Reviews

Acceptor-type graphite intercalation compounds and new carbon materials based on them

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The problems of synthesis and study of the physicochemical properties of graphite intercalation compounds (GIC) formed upon insertion of various molecules into the interplanar space of graphite are considered. Binary and ternary intercalation compounds with protonic acids (HNO_3, CH_3COOH, H_3PO_4, H_2SO_4, *etc.*) are described. The results of systematic research into graphite intercalation by potentiometry, calorimetry, powder X-ray diffraction, conductivity measurements, DTA, chemical analysis, and other methods are given. These results underlie elucidation of the characteristic and peculiar features of acid insertion into graphite. The physicochemical properties and practical applications of GIC and low-density carbon materials are analyzed.

Key words: graphite intercalation compounds (GIC), binary GIC, ternary GIC, acids, exfoliated graphite.

Introduction

In recent years, considerable attention has been devoted to the synthesis and study of the physicochemical properties of graphite intercalation compounds (GIC), which have a regular layer structure, high anisotropy of physical properties, and an unusual type of bonding between the intercalated compounds and graphite. The carbon network almost does not change upon chemical transformations that accompany the insertion of substances of different nature in the graphite matrix, only the distances between them increasing substantially. This increase is determined by the properties of the incoming substances (intercalates), while intercalation proceeds under relatively mild conditions. The existence of compounds differing in the number of carbon atom layers between the two closest layers of the intercalate (stage number *n*) is the most general and typical feature of the GIC structure. The most saturated first-stage GIC contains the intercalate in all interlayer spaces of the graphite matrix.[1—4]

The scientific and applied interest in the GIC and their derivatives is due to the opportunities of targeted formation of properties for the materials based on them. For example, acceptor GIC with strong acids such as

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sulfuric or nitric acid are currently used in practice, because their subsequent treatment involving hydrolysis and thermolysis gives a new material, exfoliated graphite (EG). Owing to a number of unique properties, determined first of all by the nature of the intercalate and the structure of the initial GIC,[5,6] EG finds extensive use in industrial engineering.

Previously, the attention has been focused on the binary GIC containing only one intercalate in the graphite matrix. In recent decades, the range of intercalation compounds has markedly extended due to the achievements in the preparative chemistry and new investigation techniques. In particular, compounds with two different intercalates in the interplanar space have been investigated. These compounds form the class of ternary GIC (TGIC). Depending on the position of the intercalates, graphite co-intercalation compounds (intercalates are located in the same interlayer space) and bi-intercalation compounds (two intercalates occur in different interlayer spaces) are distinguished.[7]

Due to the diversity of the physical and chemical properties, the fundamental and applied research of TGIC can be carried out over a broader range than in the case of binary GIC. However, the data on their properties and preparation methods[8—10] are scarce, which restricts the scope of systematization of experimental facts and prediction of the properties of new compounds.

The published data[11—16] on the synthesis of TGIC with acids indicate that Brönsted acids are mainly used, for example, HNO_3 and H_2SO_4. Currently, less than ten TGIC of this type, synthesized mainly by the electrochemical method, are known.

This review considers the formation of intercalation compounds in two aspects. The first one includes the procedural, thermodynamic, and kinetic features of the synthesis of binary GIC, graphite hydrogensulfate and graphite nitrate, which serve as the initial matrices for the preparation of new TGIC. Then various methods for the introduction of the second intercalate into the prepared graphite matrix and the effect of the synthesis conditions on the processes in the graphite—acid A—acid B system are described. In addition, we analyze the results of our studies dealing with the properties of binary and ternary GIC with inorganic acids and consider the possible applications of the new carbon materials.

Synthesis and main features of intercalation of acids into graphite matrix

The data on the synthesis of binary GIC with acids published to date are summarized in Table 1. A necessary condition for the formation of GIC is the use of chemical oxidizing agents or anodic polarization of graphite in a solution of an appropriate acid. The feasibility and the degree of intercalation are largely determined by the acidic properties of the intercalate and by the conditions of oxidation of the graphite matrix. For example, strong inorganic acids (HNO_3, H_2SO_4, $HClO_4$) form highly saturated first-stage GIC. Weaker acids (H_3PO_4, $H_4P_2O_7$) are intercalated into graphite only upon long-term heating in the presence of an oxidant to give only second-stage GIC. Acids like CH_3COOH or H_3BO_3 are not intercalated into graphite at all.[1—3] In a number of publications,[4,5] it has been noted that the higher the degree of dissociation of the acid, the lower the threshold concentration for its insertion into the graphite matrix and the lower the redox potential for the formation of this GIC.

The chemical model of formation of GIC implies oxidation of the graphite matrix (C) conjugated with inser-

Table 1. Conditions and products of synthesis of binary GIC of various stages (n) in the graphite—acid systems

Acid	Dissociation constant, pK_a	Chemical synthesis		Electrochemical synthesis		Thickness of the filled layer, d_i/Å	References
		Reagents and conditions	n	Reagents	n		
$HClO_4$	−6.15	70% $HClO_4$ + CrO_3	II	72% $HClO_4$	I	7.94	17, 18
		~100% $HClO_4$	I				
H_2SeO_4	−3	CrO_3, 333 K	I	—	—	8.25	19
H_2SO_4	−2.80	$K_2Cr_2O_7$, $KMnO_4$	I	60—98% H_2SO_4	I	7.98	20—22
HNO_3	−1.64	85—98% HNO_3	II	75—98% HNO_3	I	7.84	23, 24
		98% HNO_3 + N_2O_5	I				
$H_4P_2O_7$	1.0	CrO_3, 343 K	II	—	—	8.19	25
H_3PO_4	2.12	100% H_3PO_4 + CrO_3, 353—373 K	II	—	—	8.03	19
$HReO_4$	—	—		65—70% $HReO_4$	III	—	18
CF_3COOH	0.56	99% CF_3COOH + $KMnO_4$	II	>99% CF_3COOH	I + II	—	26
HCOOH	3.75	—		—	III	—	27
CH_3COOH	4.76	No intercalation		—	—	—	19

tion of the intercalate (HA = HNO_3, H_2SO_4, $HClO_4$, H_3PO_4, $H_4P_2O_7$) in the presence of an oxidant (Ox).[2,3]

$$k\,C \xrightarrow{[Ox]} C_k^{\ +}, \qquad (1)$$

$$C_k^{\ +} + A^- + m\,HA \longrightarrow C_k^{\ +}A^-\cdot mHA. \qquad (2)$$

The electrical neutrality condition for GIC is met by insertion of solvated acid anions into the positively charged graphite matrix. The oxidant is required due to the low redox potentials of most of the inserted acids, which are unable to detach electrons from the graphite network themselves (except for concentrated nitric and perchloric acids). Nitric and perchloric acids function as both intercalates and oxidants, *i.e.*, they are spontaneously intercalated compounds.

It is noteworthy that for most GIC with acids, only the identity period (I_c) of the crystal structure along the trigonal axis c (see Refs 25, 26) is known:

$$I_c = d_i + (n-1)d_0, \qquad (3)$$

where d_i is the thickness of the layer filled by the intercalate, d_0 = 3.35 Å is the interplanar spacing in graphite, n is the stage number.

The GIC compositions were determined reliably only for graphite hydrogensulfate or bisulfate (GB) and graphite nitrate (GN): $C^+_{24n}HSO_4^-\cdot(2-2.5)H_2SO_4$ and $C^+_{24n}NO_3^-\cdot(2-3)HNO_3$,[19,28] which are described by the gross formulas $C_{(7-8)n}H_2SO_4$ and $C_{(6-8)n}HNO_3$. Substantial deviations from these formulas are possible, because GIC with acids have broad homogeneity regions and their composition depends on the method of synthesis.

Binary GIC with acids: graphite bisulfate and graphite nitrate

Most of publications dealing with the synthesis of binary GIC are devoted to electrochemical intercalation of graphite in H_2SO_4 solutions (see Ref. 29) and spontaneous gas-phase intercalation of fuming HNO_3 into graphite.[23] Unlike the widely used electrochemical synthesis of GB, the insertion of H_2SO_4 into graphite in the presence of a chemical oxidant has received much less attention. The intercalation of H_2SO_4 into graphite is initiated only by strong oxidizing agents: $K_2Cr_2O_7$, $(NH_4)_2S_2O_8$, HNO_3, CrO_3, $KMnO_4$, H_2O_2, PbO_2, and so on.[30–36] Studies aimed at elucidating the effect of the oxidant on the intercalation reaction are virtually missing. Therefore, in our opinion, elaboration of a criterion for predicting the probability of formation of a definite-stage GIC on the basis of known properties of the oxidizing solution is a fairly topical task.

The quantitative comparison of the two synthetic methods (chemical and electrochemical ones) carried out independently by our[37] and another[38] research groups demonstrated a common mechanism of graphite intercalation for chemical and electrochemical oxidation. The difference is only in the way of electron transfer from the graphite network. It was suggested that for ensuring the thermodynamic conditions for the synthesis of definite-stage GB, one must use sulfuric acid solutions of chemical oxidants whose redox potentials are correlated with the potentials needed for the formation of GIC of the same stage upon anodic oxidation.

We proposed using the scale of standard redox potentials[39,40] for the qualitative estimation of applicability of a particular oxidant for GB synthesis. For a series of chemical oxidants, the correspondence of the standard redox potentials of reagents to the stage numbers of graphite bisulfate formed in their presence was verified experimentally. First, the redox potentials of traditional oxidizing agents used for the synthesis of graphite bisulfate, namely, $K_2Cr_2O_7$ and $KMnO_4$, were measured in 94% sulfuric acid. The resulting values were compared with the potentials needed for the electrochemical synthesis of GB (see Ref. 29) and with the standard redox potentials $E°$ of the oxidants.[41] Second, the synthesis of GB with seldom used oxidants such as $(NH_4)_2S_2O_8$, H_2O_2 and Cl_2 was carried out.[30,35] Third, in conformity with the standard redox potentials, new oxidants that had not been used earlier for GB synthesis were proposed and tested; most of all, this refers to cerium(IV) and O_3 compounds.[34,42]

The experimental results showed the following:

— stage number of GB is determined by the redox potential of the oxidizing solution and the amount of the oxidizing agent added to the solution in strict correspondence with the reaction stoichiometry;

— role of the chemical and electrochemical oxidants in the GIC synthesis is the same;

— scale of standard redox potentials can be used for qualitative considerations when selecting the oxidant.

The results obtained were used to propose and apply potentiometry for predicting and monitoring the synthesis of GIC of a specified stage for the preparation of binary and ternary compounds.

It is known that the major difference between concentrated nitric and sulfuric acids is that the former acts as both an oxidizing agent and an intercalate in the reaction of graphite with the acid, and the latter is only an intercalate. The oxidative behavior of HNO_3 depends on its concentration. We found[43,44] a regular increase in the steady-state potential of HNO_3 following an increase in the concentration, in particular, $E_{Ag/AgCl}$ = 0.94 V (50% HNO_3) to $E_{Ag/AgCl}$ = 1.27 V (98% HNO_3) (Fig. 1).

It was expected[46] that spontaneous insertion of HNO_3 into graphite is impossible in solutions with HNO_3 concentration of <75% (region *A*) because of the lack of $NO_2^{\ +}$. When the HNO_3 concentration is >75%, the oxidizing properties of the solution are provided by the nitronium ion $NO_2^{\ +}$ and, probably depending on the ion

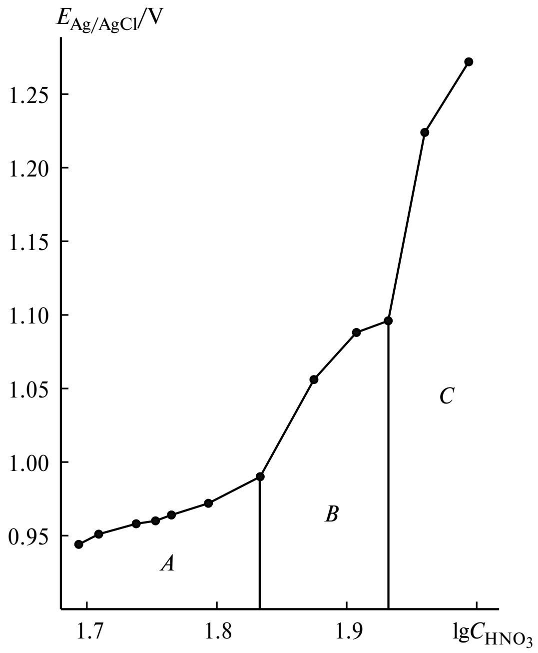

Fig. 1. Steady-state $E_{Ag/AgCl}$ potential of a 50—98% solution of HNO_3 *vs.* logarithm of the HNO_3 concentration.[45]

concentration, spontaneous formation of higher-stage (region *B*) and second-stage (region *C*) intercalation compounds is possible. Our assumptions were confirmed by experimental data (Table 2).[43,44,47—50]

It can be seen from Table 2 that the phase composition of the reaction products and the reaction rate depend appreciably on the acid concentration. As expected, the threshold concentration for the spontaneous intercalation of nitric acid was ~75%. At lower concentrations, no GN was formed.

The potentiometric measurements of the GN potential during intercalation showed for the first time that it corresponds to the solution redox potential, which, in turn, depends on the acid concentration. Thus,

— in the graphite—H_2SO_4—oxidant and graphite—HNO_3—H_2O systems, the redox potential of the solution correlates with the stage number of the GIC formed;

— in the graphite—acid systems, the GIC stage number depends not only on the oxidizing properties of the solution but also on the nature and the concentration of the acid;

— there exists a threshold concentration of the acid below which no GIC is formed.

Table 2. Conditions of synthesis and characteristics of graphite nitrate obtained by spontaneous HNO_3 intercalation into graphite[43,44,47—50]

C_{HNO_3} (%)	t/h	n	I_c/Å	$E_{Ag/AgCl}$/V	Δm (%)
98	0.2—0.5	II	11.19	1.27_2	50
95	0.6	II	11.25	1.26_6	49
90	0.8	II	11.26	1.22_0	50
85	1.0	II	11.27	1.10_5	50
83	1.0	III	14.66	1.09_5	33
80	1.5	IV	17.92	1.09_0	26
75	~10—50	V	21.56	1.06_1	20
≤71	720	Graphite	d_{002} = 3.37	—	—

As shown above, at 298 K, the chemical reaction of graphite with HNO_3 starts when the HNO_3 concentration is >75%. The oxidizing properties of nitric acid are adequate for the preparation of only second-stage GN.

The electrochemical oxidation of graphite in aqueous solutions of HNO_3 allows the synthesis of various-stage intercalation compounds, except for the first stage. A detailed study of the anodic oxidation of graphite in 50—98% HNO_3 has been carried out[44,45,50] with variation of the current intensity from 30 to 1500 μA. These data were used to define the concentration regions and the potentials of GN formation. Note that the threshold concentration for HNO_3 intercalation decreases to 55%. Unlike the electrochemical oxidation of graphite in sulfuric acid, low-current (30—100 μA) anodic polarization of graphite in nitric acid solutions does not result in the synthesis of the first-stage GIC.[45] Specific features of HNO_3 intercalation at concentrations of >75% during the galvanostatic oxidation of graphite were noted. It was found that oxidation of graphite (I = 30—100 μA) in 90—98% HNO_3 is not accompanied by a substantial increase in the GN potential (Fig. 2); hence, the formation of first-stage GN is impossible under these conditions. Apparently, in 90—98% HNO_3, the greatest contribution

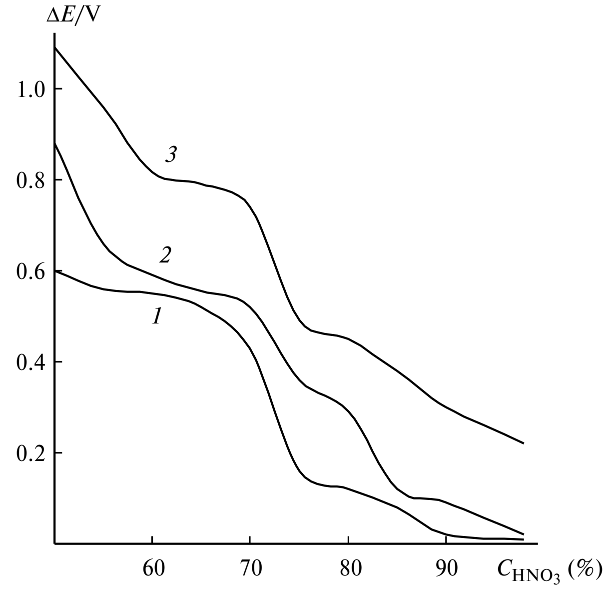

Fig. 2. Change in the limiting potentials of GN during galvanostatic oxidation *vs.* HNO_3 concentration for I = 30 (*1*), 100 μA (*2*), and 1.5 mA (*3*).[45]

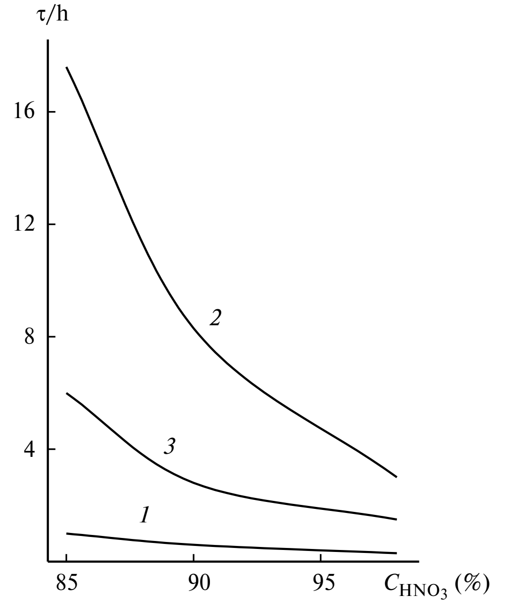

Fig. 3. Effect of the current load on the formation time of the second-stage GN: I = 0 (*1*), 30 (*2*), and 100 μA (*3*).[45]

to the formation of second-stage GN is due to spontaneous intercalation; conversely, anodic oxidation of graphite at low currents retards the process, which is manifested as a decrease in the reaction rate (Fig. 3). An experiment showed that an increase in the anodic current to 1.5 mA in 75—98% HNO_3 gives rise to a single-phase first-stage GN sample. In our opinion, during the electrochemical oxidation of graphite (current intensity >1.5 mA), the major contribution to intercalation over the whole range of HNO_3 concentrations is made by the electric current; in the HNO_3 concentration range of 75—98%, this allows overcoming the energy barrier to the formation of first-stage GN.

A typical dependence of the potential of HNO_3 intercalation on the quantity of electricity passed $E(Q)$ during the anodic polarization of graphite is shown in Fig. 4. In this case, the charging curves for the graphite—HNO_3 system acquire a typical stepwise pattern over the whole range of GIC formation, like those for the graphite—H_2SO_4 system. Apparently, the oxidative role of NO_2^+ is leveled under these conditions, because it is more prone to be reduced at the cathode than to oxidize graphite.

The first stage GN is formed upon anodic polarization of graphite (I = 1.5 mA) at the potentials $E_{Ag/AgCl}$ = 1.49 (98% HNO_3), 1.54 (80% HNO_3), and 1.55 V (75% HNO_3).

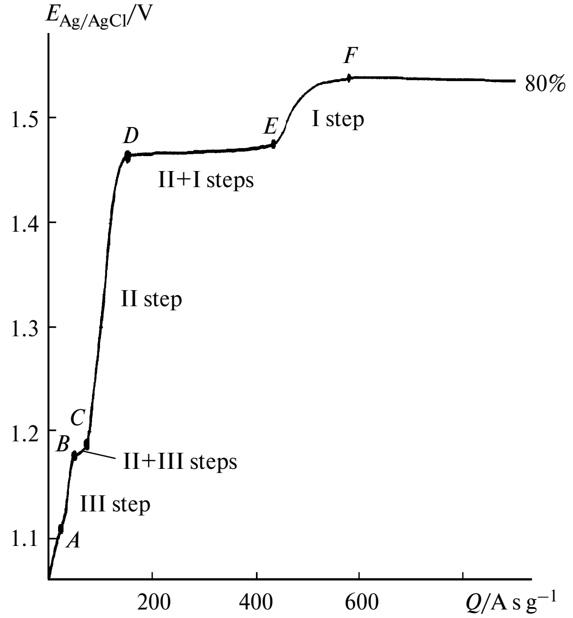

Fig. 4. Charging curve of a graphite sample in 80% HNO_3 (I = 1.5 mA).[49]

Thus, the studies revealed the fundamental distinctions between the electrochemical behaviors of reagents capable (HNO_3) and incapable (H_2SO_4) of spontaneous intercalation during the anodic polarization of graphite by low currents. For higher current loads (>500 μA), the behaviors of the C—HNO_3 and C—H_2SO_4 systems become identical.

A study of the electrochemical oxidation of natural graphite in solutions of 10—98% HNO_3 has shown[51,52] that irrespective of the current intensity and the duration of synthesis, the process in <55% solutions of HNO_3 gives only defect phases like graphite oxide, capable of foaming at low temperatures (423—473 K) to give EG with specific properties.

The set of obtained data indicates that the GIC properties in aqueous solutions of acids can be controlled, first of all, by changing the acid concentration and by other factors, which allow one to affect the mechanism of formation of intercalation compounds. In the region of highly concentrated solutions of acids, the GIC is formed according to the generally accepted electrochemical mechanism followed by re-oxidation of GIC. In the case of medium concentrations, simultaneous intercalation and hydrolysis are likely to occur. When the acid concentration is low, the role of water increases, and the structure or properties of the initial graphite do not change. During the chemical oxidation, the possibility of the synthesis is limited by the oxidizing properties of the reagents. However, if intercalate is an oxidant itself, the intercalation rate is rather high. If the oxidant only initiates the intercalation, the reaction, although slows down, becomes easily controllable, which allows one to prevent the undesirable side processes (GIC over-oxidation, hydrolysis, *etc.*). The electric current has markedly extended the resources of researchers in the synthesis GIC; with this tool, a broad range of compounds possessing unique properties have been prepared.

After discussing the regular features observed in the graphite—acid—H_2O system (water is not inserted in graphite[19]), we will consider other systems containing one more acid as the third component.

Ternary GIC with acids: study of interaction in the graphite—HNO_3—R systems (R = CH_3COOH, H_3PO_4, H_2SO_4)

Presumably, the rules observed in the formation of binary GIC with acids would also be valid for the synthesis of GIC in the graphite—HNO_3—reagent (R) ternary systems. The graphite—98% HNO_3 system studied previously in detail served as the basis system. The reagent R was represented by acids with different reactivities as regards intercalation into the graphite matrix: 96% H_2SO_4, 100% H_3PO_4, and glacial CH_3COOH.[53—55]

It was established by potentiometry that the $E_{Ag/AgCl}$ potential in 98% HNO_3—R solutions for R = H_2O, CH_3COOH, and H_3PO_4 is determined by the concentration of HNO_3: the potential regularly increases with an increase in the HNO_3 concentration (Fig. 5). The $E(C_{HNO_3})$ dependence for these systems is a broken line in which two main sections can be distinguished. By analogy with HNO_3—H_2O solutions, one can conclude that the right branches represent the concentration regions of spontaneous formation of GIC. It was confirmed experimentally that the boundary of GIC formation lies near the inflection point in the E *vs.* C_{HNO_3} dependence for each of these systems. In the HNO_3—H_2SO_4 system, the potential depends only slightly on the HNO_3 concentration, being equal to $E_{Ag/AgCl} = 1.4\pm0.1$ V. Probably, this is due to the formation of substantial amounts of NO_2^+, exceeding the content of the nitronium ion in fuming HNO_3 by a factor of several tens.[46]

It was found experimentally that only nitric acid is spontaneously intercalated into graphite in the HNO_3—CH_3COOH solution. Comparison of the obtained results with data for the graphite—HNO_3 system shows that the concentration range for the formation of intercalation compounds has markedly extended. The threshold concentration of HNO_3 intercalation in CH_3COOH solutions is at the inflection point (see Fig. 5). It is noteworthy that even by the electrochemical method, it proved impossible to insert acetic acid into graphite nitrate to give ternary GIC.[56—58]

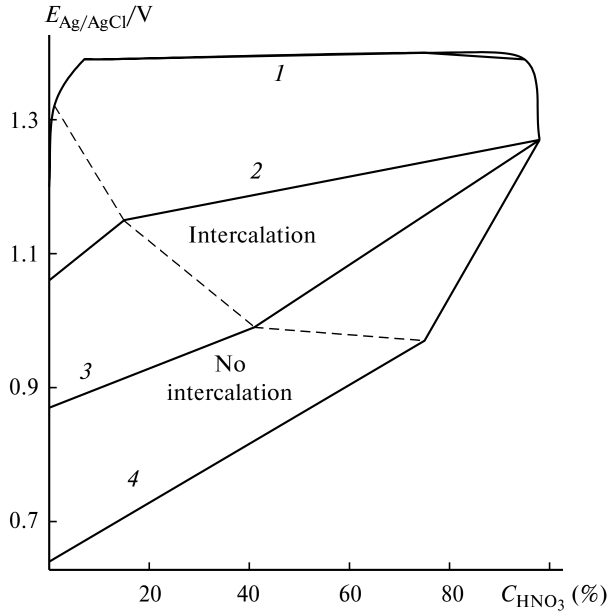

Fig. 5. Schematic concentration dependence of the redox potentials of HNO_3—R solutions: R = H_2SO_4 (*1*), H_3PO_4 (*2*), CH_3COOH (*3*), and H_2O (*4*).[53]

The results of spontaneous intercalation in the graphite—HNO_3—H_3PO_4 system at 313 K are summarized in Table 3. Second-stage TGIC with nitric and phosphoric acids have been synthesized.[59—65] An HNO_3 content of 28—44% is the best for the preparation of the TGIC with I_c = 11.55 Å. After chemical treatment of graphite in these solutions for 1—3 h, only the graphite nitrate phase was found by powder X-ray diffraction. Long-term (>30 h) keeping of samples in the reaction medium yields graphite co-intercalation compounds. Using the powder X-ray diffraction data, one can clearly follow the dynamics of formation of the second-stage GN and the appearance of the diffraction lines, indicating the formation of a new phase. The H_3PO_4 molecule has a larger effective size than

Table 3. Spontaneous intercalation in the graphite—HNO_3—H_3PO_4 system[53,59]

C_{HNO_3} (%)	n	I_c/Å	$E_{Ag/AgCl}$/V	Δm (%)	Phase composition
≥61	II	11.21—11.24	$>1.24_2$	49—53	GN
44	II + II*	11.22 + 11.55*	1.21_1	50—52	GN + TGIC
28	II*	11.55*	1.20_5	53	TGIC
21	III	14.53	1.17_3	35	GN
17	IV	18.03	1.15_0	28	GN
14	Graphite + V	d_{001} = 3.38, 21.49	1.14_3	5	Graphite + GN

* Refers to ternary GIC with HNO_3—H_3PO_4.

HNO_3; therefore, the thickness of the filled layer (d_i) of the new phase is ~0.3 Å greater than that in GN. According to the chemical and gravimetric analyses, the composition of the TGIC is given by $C_{5.6n}(HNO_3)_{0.75}(H_3PO_4)_{0.25}$. The transformation of GN into co-intercalation GIC occurs at an invariable potential. This transformation takes place only for the GN second stage, which is less stable than higher-stage compounds. Thus, spontaneous interaction in the $C—HNO_3—H_3PO_4$ system includes two steps: the formation of the GN and the subsequent partial exchange reaction between GN and phosphoric acid.

By using electrochemical synthesis, one can extend the concentration region (28—61% HNO_3) where the conditions for the formation of the first-stage TGIC are met. In this region, the first-step GN is formed initially during anodic oxidation, while subsequently, an increase in the sample potential $E_{Ag/AgCl}$ from 1.60 to 1.75 V gives rise to two first-stage phases: GN and the ternary GIC (Fig. 6). As the duration of synthesis increases, a single-phase ternary GIC sample appears. The initial formation of a binary GIC is followed by the simultaneous intercalation of two components. A similar mechanism of formation of a co-intercalation compound with the strong sulfuric and weak formic acids has been proposed in a publication.[66]

A study of a system involving two strong Brönsted acids (HNO_3 and H_2SO_4) has shown that, depending on the solution composition, spontaneous synthesis of either binary GIC (second-stage GN or first-stage GB) or the first-stage ternary compound is possible. As the H_2SO_4 content in the mixture increases, the d_i value and the overweight caused by the formation of ternary GIC (Δm) gradually increase. In our opinion, this is due to the fact that co-intercalation GIC have a variable composition, which is largely determined by the composition of the reaction mixture.[67,68]

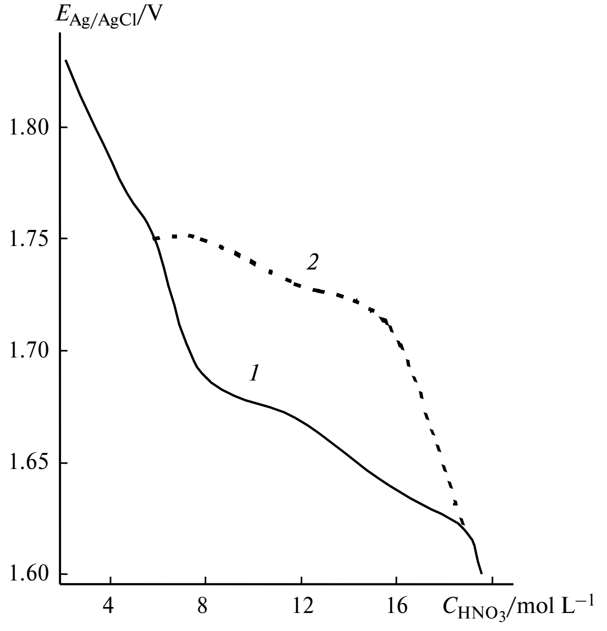

Fig. 6. Formation potentials of GN (*1*) and TGIC (*2*) *vs.* HNO_3 concentration in the $HNO_3—H_3PO_4$ solution.

It was shown that in both binary and ternary systems, the crucial role in the intercalation is played by the nature of the acid. During spontaneous intercalation, the GIC potential in all the systems studied strictly corresponded to the redox potential of the solution.

The results of investigation of the electrochemical behavior of graphite in the $H_2SO_4—CH_3COOH$ and $H_2SO_4—H_3PO_4$ electrolytes confirmed the influence of the nature of intercalates on the intercalation mechanism.[69—71] The anodic oxidation of highly oriented pyrolytic graphite in acetic acid solutions containing 60—80% H_2SO_4 affords ternary GIC. The electrochemical graphite intercalation in $H_2SO_4—[1-^{14}C]CH_3COOH$ solutions was first studied using radioactive tracers in combination with the autoradiography technique. A uniform distribution of the acetic acid radionuclide in the graphite sample was demonstrated. Thus, direct experimental evidence was obtained for the formation of a co-intercalation compound. This is consistent with the results of another study,[27] which suggested that the central bisulfate anion in the intercalate layer is surrounded by a mixed solvation shell formed by both H_2SO_4 and CH_3COOH.

In the graphite—$H_2SO_4—H_3PO_4$ system, we performed the first synthesis of co-intercalation GIC. In this case, two acids are intercalated simultaneously from the solution, the composition of the intercalated layer being determined by the H_2SO_4 to H_3PO_4 concentration ratio in the electrolyte. The thickness of the intercalated layer smoothly increases from the value typical of the bisulfate ion (d_i = 8.08 Å) to the value typical of the phosphate ion (d_i = 8.20 Å). The profile of the charge curves and the GIC stage number also depend on the solution composition: as the concentration of the active intercalate decreases (H_2SO_4), the stepwise pattern of the curves smoothes down.

Study of formation of intercalation compounds by potentiometry and calorimetry

Using potentiometric and calorimetric measurements, the process dynamics can be studied quickly and reliably, the time of GIC formation, the potentials of particular stages, and the corresponding reaction heats can be determined, and the differences between the behaviors of systems containing reagents either capable or incapable of spontaneous intercalation into the graphite lattice can be revealed. This section covers the studies in which potentiometric and calorimetric measurements were used to study the intercalation dynamics in binary and ternary

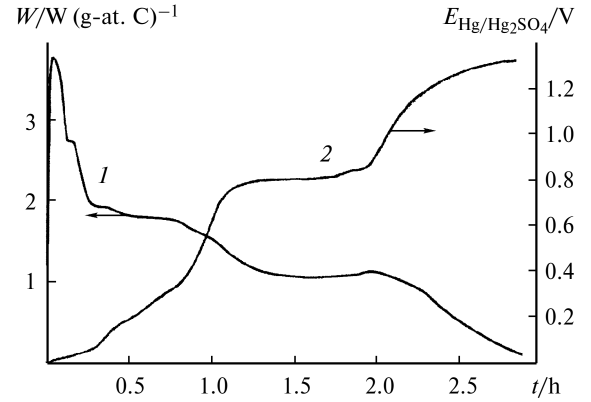

Fig. 7. Time dependences of the heat flow *W*(*t*) (*1*) and potential of the formation of graphite hydrogensulfate *E*(*t*) (*2*) in the graphite—96% H_2SO_4—$K_2Cr_2O_7$ system.[45]

systems. The time dependence of the heat flow *W*(*t*) for the formation of GB in the presence of an oxidizing agent and the time dependence of the GB potential *E*(*t*), observed *in situ* (graphite—H_2SO_4—$K_2Cr_2O_7$ system)[72—74] are shown in Fig. 7. Similar curves were recorded for the graphite—H_2SO_4—$KMnO_4$ system. As can be seen from Fig 7, the time dependences of the heat flow *W*(*t*) and the GIC potential are stepwise. According to powder X-ray diffraction, the plateaus in the *W*(*t*) and *E*(*t*) dependences correspond to the formation of a mixed-stage GIC, while the slopes describe the single-phase stages. Attention is attracted by the fact that the breaks in the heat flow curve and in the potentiometric curve are in good agreement with each other. A similar stepwise pattern of the curves was observed for the anodic oxidation of graphite in a H_2SO_4 solution.[29]

Thus, it was first demonstrated convincingly that the formation of GB upon the chemical (using $K_2Cr_2O_7$ or $KMnO_4$) and electrochemical oxidation involves consecutive transformation of higher stages into lower ones, which confirms the domain model of the GIC.

Typical time dependences of the heat flow *W*(*t*) and the potential *E*(*t*) observed during graphite interaction with concentrated solutions of HNO_3 are shown in Fig. 8. The potential can be seen first to increase monotonically and then to reach a plateau, indicating the end of the intercalation reaction. Other characteristics of the intercalation, reflecting the course of the reaction involving a spontaneously intercalating reagent (HNO_3), for example, the time variation of the GIC weight[23,24] and the descending branch of the heat flow curve (*W*(*t*)), are monotonic. Probably, the monotonic pattern of the curves is characteristic of graphite reactions with spontaneously intercalating compounds. A similar course of the heat flow curve has been found[35,40] for the graphite—oleum system in which oleum also functions as a spontaneously intercalating reagent.

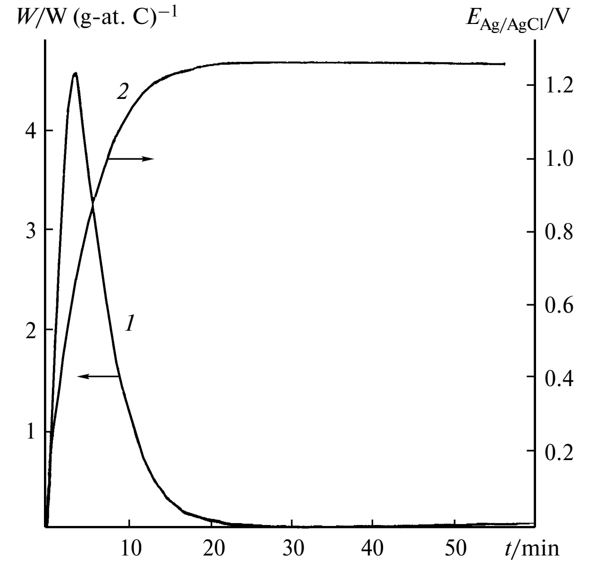

Fig. 8. Variation of *W*(*t*) (*1*) and *E*(*t*) (*2*) during spontaneous intercalation of 98% HNO_3 into graphite.

Similar *E*(*t*) and *W*(*t*) patterns are typical of the spontaneous graphite intercalation with HNO_3—R solutions. In the region of highly concentrated solutions of HNO_3, the potential increases monotonically and then reaches a plateau.

The potentials of the formation of like GN steps in HNO_3—R solutions increase in the series H_2O, CH_3COOH, and H_3PO_4 (Fig. 9). Thus, the higher the acidity of the reagent R, the milder the conditions for GIC formation.

As HNO_3 is being diluted with the reagent R, the pattern of the *E*(*t*) curves changes, which is indicative of a change in the intercalation mechanism. In the HNO_3—R systems containing sulfuric or phosphoric acid, the potentiometric curves acquire a stepwise form typical of systems with an acid incapable of spontaneous intercalation; in this particular case, these are H_2SO_4 or H_3PO_4. As their content in the HNO_3—R solution increases, the stepwise pattern of the potentiometric curves may be indicative of intercalation of these acids, together with HNO_3, into the graphite matrix. The content of nitric acid in the mixed solution has a pronounced influence not only on the pattern of *E*(*t*) dependences for the spontaneous intercalation but also on the charging curves. Typical *W*(*t*) plots for the graphite—HNO_3—CH_3COOH system are shown in Fig. 10. Powder X-ray diffraction analysis of samples formed after completion of the exothermic effect showed the presence of only GN in the graphite—HNO_3—CH_3COOH and graphite—HNO_3—H_3PO_4 systems. Thus, the shape of the curves and the phase composition of the reaction products are indicative of insertion of only nitric acid. In HNO_3—H_3PO_4 solutions (27—44% HNO_3), a second exothermic effect is

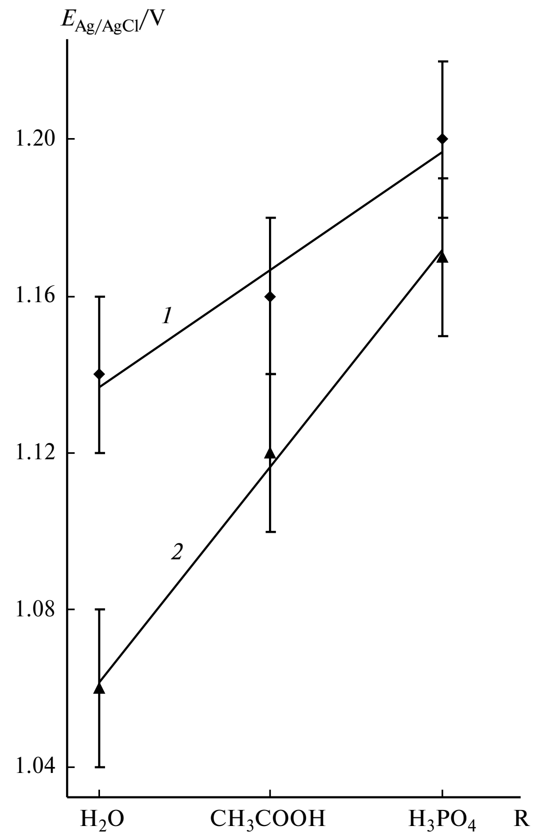

Fig. 9. Minimum potentials of the formation of the second (*1*) and third stages (*2*) of GIC in the C—HNO_3—R systems on the reagent R.

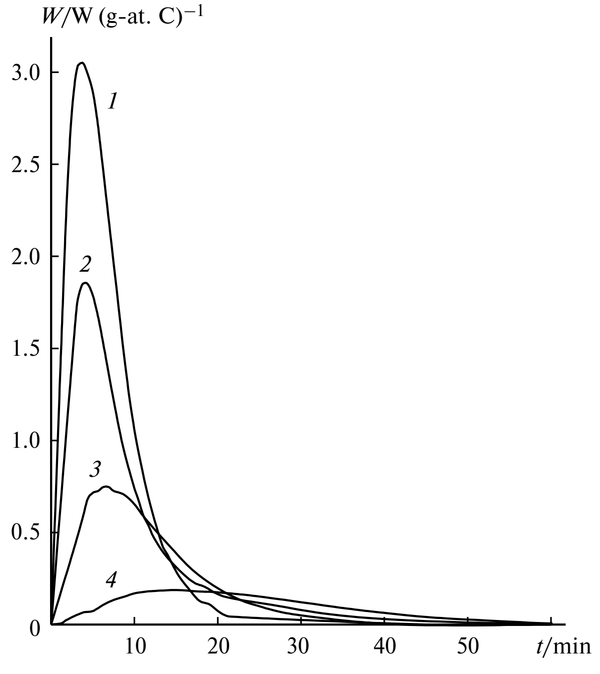

Fig. 10. Heat flow curves in the graphite—HNO_3—CH_3COOH system for different contents of the active intercalate HNO_3: 84 (*1*), 73 (*2*), 67 (*3*), and 58% (*4*).[45]

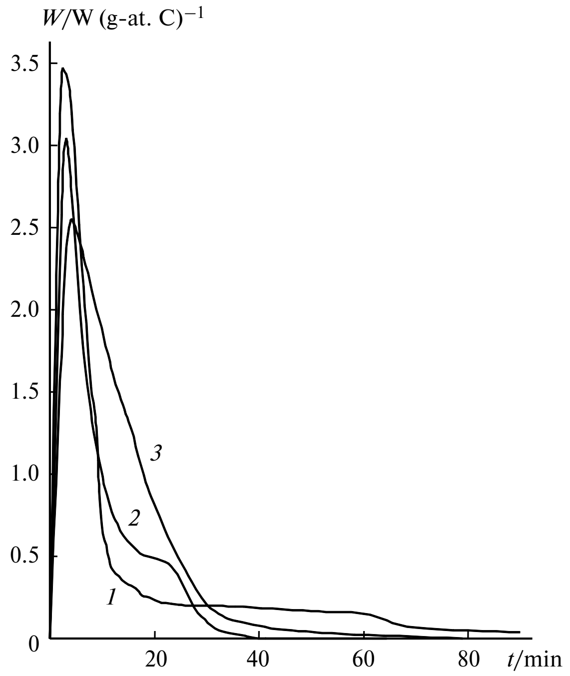

Fig. 11. Heat flow *vs.* time for the C—HNO_3—H_2SO_4 system for a HNO_3 : H_2SO_4 ratio in solution of 10 : 1 (*1*), 1 : 1 (*2*), and 1 : 10 (*3*).

observed after long-term (4—5 h) keeping of the samples; the heat flow curve does not reach a baseline. This is apparently due to the partial exchange reaction between HNO_3 and H_3PO_4 after the formation of the second-stage GN.

It was found that the formation of the first-stage TGIC in the C—HNO_3—H_2SO_4 system is described by different heat flow curves $W(t)$ (Fig. 11) and potentiometric curves $E(t)$ (Fig. 12), depending on the composition of the oxidative solution. This is due to specific features of the intercalation reactions in HNO_3—H_2SO_4 systems and to the formation of TGIC with variable composition.

The generalized data on the phase composition of the reaction products in the C—HNO_3—R systems are shown in Fig. 13.

Physicochemical properties of intercalation compounds

For GIC with acids, the thickness of the filled layer d_i lies in the 8.0±0.3 Å range, being determined by the effective diameter of the intercalate molecule. In addition, d_i may slightly vary depending on the method of synthesis of the GIC. For example, the use of different oxidants for graphite treatment in sulfuric acid gives rise to a GB with 7.94—8.10 Å-thick filled layer. The gross composition of the GIC and the composition of the C_p^+ cation may vary depending on the synthesis conditions. Relying on the results of gravimetry and iodo-

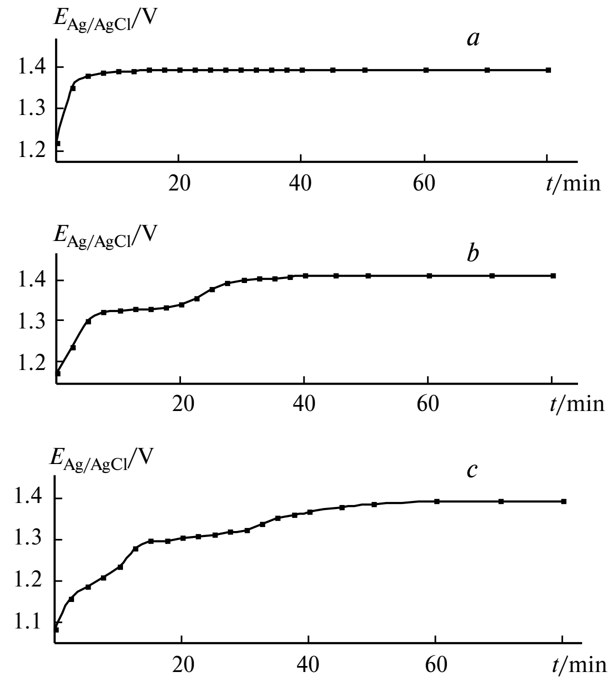

Fig. 12. Potentiometric dependences in the graphite—H_2SO_4—HNO_3 system for a $HNO_3 : H_2SO_4$ ratio in solution of 10 : 1 (*a*), 1 : 1 (*b*), and 1 : 10 (*c*).

Table 4. Thickness of the intercalated layer of GIC (d_i)[53]

System	Composition	d_i/Å
$C—H_2SO_4$	$C_{(7.3—7.8)n}H_2SO_4$	$7.95_6—8.10_5$
$C—HNO_3$	$C_{(5.3—5.6)n}HNO_3$	$7.94_2—7.98_6$
$C—HNO_3—H_2SO_4$	—*	$7.98_1—8.03_3$
$C—HNO_3—H_3PO_4$	—*	8.20_4
$C—H_2SO_4—CH_3COOH$	—*	7.94_0
$C—H_2SO_4—H_3PO_4$	—*	$8.08_2—8.23_2$

* Co-intercalation compound of variable composition.

metric titration, the composition of the GB is described as $C_{(7—8)n}H_2SO_4$ and the macrocation composition for the first stage is $C^+{}_{17—23}$. A similar behavior of these characteristics was noted for other GIC (Table 4).[30,45,55,59,67,71,72]

The physicochemical properties of the above-indicated intercalation compounds have been studied.[75—80] A number of characteristics, namely, the overweight (Δm), the identity period (I_c), the enthalpies of formation (ΔH_f) and decomposition (ΔH_{decomp}), the conductivity along the *a* axis, the degree of expansion on heating, and the temperature of the onset of thermal decomposition were found[75—80] to be determined by the GIC stage number.

The thermochemical data for graphite intercalation with acid are virtually missing from the literature; only the enthalpies for intercalation of sulfuric acid in graphite (ΔH_f) in the graphite—H_2SO_4—oxidant systems were measured. The ΔH_f values for the first and second stages depend little on the nature of the oxidant, being equal to -2.25 or -2.80 kJ (g-at. C)$^{-1}$ for the second stage and -3.67 or -4.00 kJ (g-at. C)$^{-1}$ for the first stage for $K_2Cr_2O_7$ and $KMnO_4$, respectively. The slight differences between the values for the same stage are due to different oxidizing properties of the oxidants and possible side processes.[73] The interaction energy of the intercalate with the graphite matrix is insignificant in both binary and ternary intercalation compounds. Experimental data obtained for intercalation reactions in the $C—HNO_3—R$ systems are summarized in Table 5. The enthalpies of formation of the second-stage graphite nitrate in 98—85% HNO_3 are $-(1.1—1.7)$ kJ (g-at. C)$^{-1}$. Some differences between the ΔH_f values for the formation of the

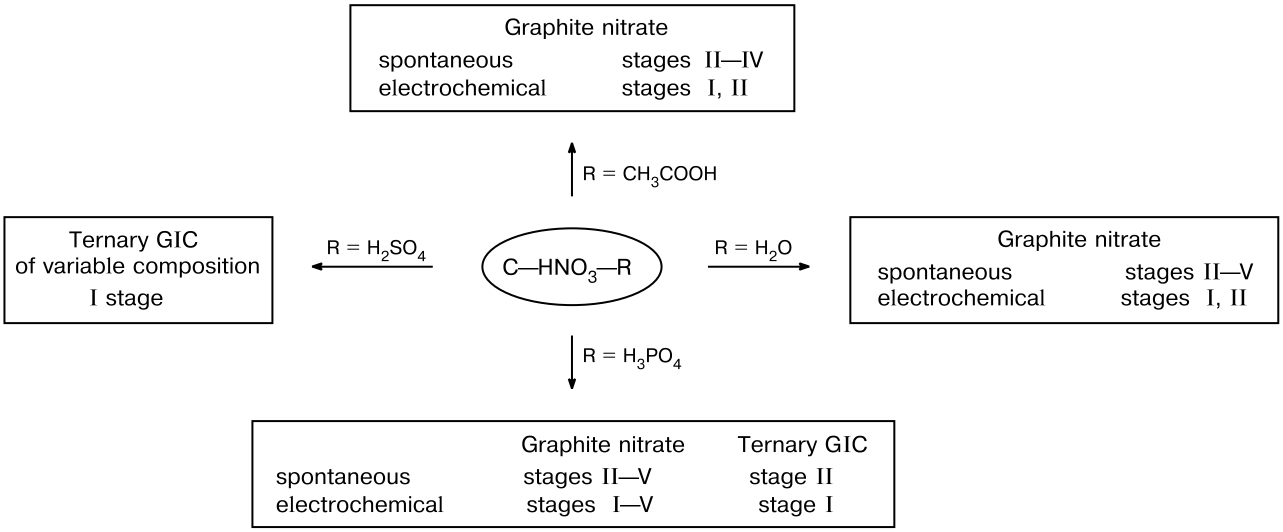

Fig. 13. Key results of investigations of graphite—HNO_3—R systems.

Table 5. Enthalpy of interaction in the C—HNO_3—R systems for R = H_2O, CH_3COOH, H_3PO_4, H_2SO_4

n	$-\Delta H$/kJ (g-at. C)$^{-1}$			
	H_2O	CH_3COOH	H_3PO_4	H_2SO_4
I	—	—	—	1.7_1—1.9_4
II	1.1_2—1.7_5	1.1_0—1.4_2	1.5_3—1.8_3	—
III	0.6_3	0.6_0	0.7_1	—
IV	0.4_0	0.3_2	—	—

second stage upon to the change in the acid concentration (85—98%) are, apparently, due to the different degrees of oxidation of the graphite matrix in GN.[72—77]

The enthalpies of formation of the GN in the C—HNO_3—CH_3COOH and C—HNO_3—H_3PO_4 systems are similar to the ΔH for the intercalation in the basis system, as the exothermic effect corresponds in all cases to the formation of the same compound, graphite nitrate (see Table 5). The ΔH values in the C—HNO_3—R systems depend on the stage number of the GIC, and within the same stage, on the HNO_3 concentration in the solution. For the C—HNO_3—H_2SO_4 system, the values for the enthalpy of formation of ternary GIC were found to vary insignificantly (–(1.7—1.9) kJ (g-at. C)$^{-1}$) over the whole range of the HNO_3 : H_2SO_4 ratios studied. The magnitudes of ΔH are relatively small for all the systems, which attests to the van der Waals character of the interaction between the intercalated layer and the graphite matrix, regardless of the intercalate nature.

Thus, a correlation was established between the intercalation enthalpy and the stage number of the graphite intercalation compounds. As for other intercalation compounds, the heat of the reaction per g-atom of C increases in magnitude following a decrease in the stage number.

Owing to weak interaction of the intercalate with the graphite matrix, the studied GIC are relatively unstable. Whereas the preceding sections were focused on the intercalation of acids into graphite, here we consider de-intercalation of GIC, which can be accomplished efficiently by at least two methods. On heating, GIC decompose to give exfoliated graphite, while hydrolysis affords so-called oxidized graphite (OG) as the final product.

Thermal analysis of the first-to-fourth stage GB and GN in the temperature range of 373—1073 K was carried out. It was shown that graphite intensively decomposes at 573—673 K, the thermal stability of GIC increasing with an increase in the stage number. The behavior of GB at low temperatures was studied; this revealed a number of features, including the dependence of the temperature and the enthalpy of a phase transition such as two-dimensional melting on the stage number. The obtained ΔH_{decomp} values (expressed per g-mol of H_2SO_4) confirm the following rule: the highest energy of the interaction between sulfuric acid and the graphite matrix is observed for higher stages.[81—84]

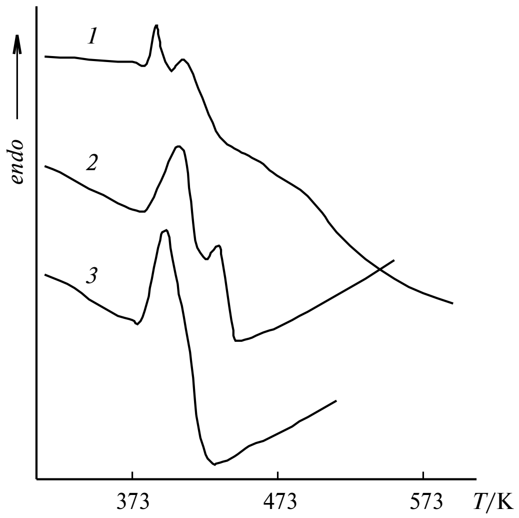

Fig. 14. Thermograms of stages II in the GIC—HNO_3—H_3PO_4 system (*1*) and acetic acid-modified (*2*) and initial GN (*3*).

Detailed investigation[82] of the thermal decomposition of GN has also confirmed the increase in the stability of intercalation compounds on passing from the first to the fourth stage. Typical thermograms of the second-stage co-intercalation GIC and graphite nitrate are shown in Fig. 14. For the binary GIC with HNO_3, only one endothermic effect was observed, which corresponds to complete de-intercalation of nitric acid. Modification of GN with acetic acid gives rise to an additional endothermic effect, which is less pronounced for higher stage numbers. In addition, this increases the temperature of the onset of decomposition, *i.e.*, the sample is stabilized on treatment with CH_3COOH. The ternary GIC with HNO_3—H_3PO_4 displays a complex pattern of thermolysis: several effects corresponding to partial de-intercalation are observed in the 293—573 K range. This is due to the fact that H_3PO_4 decomposes at higher temperature and hampers the departure of HNO_3 from the graphite matrix.

For all GIC, the temperature of the onset of decomposition T_0 and the enthalpy ΔH_{decomp} per mole of intercalate increases with an increase in the stage number; this is due to the increase in the compound stability on passing from lower to higher stages and is a general feature of GIC (Table 6).

In view of the fact that hydrolysis is a necessary intermediate reaction in the synthesis of EG, we studied the stability of GIC in water by X-ray diffraction. Hydrolysis is accompanied by destruction of GIC and de-intercalation to give the adduct (OG), which is used in the manufacture of new carbon materials. It is surprising that at a substantial weight increase (up to 30%), the OG structure retains planar, although defective hexagonal carbon net-

Table 6. Thermal properties of GIC*

n	Graphite nitrate		Modified GN		Ternary GIC with HNO_3—H_3PO_4	
	T_0/K	ΔH_{decomp}/kJ (g-at. C)$^{-1}$	T_0/K	ΔH_{decomp}/kJ (g-at. C)$^{-1}$	T_0/K	ΔH_{decomp}/kJ (g-at. C)$^{-1}$
II	373	2.5	378, 418	1.3	383, 403, 433	0.8
III	377	1.9	388, 418	0.7	410, 443	0.7
IV	391	0.9	398	0.6	—	—

* The accuracy of determination of the temperature of the onset of decomposition T_0 and enthalpy ΔH_{decomp} was ±2° and ±5%, respectively.

works with an interplanar spacing[85,86] of 3.37—3.42 Å. During hydrolysis, the intercalate molecules diffuse from the graphite lattice and anions exchange with hydroxy groups. In addition, during hydrolysis, oxygen-containing groups are formed on the graphite surface. The OG contains also some adsorbed acid, which is kept rather firmly on the defects of the graphite matrix.

The solvolysis of second-to-fourth stage GN in R = CH_3COOH, H_3PO_4, H_2SO_4 has been studied. A specific feature of the behavior of GN in glacial acetic acid is an increase in the stage number of the compound from n to $n + 1$. The degradation rate of GN in acetic acid mainly depends on the number of stage. The thickness of the intercalated GN remains virtually the same after treatment with glacial acetic acid, and the overweight Δm of the resulting GIC is at the level of Δm for the GN of the same stage,[65] although it tends to decrease. The preliminary chemical treatment of GN with acetic acid has a substantial effect on the properties of the products obtained upon subsequent hydrolysis. This is apparently due to stabilization of the intercalation compound and partial substitution of CH_3COOH for HNO_3 in the solvation shell of the central anion.

The reaction of GN with anhydrous H_3PO_4 permitted the first preparation of ternary second-to-fourth stage intercalation compounds. The numbers of stages for the TGIC and the initial GN coincide, while d_i for the TGIC exceeds this value for GN by ~0.3 Å. Thus, solvolysis of GN with phosphoric acid yields TGIC, the mechanism of its formation being consistent with that proposed for co-intercalation GIC in the graphite—HNO_3—H_3PO_4 system.

The reaction of H_2SO_4 with second-to-fourth stage graphite nitrate results in the first-stage GIC. It is quite likely that process starts with the exchange reaction in which H_2SO_4 displaces nitric acid from the interlayer space. Simultaneously, the acids react in the layer to give NO_2^+ and the graphite matrix is further oxidized. Finally, the reaction gives the first-stage graphite hydrogensulfate with a substantial overweight due to the acid adsorption on structure defects.[68]

In conclusion, it should be noted that the interaction in the GN—R system follows three pathways, resulting in graphite bisulfate (R = H_2SO_4), second-to-fourth stage TGIC with HNO_3—H_3PO_4 (R = H_3PO_4) and, apparently, modified GN (R = CH_3COOH). The subsequent hydrolysis of these intercalation compounds affords OG (Fig. 15), which shows high stability, a substantial degree of expansion, and the ability to foam up in a given temperature range (Fig. 16) to give a foam-like material, EG (Fig. 17). The methods proposed for the synthesis of oxidized graphites permit subtle adjustment of the residual content of the acid in the final product, which is highly important for practice. For example, the content of the corrosive agent, sulfur, in OG varies in parallel with the stage number of the initial GN and is much lower than this parameter for the bisulfate OG. The high residual content of sulfuric acid in the OG imparts fire protection properties to this material. The variation of the nature and the specific consumption of the second intercalate opens up extensive opportunities for the controlled synthesis of GIC based on graphite nitrate.

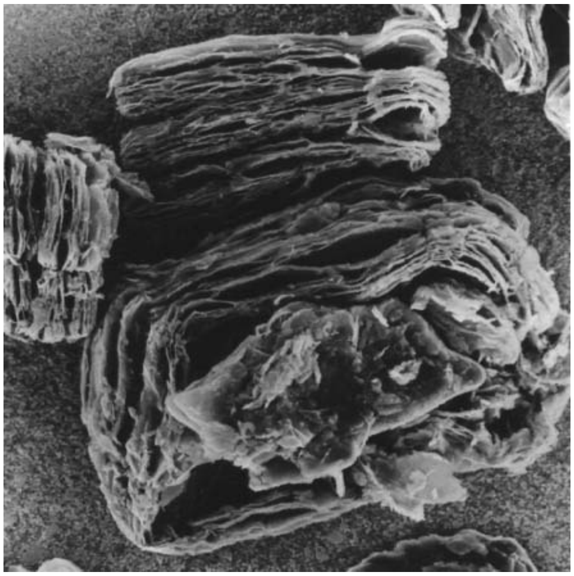

Fig. 15. Microstructure of oxidized graphite.

A comprehensive study[87—91] of the intercalation by calorimetry, potentiometry, powder X-ray diffraction, *etc.*, allowed the researchers to select the optimal conditions

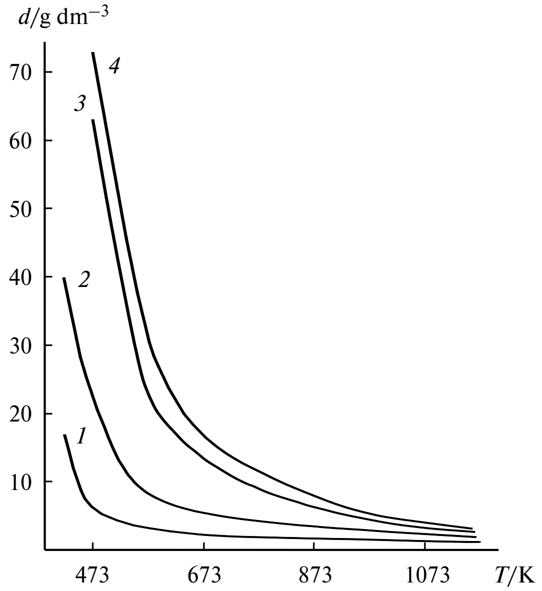

Fig. 16. Temperature dependence of the bulk density of exfoliated graphites (*d*) obtained in the GN—R systems with R = CH_3COOH (*1*), H_3PO_4 (*2*), H_2SO_4 (*3*), and H_2O (*4*).

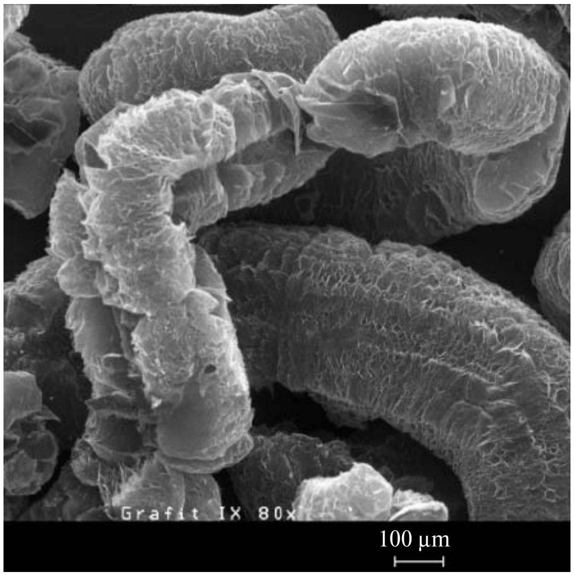

Fig. 17. Microstructure of exfoliated graphite.

for the synthesis of perfect quasi-single crystals of GIC for which the quantum oscillator effects were observed for the first time (*viz.*, the Shubnikov—de Haas effect, the Hall effect, the temperature dependence of the resistance). The data of the oscillatory effects were used to determine the topological features of the Fermi surface and to calculate the Dingle temperature, the concentration of delocalized holes, the effective weights of charge carriers, the free path, and the relaxation time. It is demonstrated that the high electrical conductivity of acceptor-type GIC is due to the increase in the concentration of free charge carriers and the decrease in the electron—phonon interaction with respect to that in graphite.

More detailed information on the physicochemical properties of the compounds can be found in original publications.[78—91]

Applications of GIC-based carbon materials

Some sorts of natural and artificial graphites and other carbon materials and composites based on them have been long used rather extensively in the ferrous and non-ferrous metallurgy, nuclear power engineering, aerospace engineering, electronics, and chemical engineering.[92,93] In recent years, considerable attention has been devoted to the application of GIC in various branches of industry, science, and engineering as components of electrode materials for fuel cells. It should also be noted that GIC can be used for the production of infrared polarizers, monochromators for low-energy neutrons, optical filters adjusted to a specified wavelength, electrochemical devices in optical displays, and in heat-protection systems. Of considerable interest for practical purposes is thermoexfoliated graphite or EG obtained by thermal destruction of either acceptor-type GIC or OG. Owing to a number of unique properties (low density, large specific surface area, pressability without a binding agent, resistance against corrosive media, low heat conductivity, *etc.*), EG could find application in various fields of industrial engineering (Fig. 18).

The dependences of the physicochemical properties of EG and OG on the sort of the initial graphite (natural, pyrolytic, or kish graphite), the fractional composition of graphite, conditions of GIC synthesis, the stage number, the GIC chemical composition, the type of the oxidizing agent, and the morphology of EG particles were elucidated (Figs 19—21). The physicochemical properties of graphite foil (compressibility, restorability, Young´s modulus, specific conductivity, heat conductivity, *etc.*) were studied as functions of the preparation conditions of GIC, the fractional composition of the initial natural graphite, the temperature mode of foaming of the GIC hydrolysis products (Figs 22—25). This made it possible to choose the best conditions for the synthesis of sealing materials with specified properties and to issue recommendations for the design of an industrial process for their manufacture.

In order to develop a new generation of sealing materials, a comprehensive study of all stages of the preparation of low-density carbon materials was carried out.

Graphite foam underlies the production of new structural materials (graphite foil, plaited sealing cord, reinforced graphite sheet, *etc.*), which retain all properties

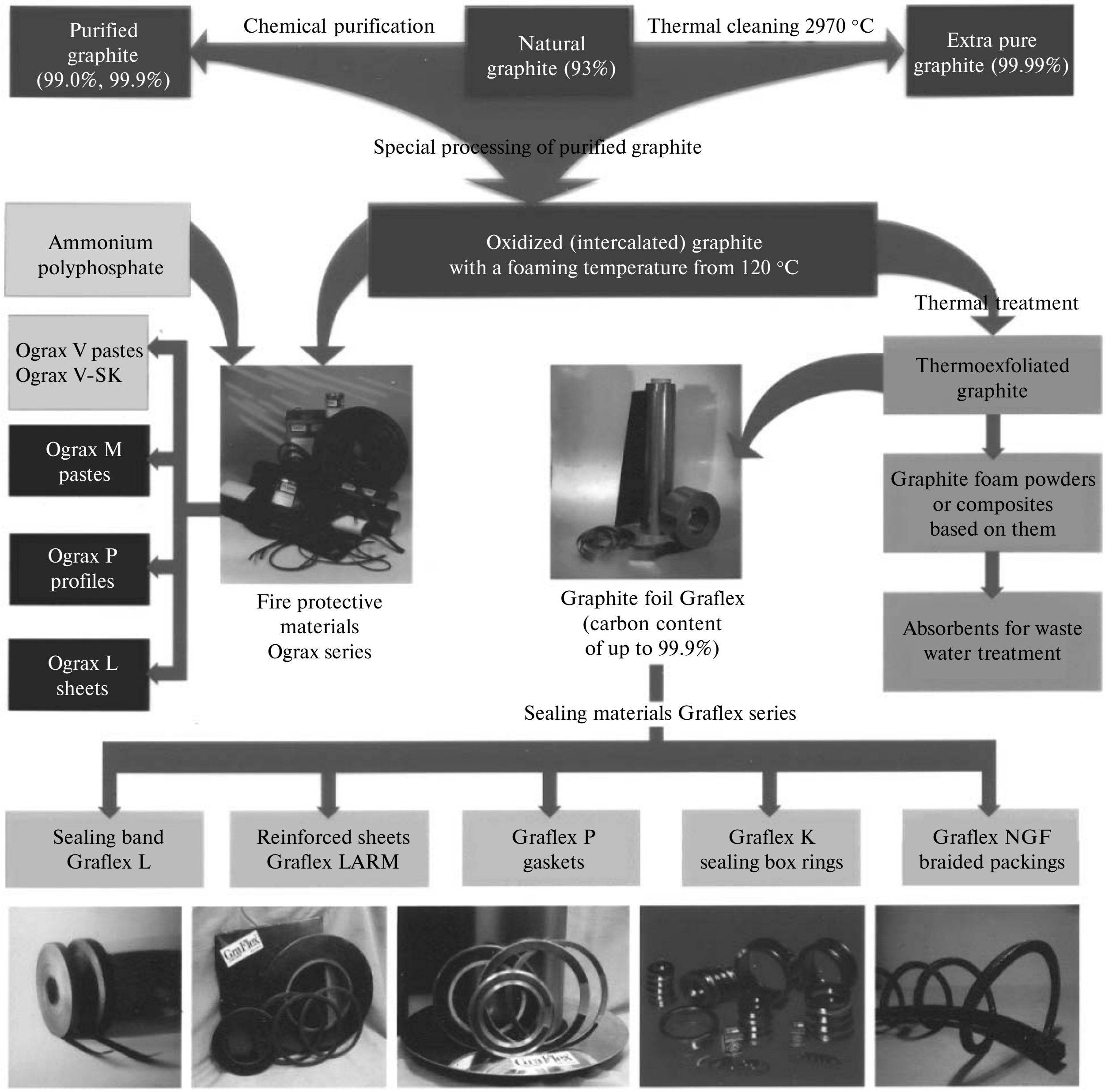

Fig. 18. Sealing and fire protective materials based on graphite.

inherent in graphite and also have new consumer properties absent in graphite or other carbon materials, *i.e.*, elasticity and plasticity.

The use of materials based on graphite foil (unique sealing material as regards the whole set of operation properties) at the fuel-and-power and mechanical engineering plants and refineries would contribute to the leak tightness and reliability of connections and process equipment, reduction of the amount of hazardous emissions; this would sharply decrease the loss of energy carriers and eliminate the use of carcinogenic asbestos materials prohibited in almost all developed countries of the world. Moreover, GIC are widely used for the design of thermally expanding fire-protective materials. Under flame, these materials sharply (several-tenfold) increase their bulk and form layers of foam with a low thermal conductivity and high thermal stability. This foam covers the surfaces to be protected, fills the holes and chinks, which results in isolation of the seat of fire. High efficiency of thermally expandable materials is due to the fact that fire protection requires application of coatings with a thickness of only several tenths of mm to several mm, which are converted under the action of fire into several cm-thick foam layers. We developed a number of thermally expandable fire-protective materials: pastes and flexible materials meant for the protection of electrical and communication cables,

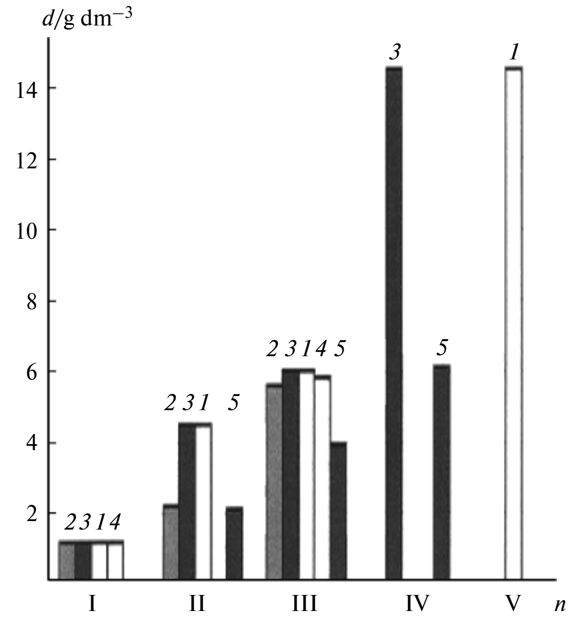

Fig. 19. Bulk density (*d*) of foam graphite *vs.* stage number (*n*) of the initial graphite bisulfate prepared electrochemically (*1*) and using oxidizing agents: $K_2Cr_2O_7$ (*2*), oleum (*3*), $KMnO_4$ (*4*), and HNO_3 (*5*).

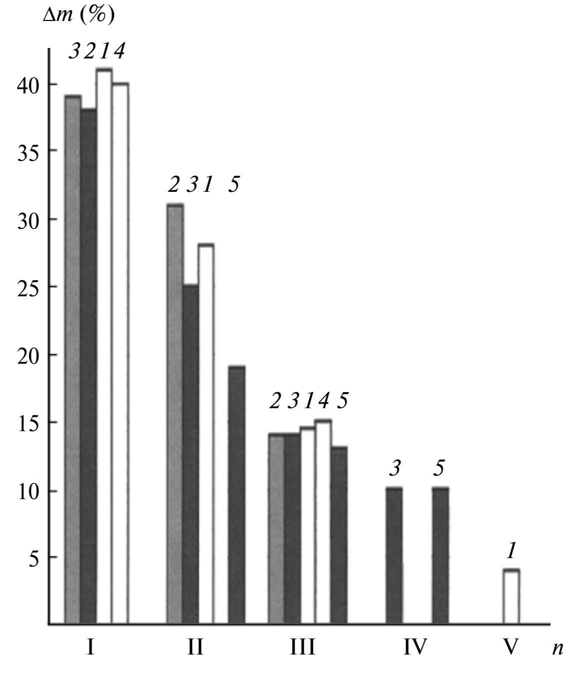

Fig. 20. Weight increment (Δm) of the oxidized graphite *vs.* stage number (*n*) of the initial graphite bisulfate obtained electrochemically (*1*) and using oxidizing agents: $K_2Cr_2O_7$ (*2*), oleum (*3*), $KMnO_4$ (*4*), and HNO_3 (*5*).

metallic and wooden building units, and polymeric materials.

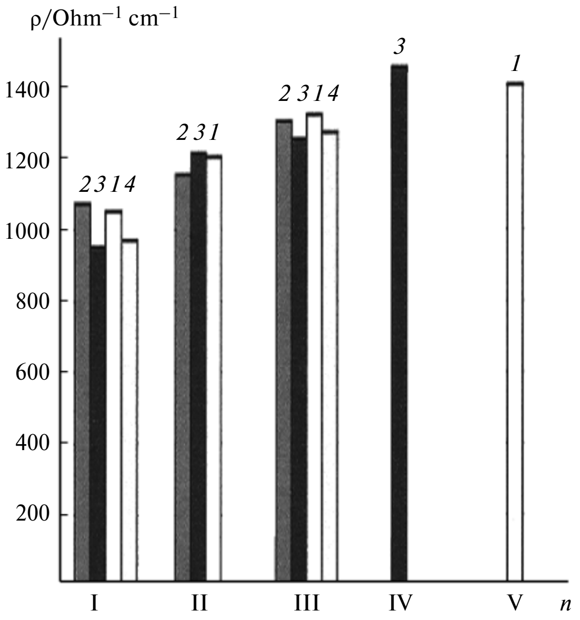

Fig. 21. Electrical resistivity (ρ) of graphite foil *vs.* stage number (*n*) of the initial graphite bisulfate prepared electrochemically (*1*) and using oxidants: $K_2Cr_2O_7$ (*2*), oleum (*3*), $KMnO_4$ (*4*), and HNO_3 (*5*).

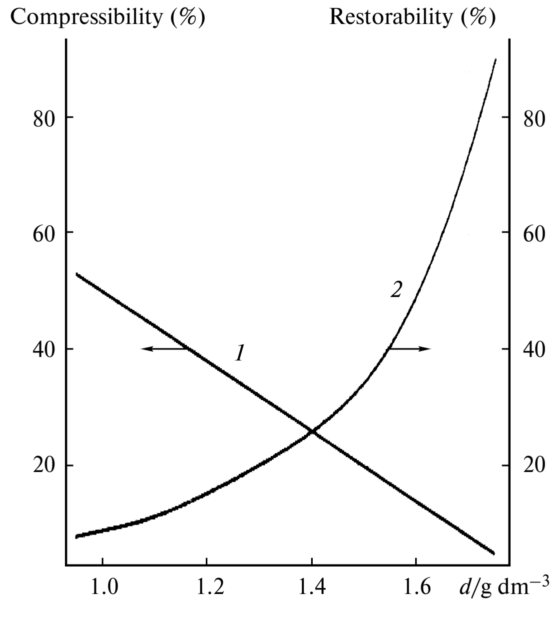

Fig. 22. Compressibility (*1*) and restorability (*2*) of graphite foil *vs.* density (*d*).

As regards the environmental safety, a topical problem is water purification from black product, oils, other organic compounds, and heavy metals. Owing to the highly developed specific surface area (50—250 m^2 g^{-1}), low density (1—10 kg m^{-3}), the microporous structure, and the ability to form composites with a broad range of substances, EG has a high absorption capacity with respect to petroleum products and other hydrophobic organic compounds such as oils, fats, toluene, xylene, chlorinated

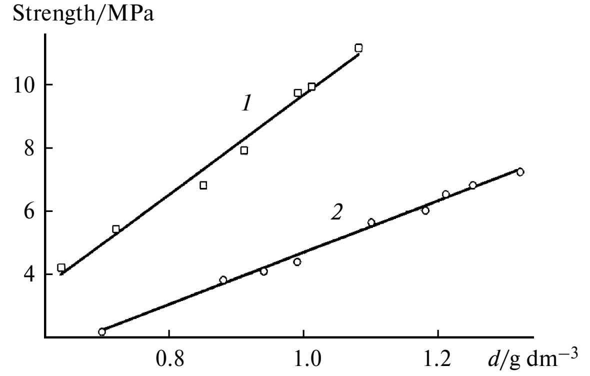

Fig. 23. Strength of graphite foil produced from graphite bisulfate (*1*) and graphite nitrate (*2*) *vs.* density.

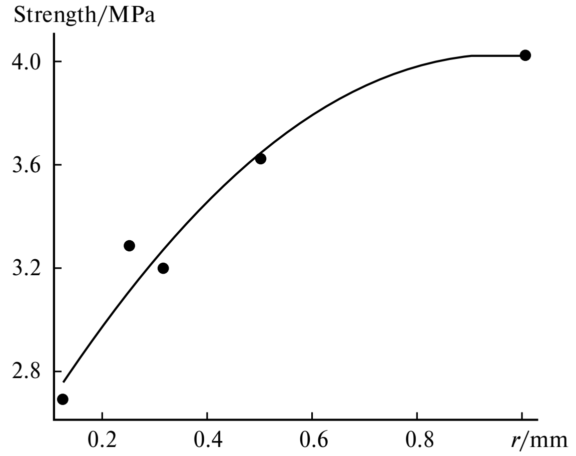

Fig. 24. Strength of graphite foil *vs.* graphite particle size (*r*).

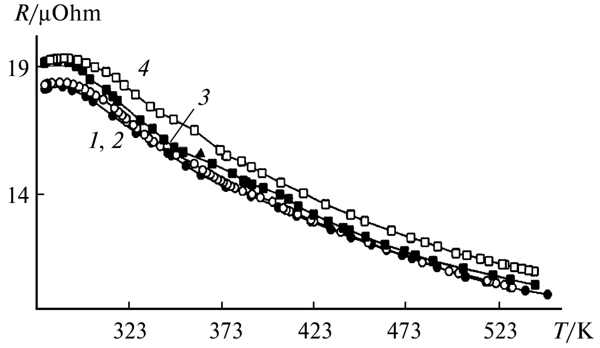

Fig. 25. Temperature dependence of the electrical resistance (*R*) of graphite foil for oxidized graphite particles with sizes of 1 (*1*) and 0.5 mm (*2*), mixture of all fractions (*3*), and 0.125 mm particles (*4*).

phenols, dichlorodiphenyltrichloromethylmethane, *etc.* (1 g of EG can absorb up to 80 g of organic compounds). An advantage of EG over the conventional sorbents is low consumtion and high regeneration ability. Light and hydrophobic EG can float on the surface of water for tens of hours and, after absorption of petroleum products, for several days. Graphite foam is able to clean water both from the surface and from the bulk.

The functional characteristics of GIC-based materials are largely determined by the properties of initial GIC. Convenient and effective methods for the preparation of graphite hydrogensulfate in the graphite—H_2SO_4—oxidant system and an electrochemical synthesis based on the use of suspension electrodes have been proposed. A new in principle class of electrochemical reactors providing continuous synthesis of GIC has been developed.[94—105] From the economic and environmental standpoints, of great significance in the manufacture of graphite intercalation compounds with acids is the specific consumption of the intercalate in the GIC synthesis. We proposed methods of synthesis in which the consumption of protonic acids has decreased 2—4-fold.

A highly important problem is the development and perfection of the process of production of GIC with controlled foaming temperature, bulk density, and specific surface area. These materials are meant for the production of fire protective and low-density carbon materials. For solving this problem, a process for the manufacture of modified OG in the graphite—nitric acid—R system, where R = CH_3COOH, H_3PO_4, H_2SO_4, has been developed.

The practical use of GIC is far from being exhausted by the above-described fields. They can be used to design flexible and bulk heating elements, protective screens from heat and electromagnetic radiations, thermal insulators, antifriction oil additives, carbon—carbon composite materials, low-density structural high-temperature heat-insulating materials for aerospace engineering, *etc.*

It is beyond doubt that further research into the synthesis and physicochemical properties of GIC and low-density carbon materials based on them would extend the fields of application of these unique materials.

References

1. A. Herold, *Les Carbons par le Groupe Francais d´Etude des Carbons*, Masson et C^{ie}, Paris, 1965, **11**, 356.
2. U. Rudorff, *Adv. Inorg. Chem. Radiochem.*, 1959, **1**, 223.
3. A. Herold, *NATO ASY, Ser. B*, 1987, **172**, 3.
4. A. Herold, G. Furdin, D. Guerard, L. Hachim, N. Nadi, and R. Vangelisti, *Ann. Phys.*, 1986, **11**, 3.
5. I. G. Chernysh, I. I. Karpov, V. P. Prikhod´ko, and V. M. Shai, *Fiziko-khimicheskie svoistva grafita i ego soedinenii* (*Physicochemical Properties of Graphite and its Compounds*) Naukova dumka, Kiev, 1990, 215 pp. (in Russian)
6. F. Kang, X.-P. Zheng, H.-N. Wang, Y. Nish, and M. Inagaki, *Carbon*, 2002, **40**, 1575.
7. S. Solin, *NATO ASY, Ser. B*, 1986, **148**, 291.
8. M. Noel and R. Santhanam, *J. Power Sources*, 1998, **72**, 53.
9. P. Scharff, E. Stumpp, and C. Erhardt, *Synth. Met.*, 1988, **23**, 415.

10. M. S. Dresselhaus and G. Dresselhaus, *Synth. Met.*, 1985, **12**, 79.
11. A. P. Yaroshenko and M. V. Savos´kin, *Zh. Prikl. Khim.*, 1995, **68**, 1302 [*Russ. J. Appl. Chem.*, 1995, **68** (Engl. Transl.)].
12. H. Shioyama, K. Tatsumi, and R. Fujii, *Carbon*, 1990, **28**, 119.
13. P. Scharff, *Materials Science Forum*, 1992, **91—93**, 23.
14. J. M. Skowronski and H. Shioyama, *Carbon*, 1995, **33**, 1473.
15. H. Shioyama and R. Fujii, *Carbon*, 1989, **27**, 785.
16. P. Scharff and E. Stumpp, *Ber. Bunsenges. Phys. Chem.*, 1991, **95**, 58.
17. H. Shioyama, *Synth. Met.*, 2000, **114**, 1.
18. P. Scharff, *Z. Naturforsch., Teil B*, 1989, **44**, 772.
19. W. Rudorff and U. Hofmann, *Z. Anorg. Allg. Chem.*, 1938, **238**, 1.
20. I. G. Chernysh and I. D. Buraya, *Khim. Tverd. Topliva* (*Solid Fuel Chemistry*), 1990, **1**, 123 (in Russian).
21. T. V. Komarova, E. V. Puzyreva, and S. V. Puchkov, *Tr. MKhTI im. D. I. Mendeleeva* (*Proc. Russ. Inst. Chem. Technol.*), 1986, **141**, 75 (in Russian).
22. K. E. Carr, *Carbon*, 1970, **8**, 153.
23. N. S. Forsman, F. L. Vogel, D. E. Carl, and J. Hofman, *Carbon*, 1978, **16**, 269.
24. H. Fuzellier, J. Melin, and A. Herold, *Mater. Sci. Eng.*, 1977, **31**, 91.
25. W. Rudorff, *Z. Phys. Chem.*, 1939, **45**, 42.
26. W. Rudorff and W.-F. Siecke, *Chem. Ber.*, 1958, **91**, 1348.
27. F. Kang, T.-Y. Zhang, and Y. Leng, *Carbon*, 1997, **35**, 1167.
28. H. Selig and L. B. Ebert, *Adv. Inorg. Chem. Radiochem.*, 1980, **23**, 281.
29. F. Beck, J. Jiang, and H. Krohn, *J. Electroanal. Chem.*, 1995, **389**, 161.
30. I. V. Nikol´skaya, N. E. Fadeeva, K. N. Semenenko, V. V. Avdeev, and L. A. Monyakina, *Zh. Obshch. Khim.*, 1989, **59**, 2653 [*J. Gen. Chem. USSR*, 1989, **59** (Engl. Transl.)].
31. V. V. Avdeev, I. U. Martynov, I. V. Nikol´skaya, L. A. Monyakina, and N. E. Sorokina, *Proc. 8th Intern. Symp. on Intercalation Compounds (Vancouvere, 1995)*, Vancouvere, 1995, 53.
32. L. A. Monyakina, V. V. Avdeev, I. V. Nikol´skaya, and N. E. Fadeeva, *Shkola-seminar po khimii poverkhnosti dispersnykh tverdykh tel (Slavsk, 1989)* [*School Seminar on the Chemistry of the Surface of Disperse Solids (Slavsk, 1989)*], Abstrs, Slavsk, 1989, 102.
33. V. V. Avdeev, I. U. Martynov, I. V. Nikol´skaya, L. A. Monyakina, and N. E. Sorokina, *J. Phys. Chem. Solids*, 1996, **57**, 837.
34. T. S. Lazareva, G. I. Emel´yanova, N. E. Sorokina, I. V. Nikol´skaya, and V. V. Avdeev, *Vestn. MGU, Ser. 2. Khimiya*, 1996, **37**, 343 [*Vestn. Mosk. Univ., Ser. Khim.*, 1996, **37** (Engl. Transl.)].
35. V. V. Avdeev, N. E. Sorokina, I. Yu. Martynov, L. A. Monyakina, and I. V. Nikol´skaya, *Neorgan. Materialy*, 1997, **33**, 694 [*Inorg. Mater.*, 1997, **33** (Engl. Transl.)].
36. V. V. Avdeev, L. A. Monyakina, I. V. Nikol´skaya, N. E. Sorokina, K. N. Semenenko, and A. I. Finaenov, *Carbon*, 1992, **30**, 825.
37. V. V. Avdeev, L. A. Monyakina, I. V. Nikol´skaya, N. E. Sorokina, and K. N. Semenenko, *Carbon*, 1992, **30**, 819.
38. M. Inagaki, N. Iwashita, and E. Kouno, *Carbon*, 1990, **28**, 49.
39. N. E. Fadeeva, K. N. Semenenko, I. V. Nikol´skaya, and L. A. Monyakina, *II Vsesoyuz. shkola po fizike i khimii rykhlykh i sloistykh kristallicheskikh struktur (Kharkov, 1988)* [*II All-Union School on the Physics and Chem. of Loose and Layered Crystalline Structures (Kharkov, 1988)*], Abstrs, Kharkov, 1988, 109 (in Russian).
40. V. V. Avdeev, L. A. Monyakina, I. Yu. Martynov, I. V. Nikol´skaya, and N. E. Sorokina, *Vestn. MGU, Ser. 2. Khimiya*, 1997, **38**, 123 [*Vestn. Mosk. Univ., Ser. Khim.*, 1997, **38** (Engl. Transl.)].
41. Ya. I. Tur´yan, *Okislitel´no-vosstanovitel´nye reaktsii i potentialy v analiticheskoi khimii* [*Redox Reactions and Potentials in Analytical Chemistry*], Khimiya, Moscow, 1989, 158 pp. (in Russian).
42. L. A. Monyakina, I. V. Nikolskaya, V. V. Avdeev, and N. E. Sorokina, *Proc. 20th Biennial Conf. on Carbon (Santa-Barbara, 1991)*, Santa-Barbara, 1991, 76.
43. V. V. Avdeev, O. A. Tverezovskaya, and N. E. Sorokina, *Proc. 10th Intern. Symp. on Intercalation Compounds ISIC 10 (Okazaki, 1999)*, Okazaki, 1999, 72.
44. V. V. Avdeev, O. A. Tverezovskaya, N. E. Sorokina, I. V. Nikol´skaya, and A. I. Finaenov, *Neorgan. Materialy*, 2000, **36**, 276 [*Inorg. Mater.*, 2000, **36**, 214 (Engl. Transl.)].
45. N. E. Sorokina, L. A. Monyakina, N. V. Maksimova, I. V. Nikol´skaya, and V. V. Avdeev, *Neorgan. Materialy*, 2002, **38**, 589 [*Inorg. Mater.*, 2002, **38** (Engl. Transl.)].
46. E. Yu. Orlova, *Khimiya i tekhnologiya brizantnykh vzryvchatykh veshchestv* [*Chemistry and Technology of High Explosive Agents*], Khimiya, Leningrad, 1973, 179 pp. (in Russian).
47. V. V. Avdeev, N. E. Sorokina, O. A. Tverezovskaya, A. A. Serdan, and A. I. Finaenov, *Neorgan. Materialy*, 1999, **35**, 435 [*Inorg. Mater.*, 1999, **35**, 348 (Engl. Transl.)].
48. V. V. Avdeev, N. E. Sorokina, O. A. Tverezovskaya, I. Yu. Martynov, and A. V. Sezemin, *Vestn. MGU, Ser. 2. Khimiya*, 1999, **40**, 422 [*Vestn. Mosk. Univ., Ser. Khim.*, 1999, **40** (Engl. Transl.)].
49. N. E. Sorokina, O. A. Tverezovskaya, A. A. Serdan, and Yu. G. Kryazhev, *V Mezhdunar. nauchno-prakt. konf. "Uglerodnye materialy" (Novokuznetsk, 1998)* [*V Int. Scientific and Practical Conf. "Carbon Materials" (Novokuznetsk, 1998)*], Abstrs, Novokuznetsk, 1998, 4 (in Russian).
50. V. V. Avdeev, O. A. Tverezovskaya, and N. E. Sorokina, *Mol. Cryst. Liq. Cryst.*, 2000, **340**, 137.
51. N. E. Sorokina, N. V. Maksimova, and V. V. Avdeev, *Neorgan. Materialy*, 2001, **37**, 441 [*Inorg. Mater.*, 2001, **37**, 360 (Engl. Transl.)].
52. N. E. Sorokina, N. V. Maksimova, and V. V. Avdeev, *Book of Abstr. of VII Intern. Frumkin Symposium (Moscow, 2000)*, Moscow, 2000, 387.
53. N. E. Sorokina, N. V. Maksimova, and V. V. Avdeev, *Neorgan. materialy*, 2002, **38**, 687 [*Inorg. Mater.*, 2002, **38**, 564 (Engl. Transl.)].
54. N. E. Sorokina, V. V. Avdeev, and N. V. Maksimova, *Proc. 11th Intern. Symp. on Intercalation Compounds (Moscow, 2001)*, Moscow, 2001, 109.
55. V. V. Avdeev, N. E. Sorokina, N. V. Maksimova, I. Yu. Martynov, and A. V. Sezemin, *Neorgan. materialy*, 2001, **37**, 448 [*Inorg. Mater.*, 2001, **37**, 366 (Engl. Transl.)].

56. V. V. Avdeev, O. A. Tverezovskaya, N. E. Sorokina, L. A. Monyakina, and I. V. Nikol´skaya, *Proc. 10th Intern. Symp. on Intercalation Compounds ISIC 10 (Okazaki, 1999)*, Okazaki, 1999, 71.
57. N. E. Sorokina, S. N. Mudretsova, A. F. Maiorova, N. V. Maksimova, and A. I. Medovoi, *V Mezhdunar. konf. "Kristally: rost, svoistva, real´naya struktura, primenenie" (Aleksandrov, 2001)* [*V Int. Conf. "Crystals: Growth, Properties, Real Structure, Applications" (Aleksandrov, 2001)*], Proc., Aleksandrov, 2001, **2**, 412 (in Russian).
58. N. E. Sorokina, S. N. Mudretsova, A. F. Maiorova, N. V. Maksimova, and A. I. Medovoi, *V Mezhdunar. konf. "Kristally: rost, svoistva, real´naya struktura, primenenie" (Aleksandrov, 2001)* [*V Int. Conf. "Crystals: Growth, Properties, Real Structure, Applications" (Aleksandrov, 2001)*], Abstrs, Aleksandrov, 2001, 75.
59. N. E. Sorokina, N. V. Maksimova, A. V. Nikitin, O. N. Shornikova, and V. V. Avdeev, *Neorgan. Materialy*, 2001, **37**, 697 [*Inorg. Mater.*, 2001, **37**, 584 (Engl. Transl.)].
60. N. E. Sorokina, N. V. Maksimova, V. V. Avdeev, A. A. Khudoshin, and A. I. Medovoi, *V Mezhdunar. konf. "Kristally: rost, svoistva, real´naya struktura, primenenie" (Aleksandrov, 2001)* [*V Int. Conf. "Crystals: Growth, Properties, Real Structure, Applications" (Aleksandrov, 2001)*], Abstrs, Aleksandrov, 2001, 74 (in Russian).
61. V. V. Avdeev, N. E. Sorokina, N. V. Maksimova, A. V. Nikitin, and O. N. Shornikova, *Proc. 11th Intern. Symp. on Intercalation Compounds (Moscow, 2001)*, Moscow, 2001, 108.
62. N. E. Sorokina, N. V. Maksimova, V. V. Avdeev, A. A. Khudoshin, and A. I. Medovoi, *V Mezhdunar. konf. "Kristally: rost, svoistva, real´naya struktura, primenenie" (Aleksandrov, 2001)* [*V Int. Conf. "Crystals: Growth, Properties, Real Structure, Applications" (Aleksandrov, 2001)*], Proc., Aleksandrov, 2001, **2**, 417.
63. N. V. Maksimova, N. E. Sorokina, O. N. Shornikova, and V. V. Avdeev, *Proc. 12th Intern. Symp. on Intercalation Compounds (Poznan, 2002)*, Poznan, 2002, 93.
64. N. V. Maksimova, A. V. Nikitin, and N. E. Sorokina, *V Mezhdunar. konf. "Fundamental´nye problemy Elektrokhimicheskoi energetiki" (Saratov, 2002)* [*V Int. Conf. "Fundamental Problems of Electrochemical Power Engineering" (Saratov, 2002)*], Abstrs, Saratov, 2002, 102 (in Russian).
65. V. V. Avdeev, O. A. Tverezovskaya, N. E. Sorokina, L. A. Monyakina, and I. V. Nikolskaya, *Mol. Cryst. Liq. Cryst.*, 2000, **340**, 131.
66. E. Bourelle and A. Metrot, *Proc. Intern. Symp. on Carbon (Tokyo, 1998*), Tokyo, 1998, 108.
67. V. V. Avdeev, N. E. Sorokina, I. V. Nikol´skaya, I. Yu. Martynov, and L. A. Monyakina, *Neorgan. Materialy*, 1997, **33**, 699 [*Inorg. Mater.*, 1997, **33** (Engl. Transl.)].
68. L. A. Monyakina, N. E. Sorokina, V. V. Avdeev, I. V. Nikolskaya, and N. V. Maksimova, *Proc. 11th Intern. Symp. on Intercalation Compounds (Moscow, 2001)*, Moscow, 2001, 107.
69. V. S. Leshin, A. V. Dunaev, and N. E. Sorkina, *V Mezhdunar. konf. "Fundamental´nye problemy Elektrokhimicheskoi energetiki" (Saratov, 2002)* [*V Int. Conf. "Fundamental Problems of Electrochemical Power Engineering" (Saratov, 2002)*], Abstrs, Saratov, 2002, 91 (in Ruissian).
70. V. S. Leshin, N. E. Sorokina, and V. V. Avdeev, *1-aya Mezhdunar. konf. "Uglerod: fundamental´nye problemy nauki, materialovedenie, tekhnologiya" (Moscow, 2002)* [*1-st Int. Conf. "Carbon: Fundamental Problems of Science, Materials Science, and Technology (Moscow, 2002)*], Abstrs, Moscow, 2002, 128 (in Russian).
71. V. S. Leshin, N. E. Sorokina, and V. V. Avdeev, *1-aya Mezhdunar. konf. "Uglerod: fundamental´nye problemy nauki, materialovedenie, tekhnologiya" (Moscow, 2002)* [*1-st Int. Conf. "Carbon: Fundamental Problems of Science, Materials Science, and Technology (Moscow, 2002*)], Abstrs, Moscow, 2002, 129 (in Russian).
72. L. A. Monyakina, N. E. Fadeeva, and I. V. Nikol´skaya, *II Vsesoyuz. shkola po fizike i khimii rykhlykh i sloistykh kristallicheskikh struktur (Kharkov, 1988)* [*II All-Union School in the Physics and Chemistry of Loose and Layered Crystalline Structures (Kharkov, 1988)*], Abstrs, Kharkov, 1988, 70 (in Russian).
73. V. V. Avdeev, L. A. Monyakina, I. V. Nikol´skaya, A. Yu. Litvinenko, and N. E. Fadeeva, *Izv. Akad. Nauk SSSR. Neorgan. materialy*, 1990, **26**, 760 [*Inorg. Mater.*, 1990, **26** (Engl. Transl.)].
74. L. A. Monyakina, N. E. Sorokina, and I. V. Nikol´skaya, *I Vsesoyuz. konf. po fizike i khimii soedinenii vnedreniya (Rostov-on-Don, 1990)* [*I All-Union Conf. on the Physics and Chemistry of Intercalation Compounds (Rostov-on-Don, 1990)*], Abstrs, Rostov-on-Don, 1990, 24 (in Russian).
75. V. V. Avdeev, L. A. Monyakina, and I. V. Nikolskaya, *Carbon*, 1994, **32**, 541.
76. L. A. Monyakina, V. V. Avdeev, I. V. Nikol´skaya, and S. G. Ionov, *Zhurn. Fiz. Khim.*, 1995, **69**, 926 [*Russ. J. Phys. Chem.*, 1995, **69** (Engl. Transl.)].
77. L. A. Monyakina, N. V. Maksimova, N. E. Sorokina, I. V. Nikol´skaya, and V. V. Avdeev, *1-aya Mezhdunar. konf. "Uglerod: fundamental´nye problemy nauki, materialovedenie, tekhnologiya" (Moscow, 2002)* [*1-st Int. Conf. "Carbon: Fundamental Problems of Science, Materials Science, and Technology (Moscow, 2002*)], Abstrs, Moscow, 2002, 146 (in Russian).
78. S. G. Ionov, V. V. Avdeev, E. P. Pavlova, S. V. Kuvshinnikov, and N. E. Sorokina, *Mol. Cryst. Liq. Cryst.*, 2000, **340**, 253.
79. N. B. Brandt, V. A. Kul´bachinskii, S. A. Lapin, V. V. Avdeev, I. V. Nikol´skaya, and N. E. Fadeeva, *Fizika Tverdogo Tela*, 1990, **32**, 94 [*Sov. Phys. Sol. State*, 1990, **32** (Engl. Transl.)].
80. V. A. Kul´bachinskii, S. A. Lapin, N. E. Fadeeva, I. V. Nikol´skaya, and V. V. Avdeev, *Vestn. MGU, Ser. 2. Khimiya*, 1990, **31**, 37 [*Vestn. Mosk. Univ., Ser. Khim.*, 1990, **31** (Engl. Transl.)].
81. N. E. Sorokina, A. F. Maiorova, S. N. Mudretsova, and V. V. Avdeev, *Proc. XV Termanal 2000 (Stara Lesna, 2000)*, Stara Lesna, 2000, 47.
82. N. E. Sorokina, S. N. Mudretsova, A. F. Maiorova, V. V. Avdeev, and N. V. Maksimova, *Neorgan. Materialy*, 2001, **37**, 203 [*Inorg. Mater.*, 2001, **37**, 189 (Engl. Transl.)].
83. V. A. Kulbachinskii, N. B. Brandt, N. E. Fadeeva, I. V. Nikolskaya, S. G. Ionov, and V. V. Avdeev, *Materials Science Forum*, 1992, **91—93**, 739.
84. N. V. Maksimova, N. E. Sorokina, S. N. Mudretsova, A. F. Maiorova, and O. A. Shornikova, *1-aya Mezhdunar. konf.*

"Uglerod: fundamental´nye problemy nauki, materialovedenie, tekhnologiya" (Moscow, 2002) [*1-st Int. Conf. "Carbon: Fundamental Problems of Science, Materials Science, and Technology (Moscow, 2002)*], Abstrs, Moscow, 2002, 137 (in Russian).

85. N. E. Sorokina, K. V. Geodakyan, and G. N. Bondarenko, *I Vsesoyuz. konf. po fizike i khimii soedinenii vnedreniya (Rostov-on-Don, 1990)* [*I All-Union Conf. on the Physics and Chemistry of Intercalation Compounds (Rostov-on-Don, 1990)*], Abstrs, Rostov-on-Don, 1990, 44 (in Russian).
86. A. G. Mandrea, K. V. Geodakyan, and N. E. Sorokina, *I Vsesoyuz. konf. po fizike i khimii soedinenii vnedreniya (Rostov-on-Don, 1990)* [*I All-Union Conf. on the Physics and Chemistry of Intercalation Compounds (Rostov-on-Don, 1990)*], Abstrs, Rostov-on-Don, 1990, 54 (in Russian).
87. S. G. Ionov, N. E. Sorokina, A. A. Serdan, O. A. Tverezovskaya, and Yu. G. Kryazhev, *V Mezhdunar. nauchno-prakt. konf. "Uglerodnye materialy" (Novokuznetsk, 1998)* [*V Int. Scientific and Practical Conf. "Carbon Materials" (Novokuznetsk, 1998)*], Abstrs, Novokuznetsk, 1998, 9 (in Russian).
88. S. G. Ionov, V. V. Avdeev, S. V. Kuvshinnikov, E. P. Pavlova, and N. E. Sorokina, *Izv. vuzov. Materialy electronnoi tekhniki* [*Higher School Bull. Materials for Electronic Eng.*], 1999, **2**, 59 (in Russian).
89. S. G. Ionov, V. V. Avdeev, S. V. Kuvshinnikov, and E. P. Pavlova, *Proc. 10th Intern. Symp. on Intercalation Compounds ISIC 10 (Okazaki, 1999*), Okazaki, 1999, 70.
90. S. G. Ionov, V. V. Avdeev, S. V. Kuvshinnikov, and E. P. Pavlova, *Mol. Cryst. Liq. Cryst.*, 2000, **340**, 349.
91. S. G. Ionov, S. V. Kuvshinnikov, V. A. Kulbachinskii, N. E. Sorokina, and A. B. Prokhorov, *Proc. Eurocarbon (Berlin, 2000)*, Berlin, 2000, 833.
92. S. V. Shulepov, *Fizika Uglerodnykh Materialov* [*Physics of Carbon Materials*], Metallurgiya, Chelyabinsk, 1990, 256 pp. (in Russian).
93. A. R. Ubbelohde and F. A. Lewis, *Graphite and its Crystal Compounds*, Clarendon Press, Oxford, 1960.
94. Pat. 1747382 RF; *Byul. izobret*. [*Invent. Bull.*], 1992, 26 (in Russian).
95. Pat. 1738755 RF; *Byul. izobret*. [*Invent. Bull.*], 1992, 21 (in Russian).
96. Pat. 2090498 RF; *Byul. izobret*. [*Invent. Bull.*], 1997, 26 (in Russian).
97. Pat. 2118941 RF; *Byul. izobret*. [*Invent. Bull.*], 1998, 26 (in Russian).
98. Pat. 2130953 RF; *Byul. izobret*. [*Invent. Bull.*], 1999, 15 (in Russian).
99. Pat. 2141449 RF; *Byul. izobret*. [*Invent. Bull.*], 1999, 32 (in Russian).
100. Pat. 2161123 RF; *Byul. izobret*. [*Invent. Bull.*], 2000, 36 (in Russian).
101. A.s. 1480304 SSSR; *Byul. izobret*. [*Invent. Bull.*], 1994, 2 (in Russian).
102. A.s. 1497952 SSSR; *Byul. izobret*. [*Invent. Bull.*], 1994, 2 (in Russian).
103. A.s. 1580755 SSSR; *Byul. izobret*., 1994 [*Invent. Bull.*], 18 (in Russian).
104. A.s. 1594865 SSSR; *Byul. izobret*., 1994 [*Invent. Bull.*], 2 (in Russian).
105. A.s. 1741042 SSSR; *Byul. izobret*., 1992 [*Invent. Bull.*], 22 (in Russian).

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