

Electrochemical reactor and process conditions for the continuous oxidation of natural graphite with a capacity of 10 kg/hour

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Abstract

The scheme and the reactor for the continuous electrochemical oxidation of dispersed natural graphite with a capacity of 10 kg/h are created. The operating modes providing the steady quality of oxidized graphite for the production of the functional materials from *thermally exfoliated graphite* (TEG) are reported. The method of obtaining the intercalated graphite and the device for its implementation adaptable to industrial manufacturing that is based on the fabrication of sealing materials and products from TEG for the equipment used in nuclear and chemical industries, power engineering, metallurgy etc. are considered.

Keywords: *Electrochemical Oxidation, Intercalated Graphite Compounds, Continuous Action Reactor*

1. Introduction

As known, the sublimation of graphite is occurred at the temperature higher than 300 °C, therefore, technology of TEG is the only possibility for the production of continual material from the dispersive natural graphite avoiding the use of binding agents. The application of this technology is started during the second half of the last century [1, 2]. However, intensive development directed to TEG application in industry for manufacturing of packing materials and seals [3], scientific investigations as namely the modeling of TEG structure and properties [4], the design of new hybrid materials for electrodes [5], the production of composite carbon-carbon materials [6, 7], the synthesis of graphene nanoparticles and its materials [8-11], reinforcement of polymeric materials [12-13] is in progress.

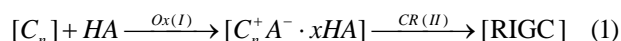
2. Intercalated graphite compounds

The synthesis of *intercalated graphite compounds* (IGC) is the first stage of the TEG technology. The following steps include their hydrolysis, drying, thermal treatment with the

rapid heating in the mode of thermal shock, rolling or pressing to get a continual material [1-4]. Such sequential processes lead to the transformation of natural graphite into nanosized “cluster-collected” system contained cone-shaped, slit-type, cylindrical and other types of defects [14] as well as the numerous unique properties. Among them, the appearance of elastic - plastic deformation as a result of nanosized porosity is emphasized and, therefore, TEG wares are widely used as seals in almost all branches of industry [3].

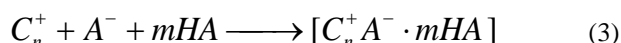
IGC are the products of incorporation of cations or anions and compounds into the layered crystalline lattice. Hydrolysis of IGC by sulfuric (IGC•H₂SO₄) or nitric (IGC•HNO₃) acid results in their transformation into *residual intercalated graphite compounds* (RIGC): RIGC•H₂SO₄ and RIGC•HNO₃. They provide the strong effect of anisotropic expansion (in the direction perpendicular to graphene’ plane) and are used as the raw materials for TEG industrial production [1-4, 15].

Traditional synthesis technologies of RIGC by Brønsted protonic acids that are thermally expanded (intumescent, foamed) are based on the following scheme of sequential reactions of oxidation, intercalation and hydrolysis:



where: [C_n] – a fragment of graphene layer of graphite matrix; HA – Brønsted acid (H₂SO₄, HNO₃, H₃PO₄ etc.); Ox – an oxidizing agent (HNO₃, K₂Cr₂O₇, KMnO₄, (NH₄)₂S₂O₈, H₂O₂, O₃, CrO₃, electrical current) used due to the low Red/Ox-potentials of most acids incorporated in graphite lattice excepting concentrated nitric and hydrochloric acids exhibiting the properties both the oxidizing agent and intercalant, CR – a chemical reagent (for instance: H₂O, NH₄OH etc.).

Step (I) includes the oxidation of graphite with formation of IGC; step (II) is the treatment of IGC to final product (RIGC). Step (II) is also required to preserve the characteristics with time of the obtained graphite compounds and to provide the certain acidity or alkalinity of the product. Step (I) includes two processes: i) the oxidation reaction of graphite matrix $[C_n]$ and ii) the formation of intercalant incorporation product (HNO_3 , H_2SO_4 , $HClO_4$, H_3PO_4 , $H_4P_2O_7$ etc.) in the presence of oxidizing agent (Ox) [15]:



The structural features of TEG are determined by IGC structure (the conditions of step (I)), the state of the product obtained in step (II) and the thermal decomposition conditions. The direction and the efficiency of the processes (2) and (3) influence on the product of the reaction: formation of IGC, re-oxidation (graphite oxide formation) and “wet combustion” of carbon etc. The prediction of the product properties of oxidation and intercalation reactions is possible only when the real values of oxidation potential are known. In view of this, the determination of thermodynamic conditions of these reactions is always paid attention [3, 15-17]. The experimental determination of oxidation potentials by two- or three - electrode methods, $HA - [Ox]$ media and IGC potentials by means of a direct potentiometry in situ is reported in details [15, 16]. The experimentally obtained redox potentials (*vs.* Standard Hydrogen Electrode) of the model system with pyrolytic graphite of high degree of structure perfection (highly-ordered) as a matrix are presented in Table 1 [3, 15-18].

One of the most characteristic features of IGC is the intercalation stages. Every pair of intercalant layers in compound after n -stage is separated by n number of graphene planes. Intercalated graphite compounds of the first stage is the most concentrated and TEG as their product implements the unique properties of graphene. The composition of IGC with sulfuric acid (graphite bisulfate) can be described by empirical formula $C_{24n}^+ \cdot HSO_4^- \times 2.5 H_2SO_4$. Graphite bisulfate potentials of I-V stages in the reactions with 94% wt. H_2SO_4 and in the presence of different oxidizing agents [15-16] or anodic oxidation [17-18] are shown in Table 1.

The identity period (I_c) of crystalline structure along the c - axis is increased in the case of intercalant incorporation between the planes of graphene:

$$I_c = d_i + (n - 1)d_o \quad (4),$$

where: d_i – the layer thickness of intercalant; $d_o = 0.335$ nm – interplanar distance in graphite; n – a stage number.

 Table 1: The formation potentials (E_{IGC}) of graphite bisulfate

Stage, (n)	$E_{Hg/Hg_2SO_4}, V$ experimental	E_{H_2}, V
$H_2SO_4 + [K_2Cr_2O_7]$		
I	1.02-1.30	1.63-1.91
II	0.70-0.85	1.31-1.46
III	0.62-0.65	1.23-1.26
IV	0.61	1.22
V	0.50	1.11
$H_2SO_4 + [KMnO_4]$		
I	1.02-1.50	1.63-2.11
II	0.80-0.90	1.41-1.50
III	0.60-0.65	1.21-1.26
IV	0.60	1.21
V	0.50	1.11
H_2SO_4, electrochemically [17, 18]		
I	0.83-1.33	1.44-1.94
II	0.55-0.83	1.16-1.44
III	0.48-0.55	1.09-1.16

There are the certain potential values for implementation of every IGC stage indicating on the possibility of the chemical (or electrochemical) oxidation. As reported in [15], the formation potential E_{GIC} is the quantitative characteristic pointing on the stage number that is, in turn, realized using the oxidizing agent with $E_{H_2} \geq E_{IGC}$.

Thermodynamic conditions of IGC formation at the certain stage are determined by the potential of reaction medium, and its realization requires the stoichiometric amount of oxidizing agent in synthesis procedure. The investigation of kinetic dependencies of the potential $E(t)$ for graphite containing samples shows their stepwise character [15]. The areas parallel to the x-axis are related to the potential of the mixture of two degrees (n) and ($n+1$), while the intervals on the slopes of these relationships correspond to the degree (n). The potential of the last horizontal “area” shows the potential of oxidizing agent solution. That kind of $E(t)$ behavior is a proof of domain model of the IGC structure.

The depth of graphite matrix oxidation is depended on the potential of oxidizing agent solution taking into account that the re-oxidation of 1st stage, amorphization of product structure as well as the change in the kinetics of intercalant incorporation can take place at certain its value. So, the formation of IGC of 1st stage follows at the lowest time for [Graphite- H_2SO_4 - $KMnO_4$] system, then with $K_2Cr_2O_7$

etc. Hence, the main principle of IGC formation is that the redox potential of oxidizing agent determines the thermodynamics and kinetics of incorporation process.

3. Anodic oxidation of natural graphite

Electrochemical intercalation (or anodic oxidation) is the most ecological, resource and energy saving method for IGC production in controlled modes [8, 9, 18, 19]. The method allows to achieve the pre-set characteristics of TEG, to regulate the structure and chemical state of surface [21, 22], to synthesize the hybrid and modified nanosized materials with graphite-like lattice as the electrodes for electrochemical power sources, sensors, catalysts and other [23-25]. Theoretical loss of electrical energy (calculated using Faraday's laws) needed for oxidation of graphite matrix is 93, 62 and 46.5 A·h/kg for the formation of 1st stage [IGC·H₂SO₄], 1st + 2nd stages and 2nd stage, respectively. These values coincide with the results in [26]. Therefore, the electricity in the range of 0.37-0.74 kW·h has to be theoretically consumed for 1 kg converted graphite to obtain IGC of 1st stage at voltage about 4-8 V.

The synthesis of IGC from natural dispersive graphite in sulfuric and nitric acids using anodic oxidation process are reported in a number of publications [20, 26-31]. The electrolytic cells loaded with no more than 100 g graphite are used in some researches [26, 27, 29-31].

To create the effective electrochemical reactor for anodic treatment of dispersive carbon powders, the following key points have to be considered:

- to use the only corrosive and acid – resistant materials for the electrodes and reactors construction;
- to provide the reliable electric contact between the particles throughout the bulk of working materials;
- to remove the gases formed from the side reaction of electrolysis of water;
- to compensate the volume increase of the solid resulted from the increased interlayer distance in graphene planes of IGC.

As known from the literature (for example [28]), the schemes of the equipment for IGC industrial manufacturing are complicated and express, more likely, the theoretical rather than applied character. The batch process of electrochemical production of IGC includes the loading of graphite material in the reactor, the acid filling, the intercalation processing, the outlet of electrolyte waste, IGC unloading, and the further its conversion. The experimental results of the process in laboratory cells are presented in [26, 27]. The use of a bath filled with acid is

provided in all cases; moreover, the acid penetration across the mass of graphite material is only applied in some cases. It has to be noted that the process followed using 50% wt. sulfuric acid [29] and a mixture of 93% wt. sulfuric and 50% wt. nitric acids [26, 27]. It is recommended [28] to use the anodic current density at 50 mA/cm² and sulfuric acid with the concentration of 30-50% wt. The electricity consumption for high quality intercalated graphite production as reported in the above-mentioned papers is in the range of 60-400 A·h/kg.

The processes of batch graphite intercalation by sulfuric acid applying the electrochemical reactors of different design: a flow reactor with unlimited graphite loading; a reactor with vertical electrodes; cassette reactor with vertical position of electrodes; horizontal cassette reactor with different modes are analyzed in paper [32]. It is proposed [33, 34] the principles of new electrochemical reactor design.

The main disadvantage of batch reactor is the interruption of the process that, in turn, stimulated to the creation of the effective electrochemical reactor of continuous action [34]. One of the essential points to solve the problem is the continuous control of “graphite-acid” pulp in the gap between the anode plate and the separator to provide a tight contact of the mixture and anode-shunt. The motion of graphite material by means of piston and auger is considered in [34]. Additionally, a device based on the principle of graphite and electrolyte mixture pushing by a piston or auger is proposed [35] where the shape of the cathode provides the vibration - rotational movements that exclude the jamming occurred due to the increased volume of graphite during oxidation process. On the other hand, a forced-feed transport of the working mixture across the extended gap between the anode plate and porous diaphragm is suggested [15, 36-38]. It must be noted that the main disadvantage of such method is the use of only one grade of graphite (or the particles of the same size) as the effect of expansion depends on the size (diameter) of the graphite particles. In the case of low dispersity of particles, the jamming can occur while the contact fault in the electrical circuit takes place at high dispersity.

Therefore, the suspension of intercalated graphite compounds of II or III stage was previously obtained by exposure of graphite with 80-98% wt. nitric acid and the further anodic oxidation led to the IGC formation of 1st stage as reported in [38]. Thus, the compensation of the suspension volume increase is achieved by anodic oxidation. This process is realized using a device contained rotary reactor with the cylindrical housing, ring-shaped anode in the form of trough fixed in housing coaxially with it and cathodes designed in the form of

blades that are radially mounted on a vertical shaft and fixed on the anode's trough that can be longitudinally moved [36]. Contrary to [15], where a large amount of concentrated acid was needed, the wetted ("semi-dry") mixtures of graphite by solutions are used [35-38].

through the zone of electrochemical treatment; passing the constant current with the density of 25-42 mA/cm² across a layer of the graphite mixture.

According to the proposed technical act [39-41] (Fig. 1), the mixture of graphite and sulfuric acid are loaded into the hopper (2) with aligning device (3) that presses and smoothes the graphite mixture by means of roller. The charging hopper (2) is situated under the movable membrane (separator) (13) designed in the form of cycled conveyor belt with the fixed transverse profiles (15). The membrane (13) is moved along the cathode surface (5) with the rate in the range of 1-18 cm/min. To test the method it was used the graphite powder GSM-2 (SU Standard GOST 17022-81), sulfate acid (Ukrainian Standard DSTU 4204), as well as the device presented in the scheme (Fig. 1).

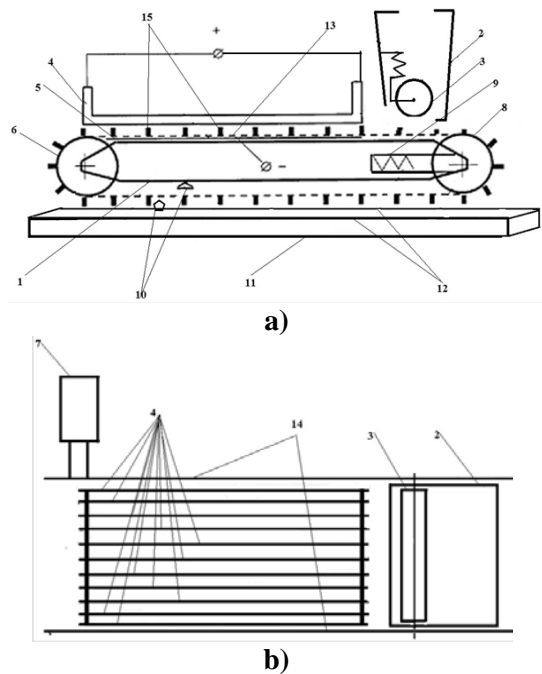


Fig. 1 The scheme of the reactor used for graphite intercalation **a** (**b** – top view): 1 – a reactor frame; 2 – a charging hopper; 3 – an aligning roller; 4 – a composite anode; 5 – the perforated cathode; 6 – the driving drum; 7 – motor means of the driving drum; 8 – a movable pulley; 9 – a device of movable pulley; 10 – rinsing collectors; 11 – a delivery tray; 12 – restrictive walls; 13 – movable membrane (separator); 14 – restrictive sides; 15 – crosscut flanks.

Continuous flow of graphite mixture along the separator (or together with it) eventually leads to the blocking of separator pores due to the presence of very small particles ("tail" of particle size distribution) present in graphite raw materials of any dispersity causing to a short circuit between electrodes. The disadvantages of the considered devices are not only the complicated design, low performance, but also insufficient efficiency of separator cleaning from IGC. There is no procedure to completely remove the tiny graphite particles from the separator pores.

The main aim of this work is to design and create the simple reactor that allows reaching the high performance at low energy costs and save the consumer characteristics of exfoliated graphite obtained from the synthesized IGC. It can be reached by the approach of IGC synthesis according to [33]: the mixing of graphite and 30-94% sulfuric acid providing 0.5-1.0 cm³ solution per 1 g graphite; transportation of the mixture of graphite and acid

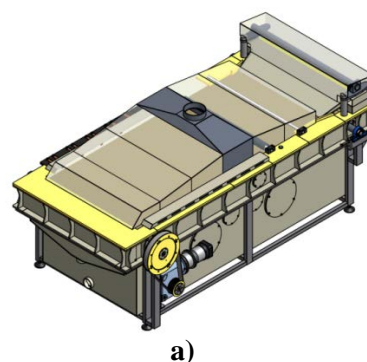


Fig. 2 3D-scheme of electrochemical reactor (a) and the view of the technological testing of electrochemical reactor with 10 kg/h production capacity (b).

3D-scheme of the electrochemical reactor and a view of the technological manufacturing testing are presented in Fig. 2.

The thermal expansion ability of obtained IGC is determined by an expansion coefficient (K_{ex}^{1000} , cm³/g). For this purpose, the washed by water and, then, dried IGC samples are used. The IGC sample (1g) placed in a quartz

glass and heated at 1000 °C for 60 s until the expansion process is completed. Afterwards, the formed thermally exfoliated graphite is cooled down. The TEG volume (V) is determined using a graduated cylinder. The thermal expansion coefficient of every sample is calculated as an average value of three measurements using the formula:

$$K_{ex}^{1000} = V / m \quad (6)$$

The anodic oxidation process using the proposed scheme can be realized as proven by the examples of particular implementation, the results of which are given in Table 2.

Table 2: Dependence of TEG expansion coefficient values on the parameters of oxidation process

Number of experiment	1	2	3	4	5	6	7	8	9
$V_{ac}/m_{graph.}$, cm ³ /g	1	1	1	0.5	0.85	0.75	0.5	0.5	1
C_{acid} , % wt.	30	55	94	55	55	94	55	55	55
L , mm	14	7	7	4	9	4	4	4	-
J , mA/cm ²	42	40	25	40	35	40	40	40	30
H , mm	14	8	8	5	9	5	5	5	-
V , cm/min	2	3.6	1.1	6.5	2.1	2.7	6.5	6.5	-
S , mm	18	18	18	18	25	10	30	8	-
E , A·h/kg	36.5	30	60	33	40	60	33	33	37.5
K_{ex} , cm ³ /kg	140	200	290	210	250	405	100	130	105

$V_{ac}/m_{graph.}$ – ratio of acid volume to graphite mass;

C_{acid} – acid concentration;

L , mm – distance between the separator and anode;

J , mA/cm² – current density;

H , mm – thickness of graphite suspension layer;

V , cm/min – rate of conveyor belt-separator movement;

S , mm – distance between the knife electrodes;

E , A·h/kg – power consumption;

K_{ex} , cm³/kg – expansion coefficient at 1000 °C.

In the case of the experiment 1 (Table 2), the natural graphite is mixed with 30% wt. aqueous solution of sulfuric acid (1 cm³ acid solution per 1g graphite). Graphite suspension is placed in the hopper 2 and roller 3 smooths and adjusts the thickness of the graphite suspension layer. The gap between the knife anode electrodes 4 is set up as 18 mm and the distance of the knife electrodes to the membrane surface is 14 mm. The motor means 7 of the driving drum 6 is turn on and the rate of conveyor belt movement (membrane) 13 is set up at 1 cm/min. Herewith, the graphite suspension is loaded from the hopper to the conveyer belt 13 and the roller 3 is used to get the uniformly distributed graphite suspension layer with the thickness equal to 14 mm. When the layer of graphite slurry reaches the anode 4, direct electric current is turn on and its density is maintained at 42 mA/cm². Then, the new portions of the slurry are added to the hopper providing the continuous process of the IGC

production. After 100 minutes, the initial portion of the graphite suspension converted to IGC slurry during electrolysis is reached the driving drum 6. During the motion of membrane 13 along the cylindrical surface of the driving drum 6, the IGC suspension is flaked off its surface and reaches the delivery tray 11 with the restrictive walls 12. Water flow from the rinsing collectors 10 washes out the rest of IGC and the product of the electrochemical treatment in the delivery tray 11 and then to Nutsch-filter. After rinsing and drying, IGC with expansion coefficient equaled to 143 cm³/g is obtained. The energy consumption of this technological process is 35.0 A·h/kg. It must to be emphasized that the procedure of IGC production described in experiments 2-6 is similar to the experiment 1 excepting the parameters of the process. The Table 2 shows the process conditions and the expansion coefficient values for the obtained product. The synthesis procedure of the product obtained according to the experiments 7 and 8 also coincides with the experiment 1 excepting the parameters of process (Table 2). In experiment 7, the distance between the knife anode electrodes is higher (30 mm) than the value reported in [39-41]. In this case, the obtained product contains the particles of non-oxidized graphite expressing the low expansion coefficient. However, the distance between the knife anode electrodes in the experiment 8 is lower (8 mm) than the values stated in the invention formula. It means that the product contains the particles of deoxidized graphite and possesses unsatisfied consumer characteristics. In experiment 9 (similar to [37]), the natural graphite with the mass equal to 200 g was mixed with 100 cm³ of 55% wt. sulfuric acid in aqueous solution (ratio of acid volume to graphite mass was 1 cm³/g). The resulting mixture was pushed into the gap between the anode and the porous membrane 13. Direct current with the density of 30 mA/cm² was passed through graphite. The energy consumption was 37.5 A·h/kg. After rinsing and drying, IGC was obtained with the expansion coefficient equal to 105 cm³/g.

4. Conclusions

Thus, the scheme and the reactor for the continuous electrochemical oxidation of dispersed natural graphite with a capacity of 10 kg/h are created. The operating modes providing the steady quality of oxidized graphite for the production of the functional materials from exfoliated graphite are reported.

The production process of the intercalated graphite and the device for its implementation adaptable to industrial manufacturing that is based on the fabrication of sealing

materials and products from TEG for the equipment used in nuclear and chemical industries, power engineering, metallurgy etc. are considered.

Acknowledgments

The work of the Project was carried out due to the financial support of the Institute of High Technologies of Heilongjiang Province, Harbin city, China.

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