

ONE-DIMENSIONAL CONDUCTIVITY AND EPR SPECTRA OF CARBON MATERIALS

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Abstract

Samples of the amorphous carbon material are shown to have EPR signals when the number of electron carriers is low and one-dimensional conductivity of the carbon material is preserved. The EPR spectra widen when the carrier concentration grows with the preservation of the one-dimensional conductivity. Such one-dimensional conductivity is supposed to be related to the presence of carbene. The observation of the EPR spectra of the amorphous carbon material is likely due to the presence of coke-like not fully condensed carbon structures.

Keywords: amorphous carbon, one-dimensional conductivity, EPR.

1. Introduction

The methods used for synthesis of amorphous carbon materials (ACM) by thermocatalytic synthesis from aromatic compounds with different functional groups (precursor carbonization at 700-800°C in the presence of an alkali – sodium or potassium hydroxide, or their equimolecular mixture) have been reported earlier [1-3]. Among specific features of such ACM samples are their EPR spectra that were not understood until now.

This effect was studied for ACM samples prepared from a mixture of phenol and 1,2,3-benzotriazol according to [1]. Sample 1 with the BET surface area 1800 m²/g was prepared by carbonization of the precursor mixture for 30 min at 900°C. Sample 2 having the surface area 2200 m²/g was prepared by carbonization of the precursor mixture for 15 min at 700°C. Sample 1 with the surface area 2900 m²/g was prepared by carbonization of the precursor mixture for 15 min at 900°C. No EPR signal was observed for Sample 1. Meanwhile, symmetric EPR signals with $g = g_e$ were observed for Samples 2 and 3. For Sample 2 the width of the signal was 15 Gs at 293 K and 10 Gs at 77 K. The signal observed for Sample 3 was wider – 34 Gs at 293 K and 24 Gs at 77 K. Both samples 2 and 3 had one-dimensional conductivity. The EPR spectra of both samples after evacuation were observed not to follow the Curie law typical for isolated or weakly interacting paramagnetic species: the integral intensity of the signal considerably decreased with the temperature decrease instead of the growth expected for the Curie law. This decrease was more significant for Sample 3 than for Sample 2 (4-fold and 1.5-fold, respectively). The analysis of these features of the EPR spectra suggests that the disappearance of the spectra at low temperatures can be related to certain localization of the electron gas in the carbon structure around some sort of structural defects where the observed unpaired electrons are localized (C-S relaxation model [5], where C – are localized electrons, and S – is the electron gas). The decrease of the measurement temperature leads to a substantial increase of the C-S relaxation efficiency accompanied by widening of the EPR spectra of localized electrons C. However, the obtained results required more careful analysis using different ACM samples. We synthesized new carbon materials with one-dimensional conductivity from 1,2,3-benzotriazol mixtures with phenol, o-nitroaniline and 8-oxyquinoline.

2. Experimental

Nitrogen-containing carbon materials were synthesized according to earlier developed methods [1, 3]. O-nitroaniline mixture with 1,2,3-benzotriazol in 2/1 molar ratio was used as a precursor for Sample 4. Sodium hydroxide was used as an alkali in the ratio organic mixture/alkali = 1.25. Carbonization was carried out at 700°C for 20 min in a sealed crucible (in the atmosphere of carbonization gases). Then, the crucible was cooled down in air. After cooling the sample was washed with water until neutral reaction and dried in air at 110-120°C until constant weight. Sample 5 was obtained by second carbonization of Sample 4 at 900°C for 10 min in a sealed crucible. After carbonization the crucible was cooled down in air (carbonization constant 0.81). The BET surface areas were 470 and 490 m²/g for Samples 4 and 5, respectively. A mixture of 8-oxyquinoline with 1,2,3-benzotriazol in 1/1 molar ratio was used as a precursor for Sample 6. Sodium hydroxide was used as an alkali in the ratio organic mixture/alkali = 2.5. Carbonization was carried out at 700°C for 80 min in a sealed crucible. Then, the crucible was cooled down in air, washed and dried similar to Sample 4. The surface area of Sample 6 was 3400 m²/g.

The textural characteristics of the ACM samples were determined using ASAP-2400 (Micromeritics) instrument by nitrogen adsorption at 77 K. Prior to the measurements the samples were evacuated at 300°C and 0.001 mm Hg pressure until the end of gas evolution from the sample without contact with the atmosphere after the pretreatment. Nitrogen adsorption isotherms were recorded in the relative pressure range from 0.005 to 0.995 followed by calculated of the surface area according to the standard BET method.

The EPR spectra of the samples were recorded using a Bruker 200 D spectrometer ($\lambda = 3$ cm) at 77 and 293 K. Before the measurements the samples were evacuated at 200°C. The conductivity temperature dependence was measured by a four-contact method in the temperature range 4.2-300 K. A powder sample was pressed into an ampoule. The contacts to the ampoule were made of 0.1 mm silver wire. To secure contact between the sample and the wire, the powder in the ampoule was additionally pressed.

Table 1. Electric conductivity σ at 300 K and evaluation of carbine concentration from the density of states

Sample	1*	2*	3*	4	5	6
T _{carb.} , °C	900	700	900	700	900	700
Time, min	23	15	15	20	10	80
S. A., m ² /g	1800	2200	2900	470	490	3400
σ (300K)	0.055	1.06	4.95	0.0002	0.78	0.33
Carbine conc., Vol. fraction	0	0.09	0.116	0.0025	0.082	0.017
Carbine conc., Vol. %	0	9.01	11.66	0.25	8.28	1.74

*Synthesis and properties of these samples are described in [1-3]

3. Results and Discussion

Localization of the conductivity electrons in limited space leads to hopping conductivity of the charge carriers between these areas of localization. When the temperature decreases, the conventional hopping conductivity between the nearest localization sites is changed for the hopping conductivity with variable hop distance (HCVHD) that is described by the generalized Mott law [6]:

$$\sigma_{\text{HCVHD}}(T) = \sigma_0 \cdot \exp(-B/T)^{1/(d+1)}$$

Here d is the charge carrier movement dimension, $B = [16a^3/k_B N(E_F)]$, a – is the reverse value of the distance where the atomic wave function goes down (usually $1/a \sim 8 \div 10$ Å), $N(E_F)$ is the density of states on the Fermi surface, σ_0 is a constant.

Figure 1 shows the temperature dependence of the electric conductivity logarithm for Samples 4, 5 and 6. Although the temperature dependences are substantially different for all studied samples, all of them can be described by the Mott law for the one-dimensional case.

$$\sigma(T) = \sigma_0 \cdot \exp(-T_0/T)^{1/2}$$

$$T_0 = [\text{const} \cdot a/k_B N(E_F)], \text{const} \sim 10, a \sim 8-10 \text{ \AA}$$

Note that one-dimensional conductivity characterized by the temperature dependence similar to the one shown in Fig. 1 ($\sigma(T) = \sigma_0 \cdot \exp(-T_0/T)^{1/2}$) was observed for carbon structures with carbine chains [7-11].

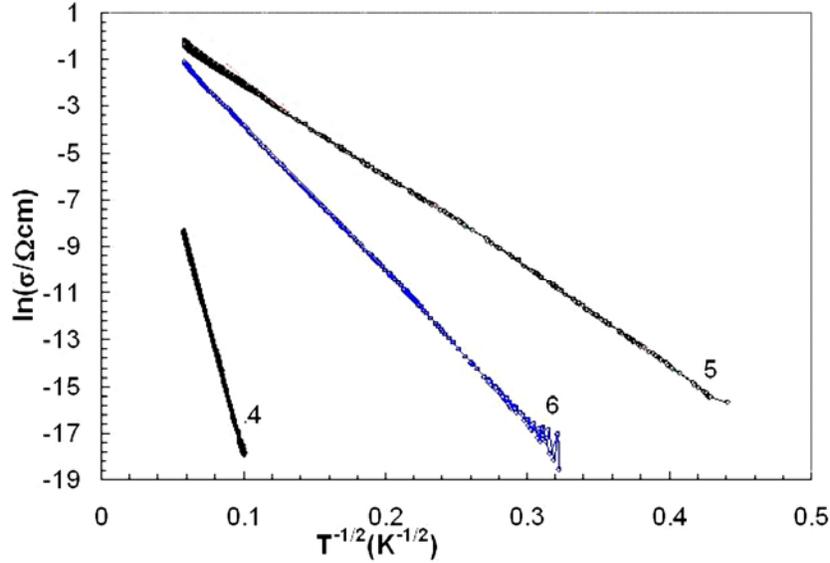


Figure 1. Temperature dependence of the electric conductivity logarithm for ACM Samples 4, 5 and 6.

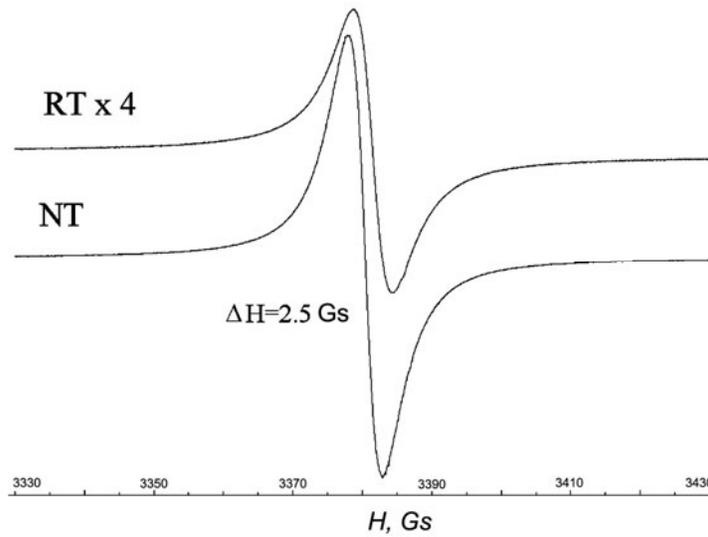


Figure 2. EPR spectra of Sample 4 after evacuation. The spectra were recorded at room temperature (RT) and liquid nitrogen temperature (NT).

Table 1 presents the calculated data on the conductivity σ_0 and carbine concentration in the samples at 300 K. As noted above, they depend on the carbonization temperature. Carbine concentration was estimated by inclination of line of experimental data of conductivity (Fig. 1) with using of Mott law for the one-dimensional hopping conductivity. Note that for Samples 4-6 the carbine concentration grows parallel to conductivity σ_0 . This means that, most likely, the carrier concentration is determined by the carbine concentration. The data on Samples 2 and 3 agree with this conclusion. The EPR spectra of Samples 4 and 6 correspond to unpaired electrons localized, most likely, on carbine chains connecting the ACM graphene fragments. Therefore, one should expect that the one-dimensional ACM conductivity would grow with the increase in the concentration of graphene fragments that is proportional to the surface area. Then, the interaction of the unpaired electron (C) with the conductivity electrons (S) described by the known C-S relaxation model is quite expected. As noted in introduction, this had been confirmed for Samples 2 and 3.

If the one-dimensional conductivity is related to carbene, an increase of the concentration of the latter will lead to the growth of the former. However, we do not see any fundamental bases for quantitative comparison of the carbene concentration with the one-dimensional conductivity (σ_0). Most likely this effect is related to not fully condensed coke-like carbon structures giving the EPR spectra. Apparently, higher temperature or longer carbonization times are required for the mixture of phenol with 1,2,3-benzotriazol to get rid of all not condensed carbon structures in comparison with the mixture of o-nitroaniline and 1,2,3-benzotriazol, as in Sample 5.

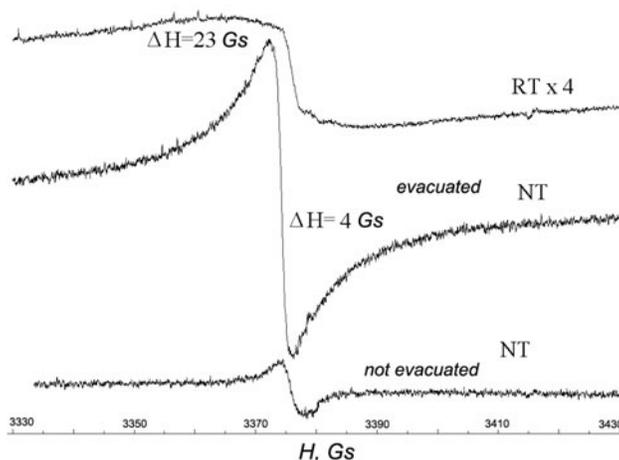


Figure 3. EPR spectra of Sample 6 after evacuation. The spectra were recorded at room temperature (RT) and liquid nitrogen temperature (NT).

4. Conclusions

One-dimensional conductivity of amorphous carbon material may be related to the presence of carbene (polyyne) in the carbon material. When the number of one-dimensional conductivity carriers (unpaired electrons) is not high, the samples show EPR signals. These EPR spectra widen when the carrier concentration grows with the preservation of the one-dimensional conductivity. The EPR spectra can also widen due to transformation of the one-dimensional conductivity to the three-dimensional one.

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