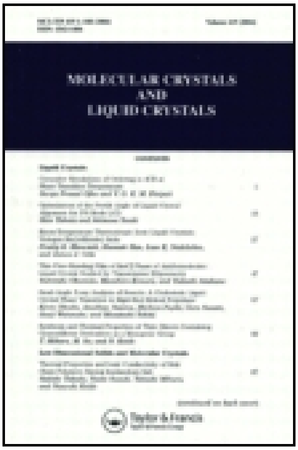

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Current Carriers Energy Spectrum of Sulfur Acid-Graphite and Graphite Foils

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Current Carriers Energy Spectrum of Sulfur Acid-Graphite and Graphite Foils

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The present work means to study the infrared spectra and to determinate energy spectra parameters of current carriers for graphite intercalation compounds of low stages with sulfur acid in the presence of different oxidizers, where oxidizers are $K_2Cr_2O_7$, $KMnO_4$, $Ce(SO_4)_24(NH_4)_2SO_4{\cdot}2H_2O$, $(NH_4)_2S_2O_8$, and for low density graphite materials (flexible graphite foils) produced on their base.

Keywords: intercalation compounds of graphite; graphite foils; infrared spectra; energy spectrum parameters

INTRODUCTION

Special place among GICs is taken by the graphite bisulfate (obtained by interaction of graphite with sulfur acid), which is the by-product for obtaining oxidized graphite, colloid graphite, thermoexpanded graphite, graphite foils etc. These materials are widely used at the fuel and energy complex, atomic, motor, oil-refining industries. The study of formation conditions, the search of new synthesis methods and the study of bisulfate graphite properties are described in many works [1-3]. However it should be mentioned that a whole number of questions, concerning the influence of methods of production of GICs with sulfur acid upon the properties of current carriers, remain open.

EXPERIMENTAL

For producing GICs the high quality single crystals of graphite (HOPG) with the angle of disordering of crystalites in the direction of trigonal axes less than 1^0, concentrated sulfur acid (with density about 1.84 g/cm^3), potassium bichromate $K_2Cr_2O_7$, potassium permanganate $KMn0_4$, ammonium complex salt $Ce(SO_4)_24(NH_4)_2SO_4{\cdot}2H_2O$, ammonium persulphate $(NH_4)_2S_2O_8$ were used. Synthesis of GICs samples was produced by the liquid phase method in the presence of different oxidizers. For producing the graphite foil the samples of GICs with sulfur acid were hydrolyzed, then dried to the constant masse at the temperature about 110 ^{0}C, then sharp heated to the temperature ≥ 950 ^{0}C and then molded without binder between cylindrical rollers. The density of graphite foils was about 0.9 g/cm^3.

The thickness of intercalat layer (I_c^0) and the identity period of crystalline structure in the direction of trigonal axes (I_c) were determined by X–ray.

The measurement of reflection coefficient was made on spectrophotometer Hitachi–330 with the device for diffusion reflection. The device provided the measurements of diffusion reflection of spectrum in the visible range of spectrum ($\lambda = 350 \div 800$ nm) and in the near infrared range ($\lambda = 900 \div 1500$ nm).

RESULTS AND DISCUSSION

The coefficient of reflection is determinated by the value of complex dielectric constant [4]:

$$R(\omega) = \varepsilon(\omega) - \frac{1}{[\varepsilon(\omega)+1]^2}\,. \qquad (1)$$

For GICs dielectric constant is equal to [5]:

$$\varepsilon(\omega) = 1 + \frac{d_0}{\left[I_c^0 + .d_0 \cdot (n-1)\right] \cdot \left[\varepsilon_\Gamma(\omega) - 1\right]} - \varepsilon\,, \qquad (2)$$

where ε is the contribution in the dielectric constant due to the transitions of electrons from valence band to conduction band. The probability of these transitions decreases due to the acceptor influence of intercalat.

The reflection coefficients in the energy range from 0.62 eV to 2.02 eV for pristine graphite, GICs of the first and the second stages with sulfur acid produced with different oxidizers: $K_2Cr_2O_7$, $KMnO_4$, $(NH_4)_2S_2O_8$, $Ce(SO_4)_2 4(NH_4)_2SO_4 \cdot 2H_2O$ and graphite foils were studied experimentally.

On the FIGURE 1 the dependence of normalized reflection coefficient for GICs of first and second stages with sulfur acid on energy is presented.

Approximation of the experimental data was made by using formulas [5]. On the base of experimental data there were calculated the hole concentration (p) and the charge transfer ratio (f/ℓ) for GICs of first and second stages.

For GICs of first stage the energy spectrum is described by the expression:

$$E = \pm\frac{2}{3}\cdot\gamma_0\cdot b_0\cdot k, \qquad (3)$$

where $\gamma_0 \sim 3$ eV is the two dimensional band parameter equal to overlapping integral of wave functions of neighbor carbon atoms in layer, $b_0 = 1.42\ \overset{o}{A}$ is the parameter of crystalline lattice of graphite in the basal plane, k is the quasi impulse of current carriers. Concentration of holes in these compounds is:

$$p = \frac{4\cdot E_F^2}{9\pi\cdot\gamma_0^2\cdot b_0^2\cdot I_c^0}, \qquad (4)$$

where E_F is the value of the Fermi energy determinated from data analysis of reflection coefficient. The charge transfer ratio for these GICs is equal to:

$$f/\ell = \frac{E_F^2}{\pi\gamma_0^2}\sqrt{\frac{1}{3}}. \qquad (5)$$

For GICs of second stage the energy spectrum is:

$$E_{VI,CI} = \pm\frac{1}{2}\left(\gamma_1 - \sqrt{\gamma_1^2 + 9\cdot\gamma_0^2\cdot b_0^2\cdot k^2}\right), \quad (6)$$

$$E_{V2,C2} = \pm\frac{1}{2}\left(-\gamma_1 - \sqrt{\gamma_1^2 + 9\cdot\gamma_0^2\cdot b_0^2\cdot k^2}\right), \qquad (7)$$

where $\gamma_1 \approx 0{,}377$ eV is the overlapping integral of wave functions of carbon atoms in neighbor layers. Holes concentration taking into account the presence of holes in the first and second valence bands is equal :

$$p = \frac{1}{9\pi\cdot\gamma_0^2\cdot b_0^2}\cdot\frac{|E_F|}{|E_F|+\gamma_1}\cdot\frac{\left(2\cdot|E_F|+\gamma_1\right)^2-\gamma_1^2}{I_c^0+d_0}, \qquad (8)$$

and charge transfer ratio for GICs of the second stage is equal:

$$f/\ell = \frac{E_F^2}{\pi\gamma_0^2}\sqrt{\frac{4}{3}}. \qquad (9)$$

Received results of measured reflection coefficient dependence approximation with theoretic curves and calculations are presented in the Table 1.

TABLE 1 Values of energy spectra parameters and characteristics of current carriers in GICs with sulfur acid

n	Oxidizer	E_F,eV	τ, 10^{-15} sec	f/l	p, 10^{20} cm^{-3}
1	$K_2Cr_2O_7$	– 0.75	2	0.011	5.0
1	$KMnO_4$	– 1.00		0.019	9.0
1	$(NH_4)_2S_2O_8$	– 1.02		0.020	9.3
1	$Ce(SO_4)_2 4(NH_4)_2$ $SO_4\cdot 2H_2O$	– 1.18		0.026	12.5
2	$K_2Cr_2O_7$	– 0.68	7	0.017	2.9

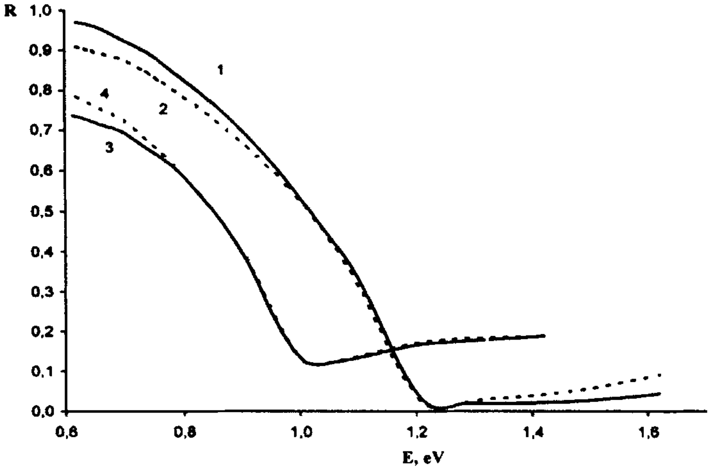

FIGURE. 1. The dependence of normalized reflection coefficient for GICs of first and second stages with H_2SO_4 (oxidizer $K_2Cr_2O_7$) on energy.

1 – GIC of the first stage (experimental), 2 – GIC of the first stage (theory), 3 – GIC of the second stage (experimental), 4 – GIC of the second stage (theory).

For the investigated samples of graphite foils the concentrations of current carries from $6.5\cdot10^{20}$ cm^{-3} to $9.7\cdot10^{20}$ cm^{-3} and values of τ from $0.3\cdot10^{-15}$ sec to $0.5\cdot10^{-15}$ sec were received.

CONCLUSION

The values of Fermi energy, charge transfer ratio and concentration of current carries for GICs with sulfur acid of the same stoichiometric composition and structure (stage number) depend on the type of oxidizer. The use of different oxidizers allows to change purposeful the electrical conductivity of GICs and graphite foils based on them. The relaxation times of current carriers in graphite foils are about an order higher than in GICs. It is an evidence that the free path length is low and concentration of defects is high in graphite foils. By this reason the electrical conductivity of graphite foils is essentially lower than that for GICs used for their production.

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