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IN SITU STUDY OF THE ACCEPTOR INTERCALATE DIFFUSION PROCESS IN GRAPHITE INTERCALATION COMPOUNDS

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INTRODUCTION

The graphite intercalation process and staging phenomena have been the focus of many experimental and theoretical works during the past years ⁽¹⁾. However, only little is known about the diffusion of the of the intercalate during the intercalation process. Conduction Electron Spin Resonance (CESR) technique is one of the most powerful methods of studying the intercalation process ^(2,3), because fact that the ESR lineshape and intensity of the bulk HOPG (highly oriented pyrolytic graphite) vary strongly during the intercalation process. In this work we present the results of an *in situ* CESR investigation of the HOPG plate intercalation mechanisms under controlled change of the HOPG plate skin-depth.

EXPERIMENTAL RESULTS

In CESR-investigations of the HOPG plate intercalation mechanisms it is possible to distinguish and investigate only the phases of reaction separated by time interval $\Delta\tau$ larger than that required to the previous reaction front to path across the skin-depth. (In the case where the HOPG plate intercalation and stage change fronts advance from the external lateral edges to the plate centre). Therefore, the $\Delta\tau$ resolution of the CESR method increases with the decrease of the conductor skin-depth. The only obvious way to do it is to decrease the microwave field frequency. Unfortunately, the problems of the ESR-experiment under consideration increase non-proportionally to the $\Delta\tau$ - resolution as a result of this process. On the other hand, our recent investigations show that in anisotropic conductors, such as HOPG and GICs plates, the more essential change of skin-depth can be implemented by the change of conduction plate orientation in the microwave field only. For instance, in ESR-experiments with the HOPG plate, the rotation of the plate investigated from the $c\perp H_{rf}$ to the $c\parallel H_{rf}$ orientation leads to the 15-fold (!) decrease of the skin-depth from the same lateral edges.

In this report we present the results of an *in situ* CESR study of the intercalation process of SbF_5 , Br_2 and F_2 molecules into the HOPG plates conducted as in the traditional configuration of such experiments with $c\perp H_{rf}$ ⁽³⁾ as by means of two-

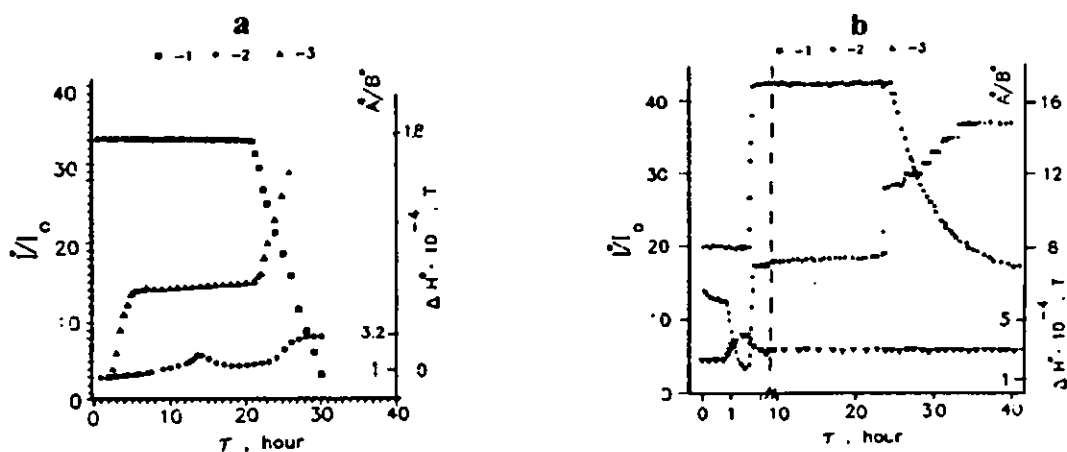


Figure 1. CCSR lineshape parameters of graphite vs. exposure time (τ) in HNO_3 atmosphere at $c \perp H_{rf}$ (a) and $c \parallel H_{rf}$ (b). 1, 2 and 3 correspond to ΔH^* , A^*/B^* and I^*/I_0 , respectively. $I^* = (A^* + B^*) \cdot \Delta H^{*2}$; I_0 is the intensity of the Mn^{2+} ESR in a standard sample, $\nu = 9.5$ GHz, $T=300\text{K}$.

zone vapor transport method. As a result, in non-traditional configuration with $c \parallel H_{rf}$ new and previously inaccessible for the study by means of the ESR method aspects and steps of the HOPG substrate intercalation process have been revealed and investigated (Fig. 1) including:

- new step of the intercalation reaction conducted only near the HOPG plate edges which precedes the extension of the intercalation process throughout the HOPG plate. It was proposed that the mechanisms of this phase formation and intercalation near external basal plane are the same;
- stage change fronts formation and their advance across the skin-depth;
- new phases which are stable between states with integer GICs index number (fractional stages ?);
- high-ohmic barrier at the direction perpendicular to the initial intercalation and the stage index change fronts.

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XPS-STUDIES OF GRAPHITE OXIDES FLUORINATED BY BrF₃

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Keywords: XPS, fluorinated carbon.

The prospective for practical applications of fluorinated graphite oxides (FGO), for instance, as a cathode materials, has led to their considerable interest. The semi-ionic bond between fluorine and carbon was found in the fluorinated carbon fibers⁽¹⁾ and fluorinated carbon⁽²⁾. The main objective of this paper was to study the type of the interaction between fluorine and initial oxidized graphite matrix with different oxygen contents.

A number of graphite oxide (GO) samples (thirteen) with different oxygen content were used to synthesize FGO. The ratio of the carbon to the oxygen (C/O) changes from 10.2 (GO N 1) to 1.5 (GO N 13). The fluorination of GO was carried out with BrF₃ at room temperature. The following hydrolysis of the fluorinated samples leads to additional oxidation and fluorination of the substances. Also, thin dispersion and subdividing of samples synthesized into two phases during hydrolysis took place (hydrophilic — bottom, «B» and hydrophobic — light, «L»). The details of the synthesis of GO and FGO and chemical analysis data were previously presented⁽³⁾.

The GO samples and both the phases of the FGO were investigated by the X-ray photoelectron spectroscopy (XPS). The calibration of the spectrometer energy scale was conducted according to the peak of carbon contamination with the binding energy (E_b) 285.0 eV. To receive more information the computer treatment of the spectra obtained was used.

For the first six GO samples (C/O for GO N 6 equal 5.2), the main components of C1s-spectra have asymmetric shapes of lines that is typical for conductors. This means that the carbon atom of the matrix keeps the sp²-hybridization of the valent electron orbitals and these compounds may be defined as a graphite hydroxide hydrate. In the GO samples with N>6, the matrix spectra lines become symmetrical. It is mean that the type of hybridization of the matrix valent electron orbitals changes from sp² to sp³.

C1s spectra of the FGO samples of both phases measured include some basic lines. An example of the FGO C1s spectra after computer simulation is presented in the Figure 1. The first line (L*) in the FGO spectra is attributed to the surface carbon contaminations. Next line (L₁) is attributed to the carbon bound with neither oxygen nor fluorine. E_b of the L₂ is close to E_b of the line of the carbon covalently bound with the oxygen-containing fragments in the GO samples. This enable to attribute the line L₂ to the carbon bound with the oxygen covalently. The line L₃ appears after interaction of samples with BrF₃. Consequently, this peak may be attributed to the carbon bound with fluorine. But one must point out that the E_b of F1s-electron in FGO (687.6 + 0.5 eV) is less than corresponding energies usually observed in covalent carbon materials (689.6 + 0.5 eV)⁽⁴⁾. Simultaneously, taking into account the E_b of L₃ in the FGO (289.3 + 0.3 eV) one may conclude that the interaction between fluorine and carbon atoms, which give the signal L₃ in the FGO, differs from that in typical covalent compounds (CF)_n and (C₂F₄)_n.

According to the XPS data the ratio of the total quantity of matrix carbon to the total quantity of oxygen (C/O) in the GO series is less than obtained from chemical analysis data⁽⁵⁾. This fact results from the reasons that we deal with the spectra of the samples surfaces wich are subjected to the influence of the oxidizing reagents to a larger extent. However, during the hydrolysis of fluorinated compounds, a thinner dispersion of the samples takes place. As a result, the domains of compounds, which were inside of

the samples before, get on the surfaces. The C/O ratio, determined from XPS-spectra of C1s- and O1s-electrons of the surfaces of the thin dispersed FGO compounds, becomes close to the chemical analysis data ⁽³⁾. Besides, the ratio of the total quantity of the matrix carbon to the total quantity of the fluorine (C/F) determined from the XPS-spectra is also less than it follows from the chemical analysis data. The facts mentioned may be explained if we will bear in mind two circumstances: 1) BrF₃ interact with the carbon of certain fragments of the structure of the initial GO matrix which are in all GO samples, and 2) the dispersion of the samples during the hydrolysis process occurs along this fragments, resulting in the increased (as compared with the bulk of substance) fluorine and fluorine-containing admixtures concentration on the surface of the thin dispersed FGO samples.

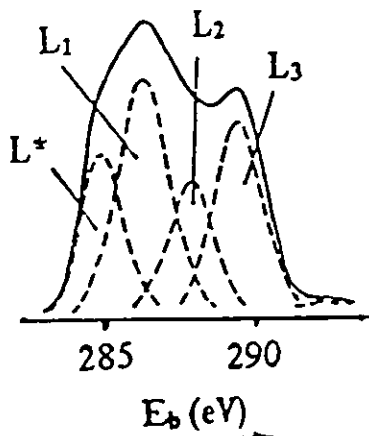


Figure 1. C1s XPS-spectrum of the FGO N 8 «B» and computer simulation of it.

In accordance with the E_b of C1s and F1s the type of the bonds formed between the fluorine and the carbon of the above mentioned structure fragments may be attributed to the so-called semi-ionic type of the bond. One may point out that the existence of semi-ionic bond is connected with the presence of the carbon bound with each other by unsaturated bond in the initial matrix. The reason of existence of these structure fragments with the unsaturated C - C bonds in the FGO may be related to the fact that in the method of the GO synthesis used the phase of the graphite hydroxide hydrate also remains in the samples with a maximum oxidation degree as well. In this case, this phase may be considered as the residual admixture phase, and its presence is related only during fluorination and following hydrolysis of the substance. But also the matrix regions of sp^2 -hybridized carbon may be the characteristic of the oxidized graphite itself.

Thus, there was found by the method of X-ray photoelectron spectroscopy that there is the peak in the F1s-spectra in FGO which E_b falls between this value in a typical ionic compounds LiF and covalent compounds of type $(CF)_n$ and $(C_2F_4)_n$. The analysis of correlation between the structure of initial substances (GO), synthesis conditions and XPS data of FGO allow us to do the following conclusions:

1. The substances under study, even at high oxidizer content on all GO synthesis stages, must preserve structure fragments with the unsaturated carbon bonds.
2. The used method of fluorination in FGO synthesis preserves the co-existence of matrix fragment containing sp^2 - and sp^3 -hybridized carbon atoms.
3. The bond formed between fluorine and these fragments is of semi-ionic type in the method of fluorination and following hydrolysis used.

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SCANNING TUNNELING MICROSCOPY OF CARBON FIBERS AND PYROLITIC GRAPHITE SURFACES

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KEYWORDS: Carbon Fibers, Highly oriented pyrolytic graphite, Scanning Tunneling Microscopy, STM.

In this paper we present the results of our investigation of the nanometric structure of carbon fibers and high oriented pyrolytic graphite (HOPG) via scanning tunneling microscope (STM). All experiments were conducted on air in constant current mode. STM was controlled by PC with original software.

CARBON FIBERS

Carbon fibers was explored via STM from the plane parallel to the fiber axis as well as from the side which is perpendicular to these axis. It was mentioned that pure carbon fibers explorations via STM are rather difficult in case of electrification processes. To eliminate this effect we have been making the same explorations of carbon fibers coated by titanium oxide. This circumstance decrease electrification.

In our investigations we have ascertained that every fiber consist of fragments, looking like microfibers composed from the cylindrical blocks of linear size 30 nm (Fig. 1).



Fig. 1. STM image of the carbon fibers in plane parallel to the fibers' axis, 900x900 nm².



Fig 2. STM image of carbon fibers in plane parallel to the fibers' axis, 225x225 nm².

Two types of pores were determined. Pores of the first type are approximately 10 nm in size and located between blocks. The second type are approximately 1 nm in size and located on the block surface (Fig. 2).

Interlayer distances are opened in blocks junctions, therefore, these locations could have some peculiarities of adsorption. The block type of carbon fibers' structure was observed from the plane which perpendicular the axis of fibers.

GRAPHITE

In (a,a) plane the flat terraces were observed on the surface. On the native (without special cleaning) HOPG surface were found some fragments with linear size up to 300 nm (Fig. 3).



Fig. 3 STM image of the HOPG surface in (a,a) plane, 1800x1800 nm².

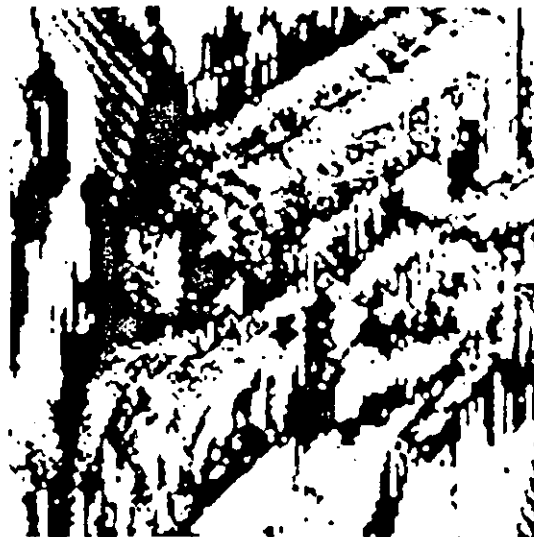


Fig. 4. STM image of HOPG surface in (a,c) plane, 1800x1800 nm².

The form of these fragments was almost true rhomb or it's parts with repeating angles 60° and 120°. Fragments orient along the terraces boundaries. We suggest that HOPG has block structure in it's bulk and when we brake the sample it brakes along the boundaries of blocks. Another possible explanation - these fragments are particles of HOPG, attracted by the electric field on the surface which orienting them such way.

In (a,c) plane we detected block structure of HOPG. The blocks are look like packages of parallel microblocks. Another observation was made in (a,c) plane - corrugation in (a,a) plane with period approximately 12 nm.

In (a,c) section we noticed angular structures with repeating angles of 60°. We suppose that these structures are the contours of the microblocks' packages, where 60°-angles are due to the displacement between one layer and the next layer. We also suggest that this packing begin from the atomic scale.

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