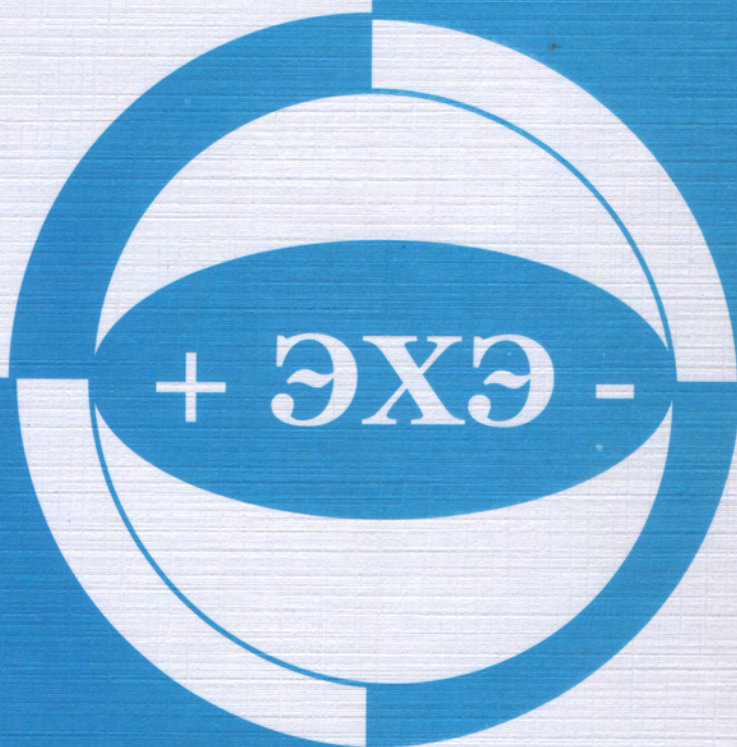


**ФУНДАМЕНТАЛЬНЫЕ  
ПРОБЛЕМЫ  
ЭЛЕКТРОХИМИЧЕСКОЙ  
ЭНЕРГЕТИКИ**

**VI Международная конференция**



**5–9 сентября 2005 года  
Саратов, Россия**

Министерство образования и науки РФ  
Российская академия наук  
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Саратовский государственный университет им. Н.Г. Чернышевского  
Российский фонд фундаментальных исследований

# ФУНДАМЕНТАЛЬНЫЕ ПРОБЛЕМЫ ЭЛЕКТРОХИМИЧЕСКОЙ ЭНЕРГЕТИКИ

*Материалы VI Международной конференции  
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Под редакцией профессора **И. А. Казаринова**

ИЗДАТЕЛЬСТВО САРАТОВСКОГО УНИВЕРСИТЕТА  
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**Фундаментальные проблемы электрохимической энергетики:**

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Сборник содержит материалы VI Международной конференции «Фундаментальные проблемы электрохимической энергетики», проведенной на базе Саратовского государственного университета им. Н. Г. Чернышевского. Представлены результаты исследований в области традиционных химических источников тока: щелочных, свинцово-кислотных, никель-металлогидридных аккумуляторов, электрохимических конденсаторов, топливных элементов.

В сборнике также приведены статьи, в которых отражены результаты научных исследований последних лет по фундаментальным проблемам литиевых источников тока. Большое внимание уделено природе процессов интеркаляции и деинтеркаляции лития в различные по природе структуры, физической химии электролитов (неводных, полимерных, гелеобразных, твердых), обсуждаются проблемы и перспективы литий-ионных аккумуляторов.

Для научных и инженерно-технических работников, занимающихся разработкой, совершенствованием и производством химических источников тока, преподавателей, научных сотрудников, аспирантов и студентов высших учебных заведений, специализирующихся в области электрохимии.

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# CONSOLIDATE NANOGRAPHITE SYSTEMS AND THEIR COMPOUNDS

*Albert M. Ziatdinov*

Institute of Chemistry, Far Eastern Branch of the Russian Academy of Sciences.  
690022, Vladivostok, Russia  
e-mail: albert\_ziatdinov@mail.primorye.ru

**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. Activated carbon fibers (ACFs), which have large specific surface areas ranging about  $1000\text{-}3000\text{ m}^2\text{g}^{-1}$ , 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  $\pi$ -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  $\pi$ -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*-poliacetylene 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  $\pi$  levels superimposed on the bonding  $\pi$  and antibonding  $\pi^*$  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  $20^\circ$ . 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  $20^\circ - 24^\circ$  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  $\sim 3 - 4$ .

The C1s spectrum of ACFs consists only of a single peak with the binding energy  $284,4 \pm 0,1$  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  $\sim 150$  K only single signal from conduction electrons with a linewidth  $\sim 40$  mT is observed. Below  $\sim 150$  K, a second narrow signal from localized spins appears with a linewidth  $\sim 1$  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.

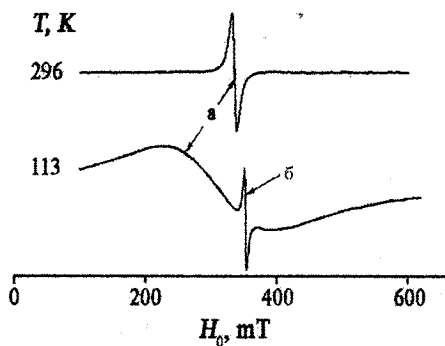


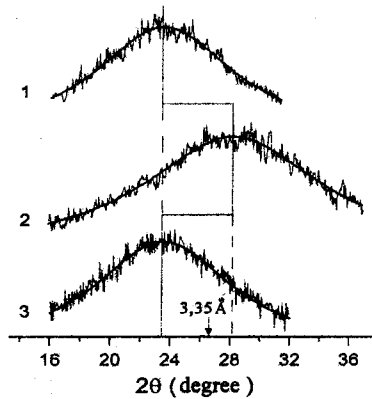
Fig. 1. The ESR spectrum of ACFs. (a – and b – the lines from conduction and localized electrons, respectively)

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

The magnetization curve shows the absence of the residual magnetization at different constant magnetic fields. The temperature dependence of the magnetic susceptibility  $\chi_g$  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  $\sim 1$  localized spin per  $\sim 10$  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

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



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

chlorine absorption is accompanied by the occurrence of localized spins and is not fully convertible. It specifies that some of absorbed chlorine molecules form covalent bonds with carbon atoms of nanographites.

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