGCs with a high degree of thermal expansion, in comparison with the chemical method, which in its turn reduces the consumption of washing water and reagents [12]. When electrochemical technology is used, the synthesis of TEGCs proceeds in a controlled manner, without the need for high purity electrolyte, which gives a radically new opportunity to use waste solutions of galvanic plants for the production of TEGCs containing anions NO_3^-, HSO_4^-. The use of such solutions will enable to solve environmental issues related to the problem of the utilization of galvanic waste products, and also significantly reduce the cost of the product [13].

In the present work, the electrochemical intercalation of graphite in an electrolyte on the basis of a spent nitric acid etching solution of copper parts containing cations of various metals has been studied. The advantages of different methods have been shown and recommendations on the choice of a mode and a method for the anodic synthesis of TEGCs have been given.

EXPERIMENTAL PART

All studies were performed on the electronic potentiostage "P-30S" of the company "Elis". Potentiostatic, galvanostatic and potentiodynamic measurements on dispersed carbon materials of the standard GB/T 3521-95 (grain size 120-250 μm) were carried out in a three-electrode cell with a moving piston-diaphragm to ensure contact with the platinum anode. Potentiodynamic measurements on a platinum electrode were carried out in a three-electrode cell with plane-parallel electrodes. In all studies, VT1-0 grade titanium was used as a cathode. The reference electrode was a saturated silver chloride reference electrode (SCRE) and all values of potentials are given relative to SCRE. A more detailed description of the equipment and methodology is presented in [14].

The electrolyte used was a nitric acid waste solution that was used for pickling copper parts with EPO "Signal", containing 63% (by weight) HNO_3 (initial concentration was 66%) and metal cations (Cu^{2+} = 16.060; Fe^{2+} = 0.067; Ni^{2+} = 0.057; Zn^{2+} = 0.010 g/l). The concentration of the solution was determined by measuring the density [15], the constituent metal cations by means of the «Kvant-2a» atomic absorption spectrometer.

Qualitative and quantitative analysis of samples for trace amounts of impurities was carried out using a «Shimadzu» «IRTracer-100» Fourier IR spectrometer.

Hydrolysis and washing of TEGCs were carried out with a tenfold volume of distilled water, after which the synthesized samples were filtered and dried to the constant weight in the oven at the temperature of 50-60 °C.

The heat treatment of intercalated graphite was carried out in a muffle furnace for 5 s at the temperature of 900 °C and for 10 min at 2500 °C. Bulk density of TEG was measured according to the standard procedure (OST 16-0689.031-74).

RESULTS AND THEIR DISCUSSION

In order to determine the electrode processes that occur during the application of anodic polarization and to identify potentials for potentiostatic synthesis of thermally expanding graphite compounds, potentiodynamic curves (PDCs) on platinum and on a graphite electrode in the investigated electrolyte were recorded (Fig. 1). The potential scan rate was υ = 0.004 V/s.

The course of the curve on the platinum electrode is due only to electrochemical processes that occur with components of the electrolyte, so on the curve 1 (Fig. 1) in the potential range 2.0-2.2 V we can see only the oxygen evolution reaction, excluding the reaction with the graphite electrode. On the graphite electrode (Fig. 1, curve 2), the oxygen evolution process is fixed at the same potentials as on platinum, with overlapping on the intercalation process. The increase in current occurs before the oxygen evolution potential is reached, which can give evidence of the oxidation of the surface functional groups (SFGs) and subsequent intercalation of the graphite matrix. The reactions of these processes were published earlier [16, 17].

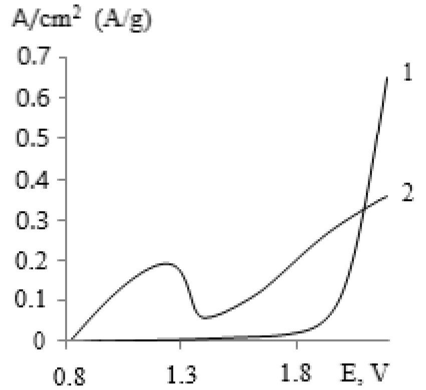


Fig. 1. Anodic potentiodynamic curves: 1 - platinum electrode (A/cm^2); 2 - disperse graphite electrode (A/g)

Рис. 1. Анодные потенциодинамические кривые: 1 – платиновый электрод; 2 - дисперсный графитовый электрод

The peak on curve 2 is due to the formation of graphite nitrate, because of the high content of nitric acid in the spent nitrate solution of etching (more than 60%) [18]. Intensive oxygen evolution (CO, CO_2) occurs after reaching a potential of 2.2 V and can lead to the annealing of the graphite matrix and an increase in its defectiveness, which subsequently has negative effects on the ability of the thermo expansion of the obtained TEGCs.

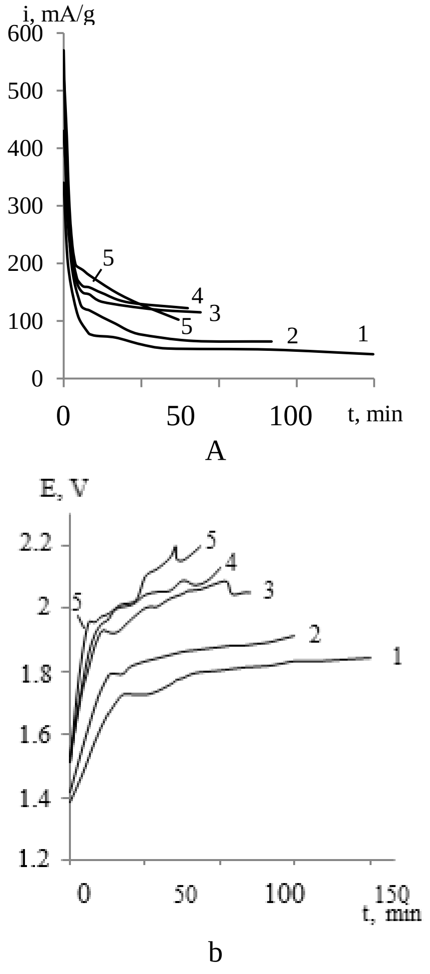
On the basis of the PDCs obtained, a potential range of 1.8-2.2 V was chosen, in which it is advisable to conduct potentiostatic synthesis in the electrolyte under study, in agreement with previously published results [19]. The upper potential threshold is limited to the region of intense oxygen evolution, and at potentials less than 1.8 V, the average current (i_{av}) of the anodic treatment sharply decreases, which significantly increases the synthesis time.

Next, we performed a series of syntheses in the potentiostatic mode at potentials of 1.8-2.2 V with a step of 0.1 V. Fig. 2a shows the characteristic potentiostatic curves on graphite for various potentials of the anodic processing. The sharp drop in the potentiostatic curve at the initial period of time is due to the induction period in which SFGs oxidation occurs, as well as the preparation of the graphite matrix for intercalation. This period is independent of the potential and is approximately 20 min for all the curves.

Today, there is no necessary equipment to apply potentiostatic synthesis to produce TEGCs on industrial scale [20]. In its turn, anodic treatment in galvanostatic mode solves this problem and makes it possible to independently determine necessary currents, which allows synthesizing with a faster report of a given specific capacity.

Based on the results of potentiostatic synthesis and literature data [21], currents of 60 - 140 mA/g with a step of 20 mA/g were chosen to conduct a series of syntheses of TEGCs in the galvanostatic mode. The synthesis time, both in the potentiostatic and galvanostatic modes was limited by reaching a specific capacity of 200 mA·h/g and was controlled using an electronic potentiostat to produce TEGCs with a high thermal expansion. The choice of this specific capacity is based on previous studies in 58% HNO_3 [16].

In galvanostatic synthesis, the results similar to the results in the potentiostatic treatment are observed. The curves (Fig. 2b) show a sharp increase in the potential with a yield to a small area, which also corresponds to the induction period. The subsequent decay for potentiostatic curves and the rise for galvanostatic curves with their yield to the area are associated with the beginning of the intercalation process.



A

b

Fig. 2. Anodic potentiostatic (a) and galvanostatic (,) curves on disperse graphite in the electrolyte under study (Q = 200 mA*h/g): a) 1 - 1.8 V; 2 - 1.9 V; 3 - 2.0 V; 4 - 2.1 V; 5 - 2.2 V; b) 1 - 60 mA/g; 2 - 80 mA/g; 3 - 100 mA/g; 4 - 120 mA/g; 5 - 140 mA/g

Рис. 2. Анодные потенциостатические (а) и гальваностатические (б) кривые на дисперсном графите в исследуемом электролите ($Q_{уд}$=200 мА·ч/г): а) 1 - 1,8 В; 2 - 1,9 В; 3 - 2,0 В; 4 - 2,1 В; 5 - 2,2 В; б) 1 - 60 мА/г; 2 - 80 мА/г; 3 - 100 мА/г; 4 - 120 мА/г; 5 - 140 мА/г

Table 1

Results of potentiostatic (PS) and galvanostatic (GS) synthesis in the electrolyte under study (Q=200 mA*h/g)

***Таблица 1.* Результаты потенциостатического и гальваностатического синтеза в исследуемом электролите ($Q_{уд}$ = 200 мА·ч/г)**

PS			d_{teg}, g/dm^3	
E_a, V	i_{av}, mA/g	t_{syn}, min	250 °C	900 °C
1.8	60	199	4.9	1.2
1.9	90	133	10.7	1.3
2.0	136	88	10.3	1.4
2.1	141	80	10.4	1.3
2.2	157	74	10.7	1.4
GS			d_{teg}, g/dm^3	
E_{gr}, V	i, mA/g	t_{syn}, min	250 °C	900 °C
1.76	60	200	7.9	1.5
1.80	80	150	6.9	1.3
1.89	100	120	6.4	1.5
1.93	120	100	9.5	1.7
1.94	140	87	10.2	1.8

The results of the syntheses in potentiostatic and galvanostatic modes, with the estimation of the properties of the obtained TEGCs are summarized in Table 1. The reproducibility of these results was confirmed by three parallel experiments, the measurement error did not exceed 5%. As can be seen from Table 1 in the potentiostatic mode (Fig. 2a), with increasing potential, the average current density of the area increases, the anodic treatment time decreasing accordingly. The average current for curve 3 corresponding to a potential of 2.0 V approximately equals to 136 mA/g, while in the galvanostatic mode (Fig. 2b) the potential for comparable currents only slightly rises above 1.9 V.

To show the results obtained on the basis of the data from Table 1, the dependence of the synthesis time on the potential of the anodic treatment of graphite was plotted in Fig. 3.

From Table 1, as well as in Fig. 3, it is seen that at comparable potentials of the anodic treatment, the 200 mA·h/g reporting rate in the galvanostatic mode is slightly higher than in the potentiostatic mode. At the same time, the quality of the TEGCs samples is at the same level and the bulk density of thermally expanded graphite varies within the limits of 1.3-1.8 g/dm^3 at 900 °C and 6.4-10.2 g/dm^3 at 250 °C.

Samples obtained in the studied electrolyte were subjected to qualitative and quantitative analysis of trace amounts of impurities. According to the results of the analysis of the composition of TEGCs, impurities in the form of metal ions contained in the solution were not detected.

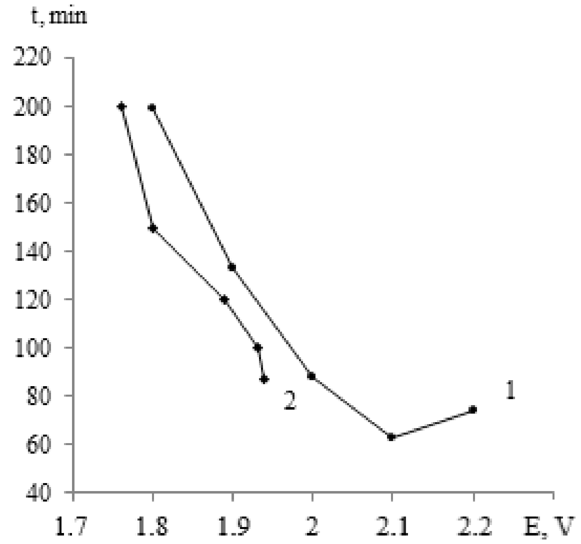


Fig. 3. The dependence of the synthesis time on the potential of anodic treatment of graphite: 1 - potentiostatic synthesis; 2 - galvanostatic synthesis

Рис. 3. Зависимость времени синтеза от потенциала анодной обработки графита: 1 – потенциостатический синтез; 2 – гальваностатический синтез

Table 2

Results of PS and GS synthesis in 58% HNO_3 (Q=200 mA·h/g)

***Таблица 2.* Результаты потенциостатического и гальваностатического синтеза в 58% HNO_3 (Q=200 мА·ч/г)**

PS			d_{teg}, g/dm^3	
E_a, V	i_{av}, mA/g	t_{syn}, min	250 ^{0}C	900 ^{0}C
1.8	65	192	5.9	1.2
1.9	88	135	9.7	1.2
2.0	145	82	11.7	1.3
2.1	152	79	11.6	1.4
2.2	154	75	12.8	1.5
GS			d_{teg}, g/dm^3	
E_{gr}, V	i, mA/g	t_{syn}, min	250 ^{0}C	900 ^{0}C
1.65	60	200	7.4	1.4
1.79	80	150	6.4	1.3
1.92	100	120	6.5	1.4
1.91	120	100	10.1	1.8
1.95	140	87	11.5	1.9

For comparative characterization, a series of syntheses was carried out under the same conditions using 58% (by weight) HNO_3 of the CC qualification as the electrolyte (Table 2). As can be seen from the comparison of Tables 1 and 2, similar results were obtained for bulk density. On the basis of the data obtained, it can be argued that the use of spent nitrate acid etching as an electrolyte makes it possible to obtain TEGs that are not inferior in characteristics obtained in pure HNO_3.

CONCLUSIONS

The principal possibility of using electroplating waste as an electrolyte for the synthesis of TEGCs (for example spent nitric acid solution of etching of copper parts) has been shown.

To obtain TEG with a bulk density of 1-2 g/dm^3, potential intervals of 1.8-2.2 V and currents of 60 - 140 mA/g have been recommended, depending on the selected mode of the anodic treatment.

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ЛИТЕРАТУРА

1. **Яковлев А.В., Финаенов А.И., Яковлева Е.В., Финаенова Э.В.** Применение терморасширенного графита в процессах водоочистки и водоподготовки. *Журн. приклад. химии*. 2004. Т. 77. № 11. С. 1833 - 1835.
2. **Финаенов А. И., Кольченко А. С., Яковлев А.В., Финаенова Э. В., Колесникова М.А.** Адсорбенты на основе терморасширенного графита. *Вестн. СГТУ.* 2011. № 2. С. 46 – 54.
3. **Финаенов А. И., Кольченко А. С., Забудьков С.Л., Финаенова Э.В., Краснов В.В.** Электрохимическое получение терморасширяющихся соединений графита для углеродсодержащих композитов. *Вестн. СГТУ*. 2011. № 1. С. 39 - 45.
4. **Караваев Д.М., Ханов А.М., Дегтярев А.И., Макарова Л.Е., Смирнов Д.В., Исаев О.Ю.** Механические свойства композиционного материала на основе терморасширенного графита. *Изв. Самар. научн. центра РАН*. 2012. Т. 14. № 1. С. 562-564.
5. **Куренкова М.Ю., Попова С.С., Финаенов А.И.** О возможности применения терморасширенного графита в электродах литиевых источников тока. Сб. статей молодых ученых по материалам Всерос. конф. «Актуальные проблемы электрохимической технологии». Саратов: Изд-во СГТУ. 2005. С. 168 - 174.
6. **Финаенов А.И., Шпак И.Е., Афонина А.В., Забудьков С.Л., Яковлев А.В.** Терморасширенный графит в электродах химических источников тока. *Вестн. СГТУ*. 2012. № 4. С. 107 – 112.
7. **Сорокина Н.Е., Никольская И.В., Ионов С.Г., Авдеев В.В.** Интеркалированные соединения графита акцепторного типа и новые углеродные материалы на их основе. *Изв. Акад. наук. Сер. хим.* 2005. № 8. С. 1699 – 1716.
8. **Стайл Э.Б.** Носители и нанесенные катализаторы. М.: Химия. 1991. 240 с.
9. **Яковлев А.В., Яковлева Е.В., Финаенов А.И.** Терморасширенный графит: синтез, свойства и перспективы применения. *Журн. приклад. химии*. 2006. Т. 79. № 11. С. 1761 - 1771.
10. **Медведева М.В., Забудьков С.Л., Яковлев А.В., Финаенов А.И.** Анодный синтез интеркалированных соединений для получения высокорасщепленного терморасширенного графита. *Изв. вузов. Химия и хим. технология*. 2013. Т. 56. Вып. 7. С. 21 - 23.
11. **Сорокина Н.Е., Максимова Н.В., Авдеев В.В.** Синтез соединений внедрения в системе графит HNO_3-H_3PO_4. *Неорг. мат*. 2001. Т. 37. № 4. С. 1 - 7.
12. **Трифонов А.И., Крамской Д.А., Краснов А.В.** Влияние температуры и концентрации сернокислого электролита на свойства и скорость анодного образования бисульфата графита. Сб. научных трудов 2-ой Междун. конф. «Углерод: фундаментальные проблемы науки, материаловедение, технология». Троицк. 2003. С. 210.

REFERENCES

1. **Yakovlev A.V., Finaenov A.I., Yakovleva E.V., Finaenova E.V.** Application of thermoexpanded graphite in water purification and water treatment processes. *Zurn. Prikl. Khim.* 2004. V. 77. N 11. P. 1833 - 1835 (in Russian).
2. **Finaeonov A.I., Kolchenko A.S., Yakovlev A.V., Finaenova E.V., Kolesnikova M.A.** Adsorbents based on thermally expanded graphite. *Vestn SGTU*. 2011. N 2. P. 46 - 54 (in Russian).
3. **Finaenov A.I., Kolchenko A.S., Zabudkov S.L., Finaenova E.V., Krasnov V.V.** Electrochemical preparation of thermally expanding graphite compounds for carbon-containing composites. *Vestn SGTU.* 2011. N 1. P. 39 - 45 (in Russian).
4. **Karavaev D.M., Khanov A.M., Degtyarev A.I., Makarova L.E., Smirnov D.V., Isaev O.Yu.** Mechanical properties of a composite material based on thermally expanded graphite. *Izv. Samar. Tauch. Tsentra RAN.* 2012. V. 14. N 1. P. 562-564 (in Russian).
5. **Kurenkova M.Yu., Popova S.S., Finaenov A.I.** On the possibility of using thermally expanded graphite in electrodes of lithium current sources. Digest of articles of young scientists on the materials of All-Russian Conference. "Actual problems of electrochemical technology", Saratov: Izd-vo SGTU. 2005. P. 168 - 174 (in Russian).
6. **Finaenov A.I., Shpak I.E., Afonina A.V., Zabudkov S.L., Yakovlev A.V.** Thermally expanded graphite in electrodes of chemical current sources. *Vestn SGTU.* 2012. N 4. P. 107 - 112 (in Russian).
7. **Sorokina N.Ye., Nikolskaya I.V., Ionov S.G., Avdeev V.V.** Acceptor-type graphite intercalation compounds and new carbon materials based on them. *Izv. Akad. Nauk. Ser. Khim.* 2005. N 8. P. 1699 - 1716 (in Russian).
8. **Style E.B.** Carriers and supported catalysts. M.: Khimiya. 1991. 240 p. (in Russian).
9. **Yakovlev A.V., Yakovleva E.V., Finaenov A.I.** Thermoexpanded graphite: synthesis, properties and prospects of application. *Zhurn. Prikl. Khim.* 2006. V. 79. N 11. P. 1761 - 1771 (in Russian).
10. **Medvedeva M.V., Zabudkov S.L., Yakovlev A.V., Finaenov A.I.** Anodic synthesis of intercalated compounds for the production of highly disintegrated thermoexpanded graphite. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* 2013. V. 56. N 7. P. 21 - 23 (in Russian).
11. **Sorokina N.E., Maksimova N.V., Avdeev V.V.** Synthesis of intercalated compounds in the graphite system HNO_3-H_3PO_4. *Neorg. Mat.* 2001. V. 37. N 4. P. 1 - 7 (in Russian).
12. **Trifonov A.I., Kramskoy D.A., Krasnov A.V.** Influence of temperature and concentration of sulphate electrolyte on the properties and rate of anodic formation of graphite bisulfate. Carbon: the fundamental problems of science, materials science, technology: Sat. scientific works of the 2nd International Conference. 2003. P. 210 (in Russian).

13. **Забудьков С.Л., Медведева М.В., Мокроусов А.А., Финаенов А.И.** Применение в электрохимическом синтезе терморасширяющихся соединений графита электролитов на основе гальванических отходов вместо растворов кислот. 8 Междун. конф. «Углерод: фундаментальные проблемы науки, материаловедения, технология». Троицк. 2012. С. 182 - 183.
14. **Забудьков С.Л., Медведева М.В., Мокроусов А.А., Финаенов А.И.** Электрохимический синтез терморасширяющихся соединений графита в отработанных азотнокислых растворах травления. *Изв. вузов. Химия и хим. технология*. 2013. Т. 56. Вып. 5. С. 115-118.
15. ГОСТ 28959-91 Кислота азотная техническая. Метод определения концентрации по измерению плотности.
16. **Медведева М.В., Забудьков С.Л., Яковлев А.В., Финаенов А.И.** Электрохимический синтез терморасширяющихся соединений графита в электролитах на основе отходов гальванических производств. *Инорг. мат.* 2014. № 9. С. 59 - 65.
17. **Тарасевич Ю.И.** Адсорбционные свойства природных углеродных адсорбентов и терморасширенного графита. *Журн. приклад. химии.* 2003. Т. 76. № 10. С. 1619 - 1624.
18. **Авдеев В.В., Сорокина Н.Е., Тверезовская О.А., Сердан А.А., Финаенов А.И.** Синтез и физико-химические свойства соединений внедрения в системе графит-HNO_3. Неорг. мат. 1999. Т. 35. № 4. С. 435-439.
19. **Забудьков С.Л., Медведева М.В., Фролов И.Н., Финаенов А.И.** Зависимость кинетики анодного интеркалирования графита и свойств полученных соединений от состава азотнокислых электролитов. *Изв. вузов. Химия и хим. технология.* 2015. Т. 58. Вып. 5. С. 62 - 65.
20. **Фролов И.Н., Забудьков С.Л., Вакулина М.В., Финаенов А.И.** Анодная обработка графита в составном нитрат-содержащем электролите для получения терморасширяющихся соединений. Актуальные проблемы теории и практики электрохимических процессов: сб. матер. III Междун. науч. конф. молодых ученых. 2017. С. 154 - 158.
21. **Фролов И.Н., Забудьков С.Л., Вакулина М.В., Финаенов А.И.** Выбор режима анодного окисления графита в составном нитрат-содержащем электролите для получения терморасширяющихся соединений. Актуальные проблемы теории и практики электрохимических процессов: сб. матер. III Междун. науч. конф. молодых ученых. 2017. С. 141 - 146.

13. **Zabudkov S.L., Medvedeva M.V., Mokrousov A.A., Finaenov A.I.** Application in electrochemical synthesis of thermally expanding graphite compounds of electrolytes based on galvanic waste instead of acid solutions. The Eighth International Conference "Carbon: the fundamental problems of science, materials science, technology". 2012. P. 182 - 183 (in Russian).
14. **Zabudkov S.L., Medvedeva M.V., Mokrousov A.A., Finaenov A.I.** Electrochemical synthesis of thermoexpanded graphite compounds in spent nitric acid etching solutions. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* 2013. V. 56. N 5. P. 115-118 (in Russian).
15. GOST 28959-91 Nitric acid technical. Method for determining the concentration by measuring the density. (in Russian).
16. **Medvedeva M.V., Zabudkov S.L., Yakovlev A.V., Finaenov A.I.** Electrochemical synthesis of thermally expanding graphite compounds in electrolytes based on galvanic waste products. *Neorg. Mat.* 2014. N 9. P. 59 - 65 (in Russian).
17. **Tarasevich Yu.I.** Adsorption properties of natural carbon adsorbents and thermally expanded graphite. *Zhurn. Prikl. Khim.* 2003. V. 76. N 10. P. 1619 - 1624 (in Russian).
18. **Avdeev V.V., Sorokina N.E., Tverezovskaya O.A., Serdan A.A., Finaenov A.I.** Synthesis and physico-chemical properties of the compounds of introduction in the graphite-HNO_3 system. *Neorg. Mat.* 1999. V. 35. N 4. P. 435-439. (in Russian).
19. **Zabudkov S.L., Medvedeva M.V., Frolov I.N., Finaenov A.I.** Dependence of the kinetics of anodic intercalation of graphite and the properties of the obtained compounds on the composition of nitric acid electrolytes. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* 2015. V. 58. N 5. P. 62 - 65 (in Russian).
20. **Frolov I.N., Zabudkov S.L., Vakulina M.V., Finaenov A.I.** Anodic treatment of graphite in a composite nitrate-containing electrolyte to produce thermally expandable compounds. Actual problems of the theory and practice of electrochemical processes with the materials of the III International Scientific Conference of Young Scientists. 2017. P. 154 - 158 (in Russian).
21. **Frolov I.N., Zabudkov S.L., Vakulina M.V., Finaenov A.I.** Choice of the mode of anodic oxidation of graphite in a composite nitrate-containing electrolyte for the production of thermoexpanded compounds. Actual problems of the theory and practice of electrochemical processes with the materials of the III International Scientific Conference of Young Scientists. 2017. P. 141 - 146 (in Russian).

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