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**STABILITY OF COMMON AND MODIFIED EXFOLIATED GRAPHITE  
TO OXIDATION****Barsukov V. Z., Chernysh O. V., Plavan V. P.**

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*Acceptor-type graphite intercalation compounds (A-GIC) can usually be obtained through electrochemical oxidation of graphite in aqueous acidic or neutral solutions. Oxygen evolution usually takes place at the anode in parallel to the A-GIC formation. It can lead to irreversible changes in the material, and consequently to a loss of reversibility of the system, caused by the partial oxidation of graphite. A special electrochemical method of prolonged sequential cyclic voltammetry was proposed for evaluation of graphite stability to oxidation. The main corrosion mechanisms for different types of graphite are estimated. Special types of TEG modified by  $P_2O_5$ ,  $B_2O_3$  and  $H_3BO_3$  are compared. A maximal cycling life (up to 550 cycles) is obtained with TEG modified by 5% of  $B_2O_3$ .*

**Keywords:** *exfoliated graphite, corrosion mechanisms, stability to oxidation, modification by  $P_2O_5$ ,  $B_2O_3$  and  $H_3BO_3$*

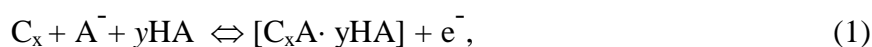
Acceptor-type graphite intercalation compounds (A-GIC) can find in principle enough wide application as electrodes for some types of rechargeable batteries and supercapacitors, electrosorption/desorption electrodes, anodes in different processes of electrochemical synthesis, etc. Nevertheless, the corrosion processes during anodic polarization of such electrodes are the main limitation for their practical using. Using of new types of graphite, more proof to oxidation, can largely increase the electrochemical stability of materials. Quite high resistivity and stability create real prerequisites for enough wide application of such graphite materials.

***Formulation of the problem***

The main targets of this paper are comparison of stability to oxidation for different grades of graphite, investigation of corrosion mechanisms and finding graphite grades with more high resistivity and stability.

***Objects and the methods of the investigation***

Graphite intercalation compounds (A-GICs) can be usually obtained at graphite anode from aqueous solutions of strong acids by the following electrochemical reaction:

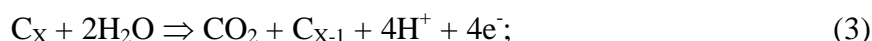


where  $C_x$  – the carbon macromolecule,  $A^-$  – the anion,  $y$  – the stoichiometric factor for solvated molecules of the acid  $HA$ . Nevertheless, in parallel to formation of GICs there usually takes place side corrosion reactions [1] connected with oxygen evolution process on anode:

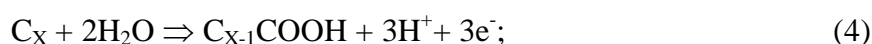
– *the anodic evolution of oxygen*



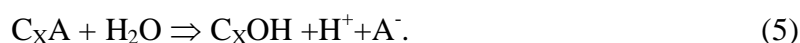
– *the oxidation of graphite to  $CO_2$*



– *the formation of surface groups*



– *the formation of graphite oxide*



It can lead to the irreversible changes in the material, caused by partial oxidation of graphite, loss of reversibility of the system along with the efficiency of reaction for intercalation-deintercalation (1).

#### *Electrodes preparation*

We have manufactured the graphite electrodes of «plug» type. An active mass (88% graphite, 10% carbon black and 2% PTFE) was pressed into a polyethylene plug of 11 mm inside diameter. We have studied the characteristics of electrodes with an equal weight of 0.280g. Before pressing, the Pt current collector was inserted into an opening, pierced in the plug wall.

#### *Graphite materials for investigation.*

We have performed comparative investigation of graphite electrodes, obtained from various types of initial natural and artificial graphites. The following materials were compared:

- #1. Natural graphites from Zavalievo (NGZ) graphite deposit, Kirovograd Region, Ukraine;
- #2. Natural graphite flakes (NGF) «Kropfmuhl Normalflocke» (BASF<sup>®</sup>, Munich, Germany);
- #3. Thermally exfoliated graphites (TEG) and their composites from Superior Graphite Co. (Chicago) and prepared from Ukrainian graphite.

*TEG preparation.* Initial natural Ukrainian graphite from Zavalievo deposit in Kirovograd Region was chemically intercalated in sulfuric acid. Potassium persulfate was used as an oxidizer. Thermal expanding of graphite was performed at 900°C [2]. Carbon content in the experimental samples was of about 99.0%.

American TEG of ABG-74 commercial grade was manufactured by similar method using, first of all, the developed continuously thermal purification process for precursor (with ability to achieve and sustain a relatively large zone of uniform temperature in excess of 2500 °C). The precursor (as minimum 98.0-99.0% carbon natural flake graphite) must have minimal ash content in order to achieve lowest possible resistivity (0.007 Ohm-cm) and ultra pure quality of a final product (99.95 %).

#### *Some structural investigations of graphite*

For investigation the micro- and macro-structural characteristics of graphite we have used a methods of X-ray analysis, SEM and studying the character of particles distribution on sizes with LASER MICRON SIZER.

#### *Consecutive galvanostatic cycling with control of the electrode mass loss*

We have used the methods of galvanostatic cycling in the 0.5-1.75V or 0.5-2.00V potential ranges vs. the Ag/ AgCl reference electrode. In some cases there was carried out the control of the loss for electrode mass during the cycling for studying the possible mechanisms of electrochemical corrosion on graphite electrodes.

#### *Consecutive voltammetric cycling*

Electrodes were manufactured of NGZ, NGF and TEG and were tested under comparable conditions. The relative resistivity of graphite electrode to corrosion was compared on stability of CVs during the N consecutive voltammetric cycling in given potential region. The relative resistivity to corrosion was estimated by the numbers of cycles for very stable cycling ( $N_{\text{stable}}$ ) and for saving of electrochemical activity ( $N_{\text{max}}$ ).

### **Results and discussion**

#### 1. Structural investigations

##### *1.1. Structural investigations in the beginning and finish of cycling for NGZ and NGF*

It is possible to make conclusion about the absence of noticeable structural changes in graphite in the beginning and finish of cycling based on X-ray data.

The parameters of an elementary crystal cell for initial and finite state are practically identical. For example, interplanar distance  $C = (6,718 \pm 0,007) \cdot 10^{-8}$  cm for NGZ (GAC-1 type) and NGF is not changes during of cycling.

##### *1.2. Comparisons the particles distribution of sizes for NGF and TEG*

We have studied the samples of TEG, NGF and TEG at a SK LASER MICRON SIZER and also from X-ray data. The particle distribution do not vary sufficiently during of cycling. The average crystal values for NGZ (GAC-1 type) and NGF is, in particular, 35-40 mic. The specific surface of such graphites in initial and finite states is also practically identical and is of about 6,8-7,0 m<sup>2</sup>/g. The average size of particles for TEG from Superior

Graphite Co. is sufficiently less ( $D_{50} \leq 10$  mic: 50% particles less than 10mic.; 90% particles less than 24 mic.). The specific surface of ABG-74 grade exfoliated graphite is  $24 \text{ m}^2/\text{g}$ . One may suppose that TEG is less oxidation-resistant than NGF and NGZ. However, we have shown TEG to be much more oxidation-resistant than NGF.

Table 1

**The main parameters of NGF and different NGZ materials (on the results of galvanostatic cycling)**

№	Type of Graphite	$N_{\text{max}}^{\text{G}}$ Cycles	$\alpha_{\text{max}}$ , %	$q_{\text{max}}$ , A·h/kg	$\mu_{\text{max}}$ , %
1	Natural graphite flakes (NGF) “Kropfmuhl Normalflocke”, Germany	>100	67,1	5,77	20,5
<i>Natural graphites from Zavalievo (NGZ) graphite deposit, Kirovograd Region, Ukraine</i>					
2	Graphite for Zn-MnO <sub>2</sub> cells (Standard #7478-75):				
2.1	GE-1	39	90	10,5	37,3
2.2	GE-2	35	90	9,3	33,1
3	Graphite for electro-carbon articles, EUZ-M type (Standard #10274-79)	26	31	12,8	40
4	Electro-carbon graphite, EUZ-E type (Standard # 21-25-156-75)	16	63,5	10,8	38,4
5	Graphite for alkaline accumulators (Standard #10273-73):				
5.1	GAC-1	10	35,2	11,1	39,5
5.2	GAC-2	7	27	8,29	25,9
6	Special graphite with a small ash content, GMS-1 type (Standard # 18191-78):	5	29	8,52	30,3
7	Special graphite, C-1 type (Standard # 113-08-48-63-90)	4	18	6,1	19,05

*In this table:*

$N_{\text{max}}^{\text{G}}$  – is the maximum numbers of cycles before the discharge electrode capacity Qd will reduce to minimal level ( $Qd^{\text{min}} = 4\text{Ah/kg}$  in our case);  $\alpha_{\text{max}} = (Qd/Q_{\text{ch}}) \cdot 100\%$  – is the maximum value of current efficiency;  $Q_{\text{ch}}$  – charge electrode capacity);  $q_{\text{max}}$  – is the maximum value of specific discharge capacity (A·h/kg) during the cycling;  $\mu_{\text{max}} = (Qd/Q^{\text{Thd}}) \cdot 100\%$  – is the utilisation factor (%);  $Q^{\text{Thd}}$  – theoretical discharge capacity.

It is clear from the data of Table 1 that the initial specific capacitive parameters of some types of NGZ are higher than NGF by factor 1.5...2.0. Nevertheless, the values of  $N_{\text{max}}^{\text{G}}$  for NGF are considerable higher than for NGZ. Thus, NGZ are less resistant to electrochemical oxidation than NGF.

## 2. Comparison of Cyclic Voltammograms

On the first stage of investigation cyclic voltammograms (CVs) were compared for the graphite electrodes during cycling in maximal possible potential range  $\Delta E_{max} = 0-2.1V$  (vs. the Ag/AgCl reference electrode) at a sweep potentials rate of 10 mV/s. As our cyclic voltammetric investigations show, the minimal resistivity to corrosion ( $N_{stable} = 20-30$ ;  $N_{max} = 50-90$  cycles) is demonstrated by the natural Zavalievo graphites (group #1).

It is clearly seen from the curves presented for TEG (Fig.1) that there is not any evidence for the electrode surface oxidation, at least during the first  $N_{stable} = 190$  cycles, whereas the oxygen evolution rate is quite high under these conditions. After 190 cycles a gradual decrease of peak currents can be noticed (see curves corresponding to 200 and 250 cycles, respectively). The service life of the electrode composed of TEG under these conditions is  $N_{max} = 250$  cycles. When cycling a NGF electrode under the same conditions (Fig. 2), the deintercalation peak current values are much higher. At the same time, under comparable conditions, a noticeable surface oxidation of NGF starts to be observed significantly earlier, after  $N_{stable} = 50-60$  cycles. The service life of the NGF electrode is  $N_{max} = 100$  cycles.

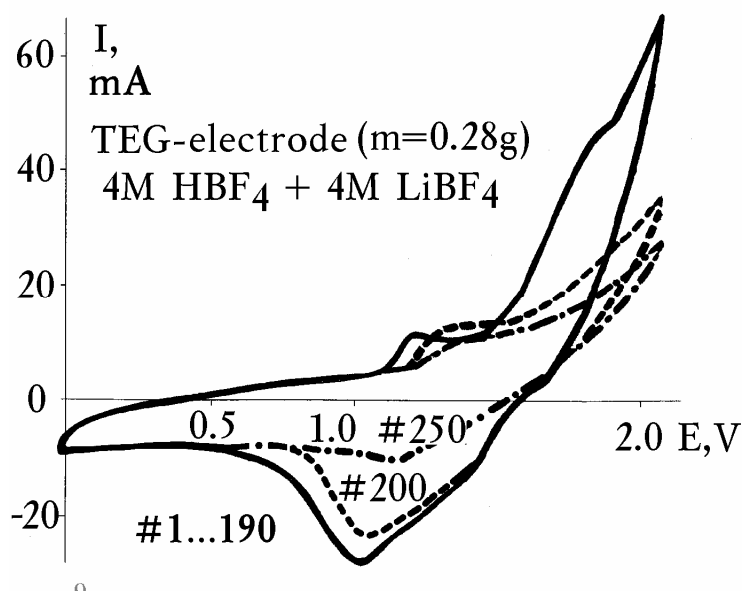


Fig.1. CVA for the TEG - electrode ( $m=0.28g$ );  $E_{max}=2.1V$ ;  $v=10mV/s$

On the next stage of investigation cyclic voltammograms were compared for the TEG modified by  $P_2O_5$ ,  $B_2O_3$  and  $H_3BO_3$  during cycling in more realistic and narrower range of potentials  $\Delta E_n = 0.8-2.1V$  at the same sweep potentials rate of 10 mV/s. Considering the

results of the comparison it is easy to conclude that the TEG electrode is more resistant to electrochemical corrosion. A maximal cycling life in such conditions (up to 550 cycles) is obtained with TEG modified by 5% of B<sub>2</sub>O<sub>3</sub>.

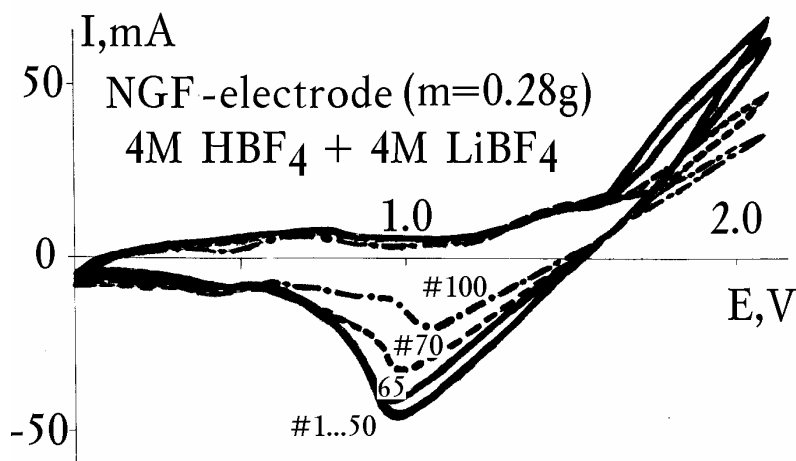


Fig.2. CVA for the NGF - electrode (m=0.28g). E<sub>max</sub>=2.1V; v=10mV/s

3. Investigation of mechanism of electrochemical corrosion of graphite electrodes.

Comparison the capacity loss with the loss of graphite electrodes mass

There is exists point of view that the main mechanism of electrochemical corrosion connected with a full step by step oxidation of graphite to CO<sub>2</sub> during the cycling according with reaction (3). For studying the possible mechanisms of electrochemical corrosion we have compared first of all the capacity loss for graphite electrodes with the loss of their mass during prolonged galvanostatic cycling (Table 2).

Table 2

**The capacity and mass loss for NGZ (GAC-1 type) and NGF («Kropfmuhl Normalflocke») during the consecutive galvanostatic cycling up to U<sub>max1</sub>=1.75V and U<sub>max2</sub>=2.00V**

Type of graphite	U <sub>max</sub> , V	The loss of electrode capacity			The loss of electrode mass		
		Q <sub>0</sub> , mA·h	Q <sub>min</sub> , mA·h	δ, %	M <sub>0</sub> ,g	M <sub>min</sub> ,g	δ,%
NGZ (GAC-1)	1.75	5.00	1.66	66.8	2.00	1.00	50.0
	2.00	9.00	0.48	94.7	2.00	0.87	56.5
NGF	1.75	5.70	3.33	67.5	1.14	1.11	2.51
	2.00	9.11	3.33	68.0	1.13	1.11	2.49

The comparison of electrode capacity loss with loss of their mass during the cycling unambiguously shows, that degradation of electrical characteristics cannot be explained only

by CO<sub>2</sub> derivation with appropriate decrease of an active material store. The main mechanism depends strongly on the type of graphite. For example, for NGZ the loss of capacity is higher but comparable with the loss of graphite mass (66.8 and 50.0%; 94.7 and 56.5%). Thus, corrosion mechanism (3) is predominant for such non stable to oxidation graphite group. For NGF the loss of capacity is much more higher (of about 68%) than the loss of graphite mass (of about 2.5%). Thus, for such type of graphite the corrosion mechanisms (4) and (5) with formation of surface groups are predominant.

The same mechanisms (4) - (5) are typical also for TEG and modified TEG. As results of additional acid-base titration shows even in the initial state the developed internal surface of TEG is covered by thin layer of -COOH and -OH groups which are the result of heat-treatment during preparation of expanded graphite. This makes TEG more stable to the electrochemical oxidation during cycling. It is well known also that chemical activity of any carbon material is less if carbon was treated at higher temperature. The stabilizing influence is connected usually with its acceptor properties and its influence for TEG can be similar as for the other carbon materials. The stabilizing influence of boron is connected obviously with its acceptor properties which appear after its implantation in a structure instead of carbon atoms. Such effects are mentioned in the literature for some types of carbon materials [2] and the influence of boron on TEG can be the similar.

### ***Conclusion***

The minimal resistance to oxidation (few dozens of cycles) is demonstrated by the natural Zavalievo graphite. Natural graphite flakes «Kropfmuhl Normalflocke» prove to possess significantly higher resistance to oxidation (up to 100 cycles). Furthermore, TEGs demonstrate even much higher resistance to oxidation (250 cycles). The main corrosion mechanism for the natural Zavalievo graphite connected with a full step by step oxidation of graphite to CO<sub>2</sub> during the cycling according with reaction (3). The main reason of graphite electrodes corrosion for NGF and TEG is the derivation and accumulation of surface groups /reactions (4), (5)/, which gradually lock «entrances» and hinder intercalation of anions in interlayer space. The evaluations show that the most probably areas, where the redundant acid centers are located, are the initial sites and «entrances» in interlayer space. Using of new types of graphite, more proof to oxidation, (in particular, TEG and TEG modified by boron) can largely increase the electrochemical stability of materials. Quite high resistivity and stability create real prerequisites for enough wide application of such graphite materials.

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**Барсуков В.З., Черныш О. В., Плаван В. П.**

**Устойчивость к окислению обычного и модифицированного расширенного графита**

Интеркаляционные соединения графита акцепторного типа А-ИСГ могут быть обычно получены путем электрохимического окисления графита в водных кислых или нейтральных растворах. Параллельно с образованием А-ИСГ на аноде обычно имеет место выделение кислорода. Это может приводить к необратимым изменениям в материале и, следовательно, к потере обратимости в системе, связанной с частичным окислением графита. Предложен специальный электрохимический метод длительной последовательной циклической вольтамперометрии для оценки устойчивости графита к окислению. Оценены основные механизмы коррозии для различных типов графитов. Сопоставлены специальные типы расширенных графитов, модифицированных  $P_2O_5$ ,  $B_2O_3$  and  $H_3BO_3$ . Наибольший срок службы (до 550 циклов) имеет расширенный графит, модифицированный 5 %  $B_2O_3$ .

**Ключевые слова:** расширенный графит, механизмы коррозии, устойчивость к окислению, модификация  $P_2O_5$ ,  $B_2O_3$  и  $H_3BO_3$

**Барсуков В. З., Черныш О. В., Плаван В. П.**

**Стійкість до окислення звичайного і модифікованого розширеного графіту**

Інтеркаляційні сполуки графіту акцепторного типу А-ІСГ можуть бути зазвичай отримані шляхом електрохімічного окислення графіту у водних кислих або нейтральних розчинах. Паралельно з утворенням А-ІСГ на аноді зазвичай має місце виділення кисню. Це може призводити до необоротних змін в матеріалі і, отже, до втрати оборотності в системі, пов'язаної з частковим окисленням графіту. Запропонований спеціальний електрохімічний метод тривалої послідовної циклічної вольтамперометрії для оцінки стійкості графіту до окислення. Оцінені основні механізми корозії для різних типів графітів. Співставленні спеціальні типи розширених графітів, модифікованих  $P_2O_5$ ,  $B_2O_3$  and  $H_3BO_3$ . Найбільший термін служби (до 550 циклів) має розширений графіт, модифікований 5%  $B_2O_3$ .

**Ключові слова:** розширений графіт, механізми корозії, стійкість до окислення, модифікація  $P_2O_5$ ,  $B_2O_3$  і  $H_3BO_3$