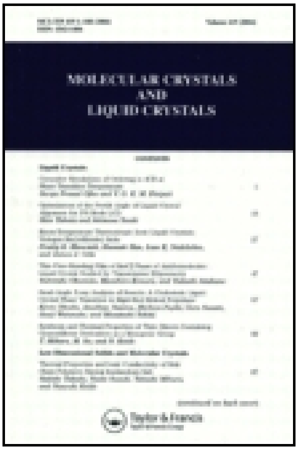

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Spontaneous and Electrochemical Intercalation of HNO_3 into Graphite

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The interaction of highly oriented pyrolytic graphite with nitric acid in a wide range of its concentrations was studied by potentiometry and X-ray. The threshold values of HNO_3 concentration for the different stages of graphite nitrate formation have been determined during spontaneous and electrochemical intercalation. At anodic oxidation of graphite in 55–98% HNO_3 the typical step-like character of the dependence of potential E(Q) is observed. The polarization of graphite (I=100μA) in 55–98% HNO_3 results in obtaining the 2nd stage graphite nitrate. The increase of a current intensity (I) up to 1.5 mA allows to carry out synthesis of the 1st stage in 75–98% HNO_3.

Keywords: graphite intercalation compounds; spontaneous intercalation; electrochemical intercalation; graphite nitrate; nitric acid

INTRODUCTION

It is known that strong Brönsted acids are capable of being intercalated into graphite matrix, forming graphite intercalation compounds (GICs). A typical example of such compounds is graphite nitrate – $C_{24n}NO_3 \cdot 3HNO_3$ (where n is the stage number). Unlike other acids, eg H_2SO_4, for the intercalation of which an oxidizer is necessary, the nitric acid relates to self–intercalated agents. In this connection it looks interesting to study interaction of graphite with nitric acid both at spontaneous intercalation, and at electrochemical oxidizing.

EXPERIMENTAL

The procedure of GIC's synthesis consisted of a treatment of graphite plates of 10-20 mg mass by 2-3 ml of 50-98% HNO_3 solution at ambient temperature. Phase composition of synthesised products was controled by X–ray on the diffractometer DRON–2 (CuK_α–radiation), mass increase was determined gravimetrically. Potentiometric and electrochemical examinations were carried out by the procedures described in ref. [1].

RESULTS AND DISCUSSION

The synthesis conditions and properties of the obtained GICs are presented in Table 1.

TABLE 1 The influence of HNO_3 concentration on phase composition of graphite nitrate

Concentration of HNO_3, %	Time of formation	Stage number, n	Period of identity, I_c, Å	Mass increase, Δm, %	Potential of graphite nitrate, E(Ag/AgCl), V
98	10-20 min	II	11.19	48	1.29
95	30 min	II	11.25	52	1.13
85	60 min	II	11.27	50	1.12
83	90 min	III	14.66	30	1.06
80	120 min	IV	17.92	26	1.02
75	7 days	V	21.57	20	1.00
71	30 days	graphite	6.74	0	–

It is established, that the threshold concentration of nitric acid spontaneous intercalation is near 75% HNO_3. With increase of nitric acid concentration the regular decrease of the stage number of graphite nitrate is observed. It is known that ions NO_2^+ are oxidizing agents in the graphite – HNO_3 system. According to literary data [2 during a dilution of the acid there is a decrease of NO_2^+concentration in solution, which is apparently accompanied by reducing of redox potential of acid, and at a ratio HNO_3:H_2O, equal to 1:1, NO_2^+ is not detected. Probably, it also explains the presence of HNO_3 concentration ranges for formation of graphite nitrate.

The dynamics of intercalation of 75-98% HNO_3 into graphite was analysed by potentiometry. Weakly expressed step–like character of E(t) curves of the reaction of HNO_3 intercalation into graphite in 90-98% nitric acid, connected with transferring of the third stage into the second has been detected. At 75-85% HNO_3 the E(t) dependence has a smooth character: a monotonic increase and exit to a plateau indicating the termination of the process. It is shown, that in the course of intercalation reaction the potential of graphite sample increases, achieving maximal value adequate to redox potential of acid solution. On the basis of obtained results it is possible to suppose, that regularity found by us during the study of graphite–H_2SO_4–oxidizer system, according to which the stage number of a GIC is determined by value of redox potential of an oxidizing solution [3], is also observed in graphite–HNO_3 system.

Systematic examination of anodic oxidation of graphite in HNO_3 was carried out for the first time. The conditions of electrochemical oxidation and phase composition of graphite nitrate are listed in Table 2.

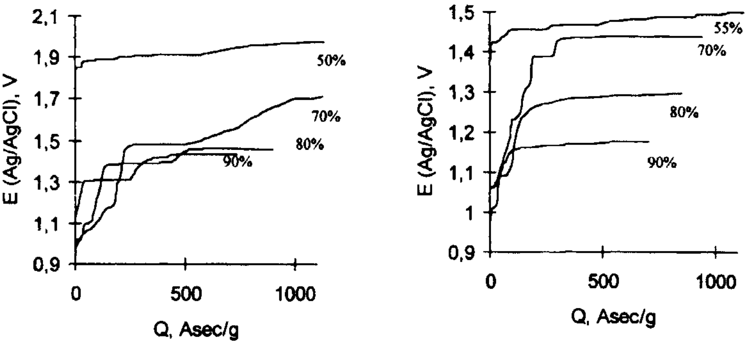
TABLE 2 Anodic oxidation of graphite in 50-98% HNO_3 by galvanostatic method

Concentration of HNO_3, %	I=100 μA		I=1.5 mA	
	n	E(Ag/AgCl), V	n	E(Ag/AgCl), V
98	2+1	1.30	1	1.54
90	2	1.21	1	1.44
85	2	1.18	1	1.47
80	2	1.30	1	1.46
75	2	1.35	1	1.48
70	2	1.55	1+2	1.73
65	2	1.53	1+2	1.77
60	2	1.61	1+2	1.80
55	2	1.71	2+ ox. graphite	1.90
50	graphite	1.78	ox. graphite	2.04

It is possible to see, that galvanostatic oxidation allows to expand considerably the concentration range of the acid: the threshold concentration of HNO_3 intercalation into graphite has decreased from 75% HNO_3 (spontaneous intercalation) up to 55% HNO_3 (electrochemical intercalation). It is established, that anodic polarization of graphite by a current I=100μA in a concentration range of 55-98% HNO_3 results in formation the 2nd stage graphite nitrate, in 98% HNO_3 – a mixture of the 1st and 2nd stages.

The essential increase of a current value I up to 1.5 mA allows to synthesize the homogeneous 1st stage in 75-98% HNO_3, in the range of 60-70% nitric acid – a mixture of the 1st and 2nd stages, and the amount of the latter increases in the course of the acid dilution. In 55% HNO_3 the 2nd stage formation in a mixture with a phase of imperfect graphite is observed and in 50% HNO_3 GIC's phase is not found. Probably, with nitric acid dilution the rate of anodic reactions, connected with participation of water, will increase, and process of electrochemical intercalation will slow down. And these processes (formation of surface functional groups, their further oxidation up to CO and CO_2, water oxidation and a participation of atomic oxygen in graphite oxidation) overlap each other and have no enough fixed borders on potential scale. In this connection anodic polarization of graphite in 50% HNO_3 solution results in obtaining imperfect phase such as graphite oxide. Earlier in the work of Krohn [4] it was mentioned about a possibility of graphite oxide formation in weak solutions of electrolytes at electrochemical treatment of graphite. It is possible to see that the potential of GIC formation and the amount of supplied electricity increases with reduction of acid concentration, which, in our view, testifies to a progressive role of anodic side-reactions.

In Figure 1a, b a dependence of potential on electric amount during anodic polarization of graphite in 50-90% HNO_3 is shown.



a) I=1.5 mA b) I=100 μA

FIGURE 1 The dependence of the potential on electric amount during anodic oxidation of quasimonocrystalline graphite in nitric acid in galvanostatic regime.

The E(Q) curves have a typical step–like form. With dilution of acid a number of steps increases, which explains sequential formation of the 3rd–2nd–1st stages GIC (Figure 1a). It is necessary to note, that a type of the E(Q) curve for 98% HNO_3 is similar to the curve published by Scharff [5]. In Figure 1a the E(Q) dependence for a treatment of graphite in 50% HNO_3 is also given. It is possible to see rather slight increase of potential in the initial period of graphite polarization and a constant value of potential at the further increase of Q. Apparently, the monotonic character of the E(Q) curve in 50% HNO_3 is a reflection of processes described above, connected with participation of water and resulting in formation of oxidized graphite phases.

CONCLUSION

The obtained results display, that in explored graphite–HNO_3 system a complex of processes attributed to an originality of nitric acid chemistry proceeds. These processes yield a variety of products easily transferring each into other. The variation of nitric acid concentration, current intensity, and time of treatment allows to change kinetics of the processes purposefully and to gain samples with given physicochemical properties.

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