

# SYNTHESIS OF GRAPHITE INTERCALATION COMPOUNDS IN THE SYSTEM GRAPHITE – HNO<sub>3</sub> – H<sub>3</sub>PO<sub>4</sub>

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## Introduction

Ternary graphite intercalation compounds (TGIC's) open wider opportunity for fundamental investigation and industrial application as compared binary intercalation compounds. During the last years there have been synthesized hundreds TGIC's, for example, with two Brønsted acids [1,2], but there are no ternary compounds with phosphoric acid.

This work is devoted to the synthesis and investigation of the formation mechanism of the TGIC's with strong acid – HNO<sub>3</sub> (pK<sub>a</sub>=-1,64) and weak acid – H<sub>3</sub>PO<sub>4</sub> (pK<sub>a</sub>=2,12).

## Experimental

Ternary system - HOPG – 98% HNO<sub>3</sub> – 100% H<sub>3</sub>PO<sub>4</sub> has been examined by X-ray diffraction and potentiometry methods with various HNO<sub>3</sub> / H<sub>3</sub>PO<sub>4</sub> ratio. The samples of graphite were treated on the solution HNO<sub>3</sub>:H<sub>3</sub>PO<sub>4</sub> = 1:0.1-10 during 2-200 h at 40°C. Galvanostatic oxidation of graphite in mixture of these acids was carried out in three electrode cell with an Ag/AgCl reference electrode with  $I = 1.5$  mA at room temperature. The intercalation of 100% H<sub>3</sub>PO<sub>4</sub> into nitrate graphite (NG) of I-IV stages is performed at 80°C.

## Results and Discussion

The interaction of graphite with mixture of these acids leads to the formation of II\*-IV\* stages of co-intercalation compounds with  $d_i = 0.43-0.47$  nm (Table 1). The H<sub>3</sub>PO<sub>4</sub> molecule has larger diameter than HNO<sub>3</sub> molecule and  $d_i$  for new phase increases on 0.02-0.04 nm over  $d_i$  for NG. Data of chemical analysis support the existence of two intercalate species HNO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub> in this ternary GIC.

The dynamics of intercalation process in this ternary system was studied by x-ray diffraction analysis. It was shown that at the first step nitrate graphite (NG) is formed. Then 001 reflections splitting is observed which is the evidence of the formation of a new phase (Fig.1). We assume that at the second step some amount of HNO<sub>3</sub> molecules are substituted by H<sub>3</sub>PO<sub>4</sub> molecules in solvate shell of the central anion. This exchange reaction taking place within

intercalate layer, practically does not influence the charge of GIC macrocation. Potentiodynamic curves of spontaneous intercalation of HNO<sub>3</sub> and the mixture of acids exhibit similar behaviour (Fig.2).

Galvanostatic oxidation of graphite in the solution HNO<sub>3</sub>:H<sub>3</sub>PO<sub>4</sub> = 1:0.5-2 results in the formation of I\* stage TGIC. In other cases different stages (I-V) of NG are formed. The threshold concentration of HNO<sub>3</sub> intercalation into graphite has decreased from 55% HNO<sub>3</sub> (C-HNO<sub>3</sub> system) to about 12% HNO<sub>3</sub> (C-HNO<sub>3</sub> – H<sub>3</sub>PO<sub>4</sub> system). The E(Q) curves for the solution HNO<sub>3</sub>:H<sub>3</sub>PO<sub>4</sub> = 1:0.1-4 have a typical step-like form. Curves have monotonic character when the content of H<sub>3</sub>PO<sub>4</sub> exceeds 85% in the solution E(Q).

The interaction between graphite nitrate I-VI stages and H<sub>3</sub>PO<sub>4</sub> allows to obtain II-VI stages of ternary GIC's. In the case of II-VI stages of NG the stage number of TGIC is equal to the number of stage of NG. Unstable I stage of NG breaks down to the III stage expanded GIC.

## Conclusions

I\* stage TGIC is synthesized by galvanostatic oxidation of graphite in the mixture HNO<sub>3</sub>-H<sub>3</sub>PO<sub>4</sub> acids. Co-intercalation GIC's of II\*-VI\* stages are formed by spontaneous intercalation in the mixture of these acids. The formation of co-intercalated GIC's with HNO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub> occurs in two steps – first, NG is synthesized and then the substitution reaction within the layer of intercalate takes place.

## References

- [1]. Solin S.A. Ternary graphite intercalation compounds. NATO ASY Ser., Ser.B. 1986;148:291-299.
- [2]. Herold A., Furdin G., Guerard D. et al. Some aspects of graphite intercalation compounds. Ann.Phys. 1986; 11:3-11.

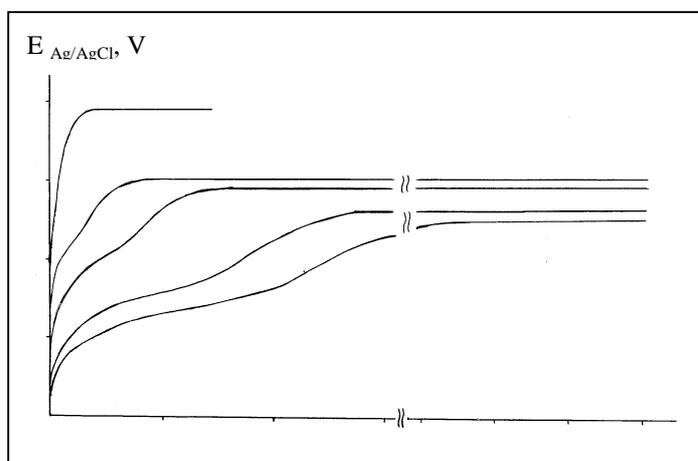
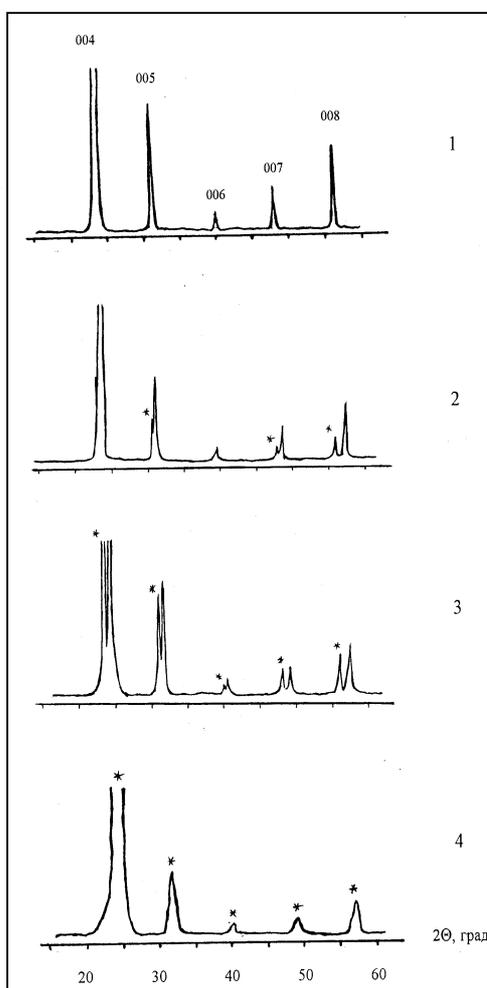
## Acknowledgments

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**Table 1.** Spontaneous and electrochemical intercalation in C–HNO<sub>3</sub>–H<sub>3</sub>PO<sub>4</sub> system

Volume ratio HNO <sub>3</sub> :H <sub>3</sub> PO <sub>4</sub>	Content HNO <sub>3</sub> , %	Number stage (spontaneous)	Number stage (electrochemical)
HNO <sub>3</sub>	98	I (I <sub>c</sub> =7.95Å)	II (I <sub>c</sub> =11.22Å)
10:1	90	I (I <sub>c</sub> =7.95Å)	II (I <sub>c</sub> =11.27Å)
5:1	80	I (I <sub>c</sub> =7.91Å)	II (I <sub>c</sub> =11.27Å)
4:1	76	I (I <sub>c</sub> =7.90Å)	II (I <sub>c</sub> =11.30Å)
3:1	73	I (I <sub>c</sub> =7.89Å)	II (I <sub>c</sub> =11.30Å) (split)
2:1	62	I* (I <sub>c</sub> =7.96*Å)	II (I <sub>c</sub> =11.30Å) (split)
1:1	45	I+I* (I <sub>c</sub> =7.76+7.87*Å)	II+II*(I <sub>c</sub> =11.28+11.66*Å)
1:2	29	I* (I <sub>c</sub> =7.88*Å)	II+II*(I <sub>c</sub> =11.16+11.66*Å)
1:3	21	II+I (I <sub>c</sub> =10.87+7.73Å)	III+III*(I <sub>c</sub> =14.53+14.87*Å)
1:4	17	II(III) (I <sub>c</sub> =11.07(14.31)Å)	IV+IV*(I <sub>c</sub> =18.12+18.69*Å)
1:6	12	V <sub>amorf</sub> (I <sub>c</sub> =21.22Å)	Graphite
1:10	7	Graphite+highly stages	Graphite
H <sub>3</sub> PO <sub>4</sub>	0	Graphite	Graphite

(\*-ternary GICs)



in the C - HNO<sub>3</sub> - H<sub>3</sub>PO<sub>4</sub> system with different ratio  
HNO<sub>3</sub>:H<sub>3</sub>PO<sub>4</sub> = 1:1 (2), 1:2 (3), 1:3 (4), 1:4 (5), HNO<sub>3</sub> (1).

**F** of intercalation in the C - HNO<sub>3</sub> - H<sub>3</sub>PO<sub>4</sub> system during 30 min (1), 15 h (2), 23h (3), 30h (4). ts