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Nanographites, Nanographite Systems and Their Intercalation Compounds

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Abstract

The structure and electronic properties of nanographites - the structural elements (blocks) of activated carbon fibers were investigated by different physical methods (X-ray diffraction, scanning tunnel microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy, ESR and magnetic susceptibility). The considerable enhancements of the intersheet distance and the density of states at the Fermi level were found. The reasons of these peculiarities are discussed.

Keywords: activated carbon fibers; nanographite; intercalation; absorption.

1. Introduction

Activated carbons are representative porous materials, which have been widely used in various technologies.¹ Activated carbon fibers (ACFs), which have large specific surface areas ranging about 1000-3000 m²g⁻¹, are microporous carbons consisting of a three dimensional disordered network of micrographites, where each micrographite has three to four graphene sheets with an average in-plane size about a few nanometers [1, 2] This particular structure makes ACFs a good model system of nanographites. There are a few reasons for an intently interest of scientists to nanographites. First, due to their intermediate position between the bulk graphite and aromatic molecules, nanographites are the potential source of new chemical substances with unusual electronic and magnetic properties. Second, while the fullerenes and carbon nanotubes are the close shaped π -electron conjugated systems [3] the electronic properties of which are mainly controlled by the quantum size and surface effects, the nanographites represent the edge-open π -electron conjugated system. The presence of open edges around the peripheral region can result in occurrence of specific features in nanographite systems, which are different from their closed-surface counterparts [4, 5]. Obviously, an arbitrary shaped graphene sheet comprises two kinds of edges: zigzag type and armchair type, while the former has a *trans*-polyacetylene type structure, while the later has a *cis*-polyacetylene type. The calculations for the model of graphite ribbons – one dimensional graphite lattices of finite width, show that ribbons with zigzag edges possess localized edge states with energies close to the Fermi level [4, 5]. These edge states correspond to the nonbonding molecular orbital (nonbonding π levels superimposed on the bonding π and antibonding π^* bands). In contrast, edge states are completely absent for ribbons with armchair edges. However, in a general finite graphene sheet consisting of both types of edges, even a few zigzag sites per sequence are shown to lead to non-negligible edge-state effects, resulting in an enhancement in the electronic density of states around the Fermi energy [5]. The theoretical investigations of the stacking effects in the zigzag nanographite sheets show that the edge states are

sensitive to the type of the graphene layers stacking and to the interlayer interaction [6, 7]. At last, it was shown that the edge states may determine the new magnetic properties in nanographene sheet, because of their relatively large contribution to the density of states at the Fermi energy [4]. The calculations show a remarkable difference in the magnetic properties between the different types of graphene layers stacking [6-8].

In this paper, we present the results of X-ray diffraction, scanning tunnel microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy, ESR and magnetic susceptibility study of nanographites - the structural elements (blocks) of ACFs, in order to clarify their structure and electronic properties.

2. Results and Discussion

The X-ray diffractograms of the ACFs show very broad peaks at the graphite (002), (100) and (101) positions, where graphite (100) and (101) peaks merge into a single broad peak around 20⁰. In order to estimate the sizes of the graphite nanoparticles in ACFs, the intensities of the experimental X-ray diffractograms were corrected by standard procedures.

Using the corrected (002), (100) and (101) peak parameters we estimate the thickness and the in-plane size of the particle grains. From the broad graphite (002) peak, we find a grain thickness of $L_c \approx 1-1,2$ nm. We deconvolute the broad feature around 20⁰-24⁰ into single (100) and (101) peaks on the assumption that each peak originates mostly from a single component. The obtained contribution to the (100) peak gives an estimate of the in-plane size of $L_a \approx 2$ nm. From the location of centre for the (002) diffraction peak the interlayer distance between graphene sheets in evacuated samples are estimated at 0,4 nm, which are considerably longer than the interlayer distance of 0.3354 nm for bulk regular graphite. From nanographite sample thickness and interlayer distance between graphene sheets, the number of graphene sheets is estimated at ~3-4.

The C1s spectrum of ACFs consists only of a single peak with the binding energy 284,4±0,1 eV. The lineshape parameters of signal considered are near the same for bulk

graphite. This fact testifies to absence or negligible amount of functional groups in ACFs.

The ESR spectrum of ACFs reveals two Lorentzian signals (Fig. 1). At temperatures above ~ 150 K only single signal from conduction electrons with a linewidth ~ 40 mT is observed. Below ~ 150 K, a second narrow signal from localized spins appears with a linewidth ~ 1 mT. The g values are estimated at $g=1,98$ and $2,01$ for the signals from conduction electrons and localized states, respectively. At lowering of the temperature the CESR signal linewidth increases at constant values of the g -factor and integral intensity.

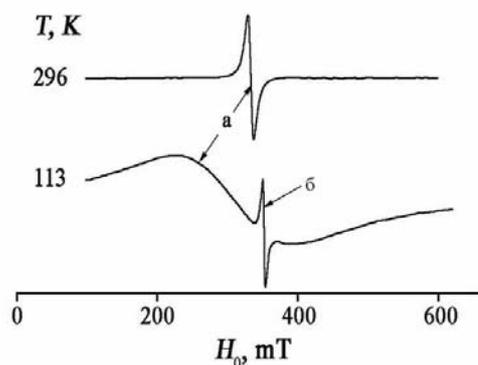


Fig. 1. The ESR spectrum of ACFs. (a – and b – the lines from conduction and localized electrons, respectively).

The magnetization curve shows the absence of the residual magnetization at different constant magnetic fields. The temperature dependence of the magnetic susceptibility χ_g for ACFs investigated is well described by the expression $\chi_g = 1.318e-5/(T+0.9) - 0.61e-6$. From this low, it follows that approximately one localized spin per 2500 carbon atoms (or ~ 1 localized spin per ~ 10 nanographites) are presented in fibers at low temperatures.

From comparison of integral intensities of signals from conduction electrons and localized spins (the concentration of latter is known from the magnetic susceptibility data), the density of states near the Fermi level in nanographites was estimated. Such calculations show, that it is more than one order of magnitude larger than in bulk regular graphite at the same value of Fermi energy [9]. The results obtained unambiguously indicate the presence of an additional band around the Fermi energy in nanographites that was proposed theoretically [4, 5]. Another reason of considered phenomenon is the deeper position of Fermi level in nanographite, than that in bulk regular graphite. Such displacement of the Fermi level in nanographites may be as the result of interaction of surface carbon atoms with some adsorbed molecules, such as water and oxygen. We shall note, that in acceptor graphite intercalation compounds a similar situation are realized and the value of displacement of the Fermi level may be significant (~ 1 eV [9]). Obviously, at the validity of the model considered, the position of the Fermi level in nanographites (as well as the sign and the value of charge on graphene layers) may be controlled by adsorption on their surface of different molecules.

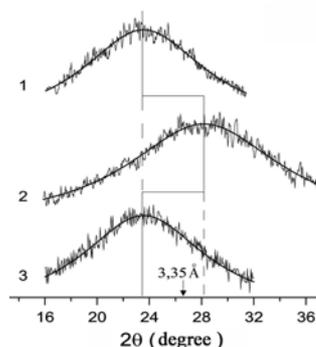


Fig. 2. The changes of (002) X-ray reflection for graphite nanoparticles – structural blocks of activated carbon fibers at absorption and desorption of water molecules. (1 – initial sample, 2 – sample after adsorption of water and 3 – sample after desorption of water).

In ACFs studied the intersheet distance in nanographites changes at the adsorption by fibers of water molecules (Fig 2). The possible reason for this is the large internal pressure from water molecules in pores, as water in the porosity of ACFs has a solid-phase structure with less density than that in the normal conditions [10]. It is obviously that the decrease of positive charge of graphene layers because of donating of electrons by the adsorbed water molecules may be another reason for this phenomenon. However, we believe, that the reason of discussed (002) X-ray reflection displacement at water absorption is the insertion of water molecules into the space between layers of nanographites.

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