

MODIFICATION OF EXPANDABLE GRAPHITE BY BORON COMPOUNDS

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Introduction

Expandable graphite (EG) is widely used in fire-protective compositions and production of exfoliated graphite (EfG). Nowadays due to its unique properties, EfG has become one of the central objects of researches in carbon chemistry. Recently, Toyoda [1] showed that sorption capacity of EfG is extremely high, 86 g of A grade heavy oil and 76 g of crude oil per 1 g of exfoliated graphite. Graphite foil (GF), received by pressing of EfG without binder, is applied to produce of new non-asbestos sealing materials. However, the application of these carbon materials is limited by oxidation temperature of elementary carbon, which is 450°C. Therefore, protection of carbon materials still remains as an ambitious goal.

A dominant method of oxidation protection of carbons is chemical vapor deposition (CVD) of inert substances, such as SiC [2], TiO₂ [3], Al₂O₃ [4] and others. Another method of oxidation protection is surface treatment (impregnation) with phosphate [5], boron oxide [6] and others. Main disadvantages of these techniques are hard conditions of processes (high temperature, continuous time and pressure).

We have attempted insertion of boron oxide into EfG and GF through the boric acid during the GIC synthesis. GIC can be prepared by two methods: chemical (in the presence of strong oxidants) and electrochemical (via anodic oxidation of graphite in solution). The electrochemical approach appears more attractive both for practical applications and fundamental studies because it provides more information, requires no additional oxidants, and offers the possibility of tuning synthesis conditions. Therefore, electrochemical synthesis of GIC was offered.

In the present paper, GIC synthesis in graphite-H₂SO₄-H₃BO₃ system and influence of boron acid insertion to fire-protective of expandable graphite are reported.

Experimental

Natural graphite ($d_1=3,35 \text{ \AA}$, particle size of 0,3-0,4mm, ashes content less than 0,2%) was used as a host material. Solutions of sulfuric acid (purity: 96%) and boric acid (chemical pure sort) were used as the initial electrolytes. Solutions H₂SO₄-H₃BO₃ were prepared by mixing of mentioned acids in the appropriate ratios and heating them until 80°C to solve of boric acid.

The synthesis of GIC were carried out by electrochemical oxidation of natural graphite out in a three-electrode cell under galvanostatic conditions at a current of I=10 mA in the H₂SO₄-H₃BO₃ mixture by varying the weight ratio H₂SO₄/H₃BO₃. The natural graphite served as the

working electrode and a platinum plate was employed the counter electrode. The saturated mercury sulfate electrode (Hg/Hg₂SO₄), 0,615 mV versus the standard hydrogen electrode, serves as the reference electrode. Then GIC was hydrolyzed by water and was dried up at 60°C to constant weight with formation of expandable graphite. Exfoliated graphite was further obtained from EG subjected to thermal shock at 900°C.

The synthesized samples have been studied by means of X-ray diffraction (XRD), scanning electron microscope, low-temperature nitrogen adsorption, thermogravimetry and elemental analysis.

Results and Discussion

3.1. Graphite intercalation compound synthesis

Charging curves E(Q) that shows sample potential from specific charge are presented in Fig. 1. As one can see, the concentration of sulfuric acid significantly influences to the curve form. The charging curve has characteristic stepwise with pronounce plateaus and ascending segments in 96% H₂SO₄. At the same time, with increasing of H₃BO₃ content (so and decreasing of H₂SO₄ concentration) in solution curves are being smoothed and the potential rise corresponding to GIC formation is weakly pronounced.

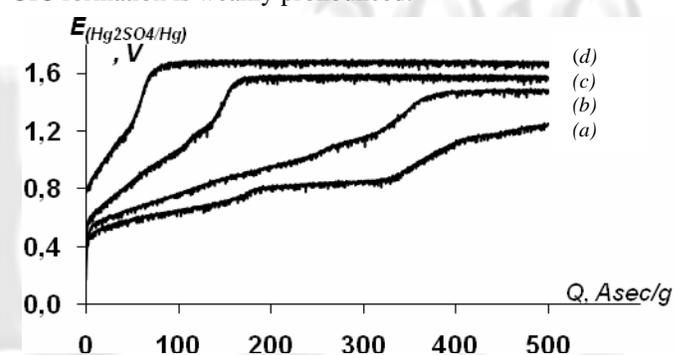


Fig. 1. Charging curves of graphite in H₂SO₄-H₃BO₃ mixed electrolytes with different weight ratios: (a) 1:0, (b) 12:1, (c) 6:1, (d) 3:1.

According to XRD patterns, mixture of GIC I and II stages were formed in solution with minimal content of H₃BO₃ (12:1), while in other mixed electrolytes GICs II stage were observed. The increase of synthesis duration (so and Q up to 1000 Asec/g) in last cases did not allow to obtain GIC I stage (table 1).

Table 1. Phase composition of GICs

Electrolytes (weight ratio)	Q, Asec/g	n (I _c , Å)	Designation
H ₂ SO ₄ (94%)	500	I (7,97)	EG(1:0)
H ₂ SO ₄ :H ₃ BO ₃ (12:1)	500	I (7,95) +II (11,23)	EG(12:1)
H ₂ SO ₄ :H ₃ BO ₃ (6:1)	500	II (11,20)	EG(6:1)
H ₂ SO ₄ :H ₃ BO ₃ (3:1)	500	II (11,17)	EG(3:1)
	1000	II (11,19)	EG'(3:1)

The concentration dependence of the formation potential of stage II E_f(II) GIC in solutions H₂SO₄-H₃PO₄

(cointercalation), $\text{H}_2\text{SO}_4\text{-CH}_3\text{COOH}$ (cointercalation) and $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ (H_2O does not insert to graphite) are -50 [7], -56 [7] and -104 [8] mV/M H_2SO_4 respectively. In the case of mixed solution $\text{H}_2\text{SO}_4\text{-H}_3\text{BO}_3$ concentration dependence comes down to -154 mV/M H_2SO_4 (Fig. 2), that indirectly argues H_3BO_3 no intercalates.

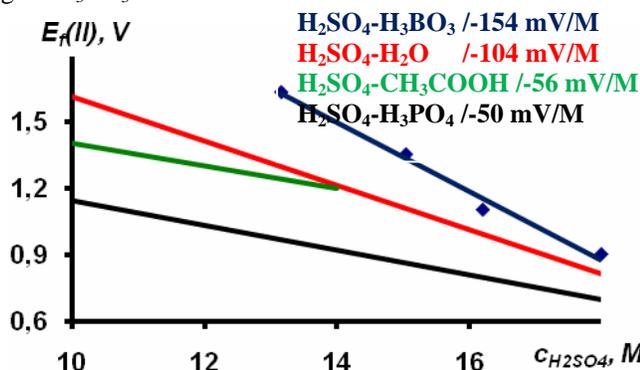


Fig. 2. Dependence of $E_f(\text{II})$ on the concentration of H_2SO_4 in $\text{H}_2\text{SO}_4\text{-L}$ ($L=\text{H}_3\text{PO}_4$, CH_3COOH , H_2O , H_3BO_3) solutions.

To understand whether boron acid inserts or not to graphite, GICs were obtained from high oriented pyrolytic in $\text{H}_2\text{SO}_4\text{-H}_3\text{BO}_3$ with weight ratio 6:1 and 3:1. To eliminate of absorption effect (absorption of boron acid on surface of graphite) all sides were cut. According to elemental analysis of obtained GICs, boron was not observed in GICs. So, boron acid does not insert to graphite.

3.2. Expandable graphite

As one can see in thermogravimetric curves (fig. 3), oxidation of modified EGs begin only at $700\text{-}750^\circ\text{C}$, that is higher for 200°C than classical EG(1:0).

According to the data of the elemental analysis, there is only $\sim 1\%$ wt. of boron in EG(6:1). But this amount of boron acid was enough to improve of thermal properties. If boron acid, as was above shown, does not insert to graphite, nevertheless it protects carbon material, consequently it adsorbs on the surface of graphite. Actually white film on SEM image of EG(6:1) is probably boron acid (fig.4).

3.3. Exfoliated graphite

Specific surface area of EfG(1:0) is $70\text{ m}^2/\text{g}$. The same value for modified samples of EfG is less for two times, which is a consequence of pores blocking by boron oxides, formed by boron acid decomposition at high temperature (900°C). This probably provokes an oxidation protection of modified samples. Although specific surface was increased, bulk density was not influenced by modifying of EfG (table 2).

Table 2. Bulk density and specific surface of EfGs.

Samples	$d_{900^\circ\text{C}}$, g/l	S , m^2/g
EfG(1:0)	1,7	70
EfG(12:1)	1,8	32
EfG(6:1)	1,8	30
EfG(3:1)	2,3	29

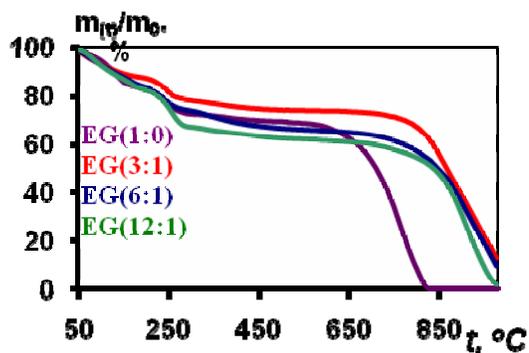


Fig. 3. Thermogravimetric curves of EGs

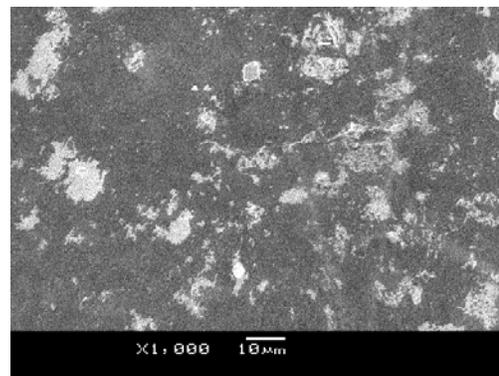


Fig. 4. SEM micrograph of EG(6:1)

Conclusions

1. Boron acid does not insert to graphite.
2. Boron acid adsorbs uniformly on the surface of graphite, so increases oxidation temperature until $700\text{-}750^\circ\text{C}$.
3. Specific surface was increased, but bulk density was not influenced by modifying of EfG

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