## Reaction of Graphite with Sulfuric Acid in the Presence of KMnO<sub>4</sub>

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**Abstract**—The reaction of graphite with sulfuric acid in the presence of  $KMnO_4$  (oxidant: graphite ratio 0.027–0.55) involves consecutive and concurrent reactions: graphite intercalation and direct oxidation of the carbon matrix. The properties of graphite bisulfate and its reaction products are determined by the stage number of the intercalation compound; the decomposition enthalpies of the stage I–IV graphite bisulfate correlate with the enthalpies of graphite intercalation with sulfuric acid.

Chemical reactions involving graphite form the basic synthetic route to an abundant and original class of compounds, viz. graphite intercalation compounds (GICs). These reactions are peculiar in that they leave the graphite structure almost intact, and simply increase the distance between graphite layers as a result of intercalation of various chemical reagents between graphite grids. The interest in GICs is primarily explained by such their features as regular lamellar structure, highly anisotropic properties, as well as unusual mode of bonding between intercalated compounds and the graphite grid. Special place among GICs belongs to graphite bisulfate, the product of graphite reaction with sulfuric acid, that, on the one hand, is a model compound for development of the classical stage structural model and, on the other, serves as the starting material for the production of oxidized graphite and a unique low-density material, foam graphite.

The intercalation of graphite with sulfuric acid can only be accomplished in the presence of an oxidant (chemical or electrochemical); in both cases, irrespective of the nature of the oxidant, graphite bisulfate is formed [1]. Depending on the nature of the oxidant and the concentration of the acid, graphite bisulfate of various composition  $C_{24s}^+HSO_4^-2H_2SO_4$  can be formed (s is the stage number equal to the number of graphite grids between two closest layers of the intercalate [1]) [2]. Later it was established that whether one or another stage forms also depends on the redox potential of the oxidizing solution [3]. Graphite reactions in C-H<sub>2</sub>SO<sub>4</sub>-[O] systems ([O] =  $K_2Cr_2O_7$  or HNO<sub>3</sub>) are the most thoroughly studied. The latter oxidants are widely used in the production of variouspurpose foam graphite. At the same time, the information on graphite bisulfate formation in the presence of  $KMnO_4$  is scarce. In this connection of mention are the works of Inagaki *et al.* [4] and Avdeev *et al.* [5], who established that the potential of a graphite sample stepwise grows in the course of intercalation with  $H_2SO_4$  in the presence of such strong oxidants as  $KMnO_4$ ,  $HNO_3$ , or  $K_2Cr_2O_7$ . The plot of potential vs. time is stepwise and is similar to that characteristic of anodic oxidation of graphite. From this observable we can conclude that both chemical and electrochemical oxidants act in a similar way. The effect of conditions of chemical treatment of graphite in the  $H_2SO_4$ - $KMnO_4$  system on the properties of the reaction products have not been considered in detail.

It the present work we have studied the reaction of graphite with sulfuric acid in the presence of  $KMnO_4$  at a widely varied  $KMnO_4$ : graphite weight ratio. By varying reactant ratio and treatment time one can control oxidation conditions and study the effect of these factors on the structure and properties of both GICs and oxidized graphite and foam graphite.

Synthesis of graphite bisulfate. The reaction of graphite with sulfuric acid in the presence of  $KMnO_4$  was assumed to occur by scheme (1).

 $5C_{24s} + KMnO_4 + 17H_2SO_4$  $\longrightarrow 5C_{24}^s HSO_4 \cdot 2H_2SO_4 + MnSO_4 + KHSO_4 + 4H_2O. (1)$ 

Here s is the stage number of the GIC.

The required quantities of the oxidant were calculated by this equation. The reaction results are given in Table 1 and Fig. 1. The experimental data provide evidence for the validity of Eq. (1) for the stage I–IV graphite bisulfate. The identity periods of the synthesized graphite bisulfate samples fit known values [2].

KMnO <sub>4</sub> : graphite	Synthesis		Graphite stag	Identity period	
weight ratio	u		expected	experiment	<i>I</i> <sub>C</sub> , Å
0.110	15	min	Ι	Ι	7.98
0.055	30	min	II	II	11.33
0.036	40	min	III	III	14.70
0.027	50	min	IV	IV	18.07
0.165	24	h	I <sup>a</sup>	Ι	7.96
0.165	72	h	I <sup>a</sup>	Ι	7.99
0.550	24	h	I <sup>a</sup>	_	-
0.550	170	h	I <sup>a</sup>	_	-
0.550	10	h <sup>b</sup>	Ia	_ LI	_

**Table 1.** Effect of graphite intercalation conditions on the stage number of graphite bisulfate

<sup>a</sup> Overoxidized I stage. <sup>b</sup> At 80°C.



**Fig. 1.** X-ray diffraction patterns of sulfuric acid– graphite intercalation compounds obtained at graphite: KMnO<sub>4</sub> ratios of (a) 0.55, (b) 0.11, and (c) 0.055–0.027 and (d) starting graphite ( $d_{002}$  3.35 Å) (2 $\theta$  is the reflection angle and *I*, reflection intensity; the same for Fig. 3).

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Probably, in the graphite– $H_2SO_4$ –KMnO<sub>4</sub> system we deal with processes characteristic of anodic oxidation of graphite [6]: oxidation of the graphite matrix to macrocation  $C_n^+$  with subsequent intercalation between the polyarene grids of sulfate anions and sulfuric acid molecules; oxidation of peripheral carbon atoms at plane edges and in defects to oxygen-containing functional groups (COH, C=O, COOH); and chemical dispersion of graphite particles to soluble compounds, such as benzenepolycarboxylic and mellitic acid, as well as wet burning of carbon to gaseous oxides [reaction (2)].

$$5C + 4KMnO_4 + 8H_2SO_4$$
$$\longrightarrow 5CO_2 + 4MnSO_4 + 6H_2O + 4KHSO_4.$$
(2)

In this system, KMnO<sub>4</sub> acts as an oxidant that favors graphite intercalation. Decreased oxidant concentration decreased the amount of KMnO4 diffusing to the graphite matrix per unit time; therefore, the time of synthesis of graphite bisulfate with a stoichiometric amount of the oxidant increases with increasing stage number. It can also be proposed that with increasing amount and, as a result, concentration of such a strong oxidant as KMnO<sub>4</sub>, the contribution of direct oxidation of the graphite matrix increases. To assess the effect of oxidant concentration, a series of experiments was performed, in which the amount of KMnO<sub>4</sub> was increased compared with stoichiometric for the first stage by 50 and 500%, and the synthesis time and temperature were, too, much increased. Figures 1b and 1c show the X-ray diffraction patterns of the graphite bisulfate samples synthesized with the stoichiometric amount of KMnO<sub>4</sub>. As seen from the figures, the intensity of reflections decreases with decreasing graphite bisulfate stage number. This observation can be explained in terms of the decreasing size of crystallites that effect coherent X-ray scattering. Treatment of graphite with an oxidizing mixture containing excess KMnO<sub>4</sub> provides a strongly amorphized stage I graphite bisulfate, as evidenced by further decrease in the intensity of reflections and their broadening.

The structure amorphization is favored by that the reaction is performed in the presence of such a strong oxidant as  $KMnO_4$  whose potential in 96% sulfuric acid is higher, as we found in [3], than that of formation of the stage I graphite bisulfate.

We also found in [3] that the increased potential will probably favor side reactions forming surface oxygen-containing groups. Moreover, in [5] we showed that the enthalpy of intercalation of sulfuric acid into a graphite matrix in the presence of KMnO<sub>4</sub> is much dependent on the amount of the latter (4–

Graphite bisulfate stage no.	$T_{i}$ - $T_{f}$ , °C	T <sub>max</sub> , °C	Δ <i>m</i> , %	$\Delta H$ , kJ mol <sup>-1</sup> C	$\Delta H_{\rm d},$ kJ mol <sup>-1</sup> H <sub>2</sub> SO <sub>4</sub>	$\Delta H_{\rm d},$ kJ mol <sup>-1</sup> C
I II III IV H <sub>2</sub> SO <sub>4</sub> + graphite	202–326 181–308 205–319 192–322 193–315	283 256 266 268 258	156 137 85 106 89	31.2 27.9 19.8 18.6 114.6	30 46 58 69 -	3.0 2.2 1.6 1.8

Table 2. Thermal properties of graphite bisulfate<sup>a</sup>

<sup>a</sup> ( $T_i$  and  $T_f$ ) Initial and final temperatures of the endo effect, respectively; ( $T_{max}$ ) maximum temperature of the endo effect; ( $\Delta m$ ) weight loss with respect to the graphite weight; and ( $\Delta H$ ) enthalpy change.

40 kJ mol<sup>-1</sup>). On this basis we suggested in the cited work that the use of  $KMnO_4$  in the synthesis of graphite bisulfate would induce side reactions. The experimental data obtained in the present work provide conclusive evidence for this suggestion.



**Fig. 2.** Thermoanalytical curves (DSC and TG) for the (a) stage II graphite bisulfate (m 3.67 mg), (b) H<sub>2</sub>SO<sub>4</sub> on the starting graphite support (m 2.85 mg) and (c) oxidized graphite obtained from the stage III graphite bisulfate (m 4.79 mg).

Thermal analysis of graphite bisulfate. A typical thermoanalytical curve in the 30–350°C [thermogravimetry (TG) and differential scanning calorimetry (DSC)] of the stage II graphite bisulfate is given in Fig. 2a. At 350°C, the graphite bisulfate decomposes completely to graphite with the interplanar spacing  $d_{002}$  of 3.36 Å.

The DSC curves contain a number of broad endo peaks. The weak effect at 50–180°C is accompanied by an inconsiderable weight loss. The strongest heat effect is observed at 180–325°C, and it is a superposition of two unresolved endo effects, the first being much stronger than the second. The strongest endo effect is accompanied by a one-stage and large weight loss. The resulting data are represented in Table 2.

The DSC curves for the I-IV stages have similar shapes. Moreover, the decomposition onset temperature is almost independent on the stage number of the starting GIC, while Matzui et al. [7] reported the tendency of the decomposition onset temperature to increase with increasing stage number. The similar DSC curves and almost equal specific decomposition enthalpies of graphite bisulfate suggest that processes associated with H<sub>2</sub>SO<sub>4</sub> deintercalation from the graphite matrix contribute little compared with another, more energetic process. The case in point is that the graphite bisulfate samples prepared on the graphite powder by the proposed procedure contain much acid on the surface. Figure 2b presents the behavior of sulfuric acid on the surface of the starting graphite under heating. As seen, the DSC pattern is similar to the above pattern for graphite bisulfate, implying that the enthalpy is mostly contributed by boiling and decomposition of sulfuric acid on the surface of the graphite sample. This is a probable reason why in our case, unlike what is observed in [7], the decomposition onset temperature of graphite bisulfate does not increase with increasing stage number.

The total heat effect of decomposition of the stage I–IV graphite bisulfate ( $\Delta H$  130 kJ mol<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>)

presumably comprises the heat of  $H_2SO_4$  deintercalation from the graphite matrix  $(\Delta H_d)$  and the enthalpy changes associated with the behavior of  $H_2SO_4$  on the surface of the graphite sample  $[\Delta H(H_2SO_4)]$ 115 kJ mol<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>]. Knowing the weight loss  $(m_1)$ we can estimate the heat of evaporation and desorption of the given amount of the acid from the surface of the graphite sample  $[\Delta H_{\Sigma} = \Delta H(H_2SO_4)^*m_1]$ . The difference between  $\Delta H_{exp}$  and  $\Delta H_{\Sigma}$  is the enthalpy of  $H_2SO_4$  deintercalation from the graphite matrix. From the composition of graphite bisulfate  $C_{24s}^+$ HSO<sub>4</sub>.  $2H_2SO_4$  [2] we can calculate the weight of sulfuric acid deintercalated on decomposition of graphite bisulfate. The experimental results and calculated deintercalation heats per mole intercalated acid  $[\Delta H_d]$ , kJ mol<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>] and per mole graphite  $[\Delta H_d, kJ \text{ mol}^{-1} \text{ C}]$  are given in Table 2.

The  $\Delta H_d$  values per mole intercalated acid vary linearly with stage number. This result can be explained by the fact that decreasing stage number of GIC results in decrease in the stage number of the latter and increase in  $\Delta H_d$  per mole graphite. It should be noted that the resulting values are small ( $\Delta H_d$  1.5–3.0 kJ mol<sup>-1</sup> C) and compare with the enthalpies of  $H_2SO_4$  intercalation into graphite [5].

Hydrolysis of graphite bisulfate. Graphite bisulfate samples were hydrolyzed using the decantation technique. As known hydrolysis results in destruction of GIC, deintercalation of sulfuric acid, and formation of oxidized graphite that contains "bound" water, various surface functional groups, and residual acid [8]. Since on treatment of graphite with a mixture of sulfuric acid and the oxidant we observe, along with the intercalation of  $H_2SO_4$  into the graphite matrix, side processes that result in sample amorphization and chemical dispersion, increase in the amount of the oxidant in the system increases the fraction of microparticles that do not drop on decantation and exist in the suspended state. Consequently, as the stage number decreases, the fraction of finely dispersed residue increases. Thus, for the IV stage this fraction is 0.3-0.5%, for the I stage it is 3.5-4.1%, and with a 5-fold oxidant excess it attains 14.5-15.5%. As seen from Table 3, the oxidized graphite synthesized with a stoichiometric amount of the oxidant gains weight by 6 to 50% as the stage number of the starting graphite bisulfate decreases. The sulfur content, too, depends on GIC stage and increases from 1.9 to 4.6% in going from the IV to I stage.

The weight gain for the oxidized graphite samples obtained with excess KMnO<sub>4</sub> is 20-24%, which is almost half the weight gain of the oxidized graphite obtained from the stage I graphite bisulfate. As would

**Table 3.** Properties of oxidized graphite

Graphite bisulfate stage no.	Weight gain Δ <i>m</i> , %	Weight gain with account for finely dispersed residue, %	Sulfur content of oxidized graphite, %			
Stoichiometric amount of oxidant						
Ι	45.8	49.3	4.6			
II	11.5	12.8	3.1			
III	10.3	11.5	3.0			
IV	5.6	6.0	1.9			
Oxidant excess						
Ι	19.6	23.6	4.3			
Ι	17.6	23.0	3.9			
_	9.2	24.1	2.8			
_	5.0	20.0	2.6			
—	2.8	18.6	3.0			

be expected, oxidative dispersion and wet burning of the graphite matrix are favored by excess oxidant and increased temperature.

As shown by X-ray phase analysis (Fig. 3), the hydrolysis product is a many-phase mixture comprising higher stage GIC and defective graphite; therewith, the graphite phase ( $d_{002}$  3.35 A) is present only in the oxidized graphite firmed by hydrolysis of the stage IV graphite bisulfate. The X-ray patterns of the



Fig. 3. X-ray diffraction patterns of oxidized graphite prepared from the stage (a) I, (b) II, and (c) III graphite bisulfate.

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Table 4. Thermal analysis of oxidized graphite

Effect	Parameter	Graphite bisulfate stage no.				
		Ι	II	III	IV	
1	T <sub>i</sub> −T <sub>f</sub> , °C	38–173	36–165	35–172	30–198	
	$T_{\rm max}, \ ^{\circ}{\rm C}$	116	97	96	101	
	$\Delta H$ ,	2.8	0.9	1.1	1.0	
	kJ mol <sup>-1</sup> C					
	$\Delta m, \%$	12.3	5.5	6.3	3.7	
2	$T_{i}-T_{f}$ , °C	173-305	165-283	172-288	198–296	
	$T_{\rm max}^{1}$ , °C	255	253	267	276	
	$\Delta H$ ,	2.5	0.9	1.2	0.6	
	kJ mol <sup>-1</sup> C					
	$\Delta H$ , kJ g <sup>-1</sup>	1.4	1.4	1.5	1.4	
	$\Delta m, \%$	15.2	5.5	6.3	3.7	
3	$T_{i}-T_{f}$ , °C	305-500	402-500	411-511	398-495	
	$T_{\rm max}$ , °C	438	443	447	443	
	$\Delta H$ ,	1.0	0.3	0.4	0.2	
	kJ mol <sup>-1</sup> C					
	$\Delta H$ , kJ g <sup>-1</sup>	1.6	0.6	0.9	0.5	
	$\Delta m, \%$	5.2	4.3	3.5	2.5	
			l		l	

oxidized graphite are impossible to assign unambiguously: Reflections can be assigned to the VII and higher stages. Residual stages cannot be completely hydrolyzed and removed only by additional washing in more severe conditions [ $T(H_2O)$  95°C], while the sulfur content therewith decreases about 1.5-fold.

Thermal analysis of oxidized graphite. Oxidized graphite samples were subjected to complex thermal analysis. A typical thermoanalytical curve (oxidized graphite prepared from the stage III graphite bisulfate) is given in Fig. 2c. It should be noted that, irrespective of stage number, the DSC curves have similar patterns. The curves show three endo effects at 30-510°C: The first endo effect is in the range 30–175°C, the second, at 175–305°C, and the third, at 305– 510°C. Once 550°C has been attained, full decomposition of the oxidized graphite to graphite ( $d_{002}$  3.36 Å). The resulting data are listed in Table 4. It can be suggested that the first endo effect corresponds to loss of "associated" water. The temperature range of the second endo effect coincides with the range of  $H_2SO_4$  deintercalation from the graphite bisulfate matrix; therefore, we assign this effect to deintercalation and evaporation of residual sulfuric acid. The last endo effect is probably associated with decomposition of surface groups and CO, CO<sub>2</sub>, and H<sub>2</sub>O evolution.

Table 4 lists the enthalpies of the three endo effects. As seen, the  $\Delta H$  of the first endo effect is the highest for the I stage, and it is higher than those for the II–IV

stages 2–3 times. The content of "associated" water in the oxidized graphite prepared from the stage I graphite bisulfate is 2–3 times higher that the respective contents for the other stages. This result is probably explained by a change in the hydrolysis mechanism in going from the stage II to stage I graphite bisulfate [9].

The enthalpies of the second effect and the weight loss decrease (from 2.5 to 0.6 kJ mol<sup>-1</sup> C and from 15.2 to 3.7%, respectively) with increasing stage number. We suggest liberation of sulfuric acid in this temperature range, since the  $\Delta H$  of the second effect is 137 kJ mol<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, which compares with the experimental decomposition enthalpy of graphite bisulfate ( $\Delta H_{exp}$  130 kJ mol<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>). The fact that the specific enthalpies (per 1 g of evolved substance) are equal to each other suggest that the decomposition processes are similar in nature. It should be noted that the weight loss associated with the second endo effect correspond to the residual H<sub>2</sub>SO<sub>4</sub> (sulfur) content in the oxidized graphite samples.

As the amount of the oxidant used in the synthesis of graphite bisulfate is increased, the content of surface functional groups increases, as seen from the weight losses for the third endo effect. As judged from the enthalpy of the third endo effect, the qualitative composition of surface functional groups changes. For example, in the oxidized graphite samples synthesized from the stage I graphite bisulfate, surface functional groups begin to decompose already at 320°C, whereas in those prepared from the stage II–IV graphite bisulfates, at 400°C only.

The oxidized graphite samples were subjected to thermal treatment under conditions of thermal shock. Analysis of the X-ray patterns of the foam graphite samples prepared from the stage I–IV graphite bisulfites shows that the major phase is a graphite with the interplanar spacing  $d_{002}$  of 3.36–3.37 Å. In going from higher to lower stages, the intensity of diffraction reflections of foam graphite changes appreciably. It is interesting to note that such a regularity in intensity changes is already observed in the stage of graphite bisulfate and oxidized graphite formation.

Figure 4a shows the plot of the bulk density of foam graphite ( $\rho_{fg}$  vs. stage number of the starting GIC).

At a stoichiometric oxidant amount, the bulk density of foam graphite decreases with decreasing stage number, in agreement with the data in [10]. Ase the foaming degree increases with decreasing stage number, the stronger burn-out of the graphite matrix enhanced, as evidenced by the fact that the yield by carbon depends on the stage number of the starting GIC



**Fig. 4.** Properties of foam graphite vs. conditions of synthesis of starting graphite bisulfate: (a) bulk density ( $\rho_{fg}$ ) vs. stage number; (b) yield by carbon vs. stage number; (c) specific surface area ( $S_{sp}$ ) vs. KMnO<sub>4</sub>: graphite weight ratio; and (d) sulfur content of foam graphite vs. KMnO<sub>4</sub>: graphite weight ratio.

(Fig. 4b). The strongest burn-out of the graphite matrix is observed with the samples obtained with a 5-fold oxidant excess: The yield by carbon decreases to 82–85%. The trend in the specific surface area [ $S_{\rm sp}$  40–90 m<sup>2</sup> g<sup>-1</sup> (Table 5)] with increasing KMnO<sub>4</sub>: graphite ratio is opposite (Fig. 4c).

The dependence of the sulfur content of foam graphite on the oxidant amount is shown in Fig. 4d. The sulfur content of foam graphite regularly increases with decreasing stage number of the starting GIC, which agrees with the data in [11]. It should be noted that the sulfur content increases with increasing oxidant amount. Under the assumption that sulfuric acid is harder to remove from defects, this fact provides one more evidence to show that increased oxidant amount in the system enhances imperfectness of the graphite matrix.

## **EXPERIMENTAL**

Natural large-flake graphite (ash content <0.04%, particle size 315–400  $\mu$ m, interplanar spacing  $d_{002}$  3.35 Å) and chemical grade H<sub>2</sub>SO<sub>4</sub> ( $\pi_{22}$  1.83 g cm<sup>-3</sup>) and KMnO<sub>4</sub> were used as starting reagents.

Graphite powder was added to a freshly prepared solution of  $KMnO_4$  in conc.  $H_2SO_4$ , and the mixture was intermittently stirred for some time. The amount of  $KMnO_4$  and reaction time were varied over a wide range. When the synthesis had been complete, excess

subjected to X-ray phase and thermal analyses. The X-ray phase analysis was performed on a URD diffractometer (Cu $K_{\alpha}$  radiation, Ni filter) in the angle range 5–80° under an X-ray amorphous film. The complex thermal analysis was performed on a Netzsch Jupiter STA-449C analyzer at 30–600°C under argon, heating rate 10 deg/min. Hydrolysis and washing of

oxidizing solution was removed, and the product was

Table 5. Properties of foam graphite

Starting graphite bisulfate stage no.	Bulk density $\rho_{\rm fg},~g~l^{-1}$	Yield by carbon with account for finely dispersed residue, %	$s_{\rm sp,m^2 g^{-1}}$	Sulfur content of oxidized graphite, %		
Stoichiometric amount of oxidant						
Ι	2.7	93.3	65.2	0.34		
II	4.8	94.0	45.2	0.19		
III	5.2	95.3	42.5	0.15		
IV	6.8	96.3	43.1	0.10		
Oxidant excess						
Ι	4.6	94.6	68.9	0.41		
Ι	5.4	94.0	79.4	0.40		
_	4.5	87.0	93.9	0.99		
_	2.9	82.0	_	1.00		
_	6.0	84.6	_	0.80		

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graphite bisulfate were performed at a graphite: distilled water weight ratio of 1:20. During hydrolysis, the graphite suspension was stirred, after which the precipitate was let to settle, and the most part of the solution was decanted (the operation was repeated). The oxidized graphite was filtered off, dried at 90°C, and weighed. The weight gain  $\Delta m$  was calculated by the following formula.

$$\Delta m(\%) = (m_{\rm og}/m_{\rm sg}) \times 100.$$

Here  $m_{og}$  is the weight of the oxidized graphite after drying and  $m_{sg}$  is the weight of the starting graphite. The weight of the finely dispersed fraction in the decanted solution was determined by the same procedure. Thermal treatment of the oxidized graphite was performed in a muffle oven (900°C) using a graduated quartz glass. The bulk density of foam graphite ( $\rho_{fg}$ ) and the yield by carbon were calculated by the following formulas.

$$\rho_{\rm fg} = m_{\rm fg}/V_{\rm fg}.$$

Here  $m_{\rm fg}$  and  $V_{\rm fg}$  are the weight and volume of foam graphite, respectively.

Yield by carbon (%) = 
$$\Delta m(\%)(m_{fo}^{\prime}/m_{oo}^{\prime}) \times 100$$

Here  $m'_{og}$  is the weight of foamed oxidized graphite and  $m'_{fg}$ , weight of resulting foam graphite [6].

The  $H_2SO_4$  contents were determined using an AC-7932 express sulfur analyzer, and the specific surface areas were estimated by the method of nitrogen thermodesorption [12].

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