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INFLUENCE OF GUEST MOLECULES ADSORPTION ON ELECTRONIC PROPERTIES OF ACTIVATED CARBON FIBERS

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Abstract. Problem of spin localization in activated carbon fibers (ACF) is discussed. Different substances were chosen to examine the influence of guest molecules on electronic properties of ACF. In comparison to purified ACF, the strongest changes in EPR spectrum were observed in two systems: ACF+H_2O and ACF+$C_6H_5NO_2$. Comparison between these two systems is presented in order to explain spectroscopic splitting factor *g* shift observed for the broader component of the EPR spectrum.

1. INTRODUCTION

Activated carbon fibers (ACF) are made up of nanometric graphite particles [1,2]. Mechanical linkage between these nanoparticles creates the porous system. ACF exhibit good adsorption properties with only weak host-guest interactions, thus are often used in research of confined systems [3,4]. Molecules confined in porous systems may show behavior of bulk material as well as nanoscale particles depending on different factors. Transition from continuum to molecular behavior of water confined in nanometer channels of closed multiwall carbon nanotubes appears for 5 and 10 nm diameter of carbon tube [5].

In presented experiments EPR silent substances were chosen to examine the influence of guest molecules on electronic properties of ACF. EPR spectrum of ACF changes significantly after guest molecules adsorption. Presence of guest molecules causes modification of the size of nanographite particles. The strongest effect is observed in case of water adsorption [6,7].

Mechanical linkage between nanographite particles is not necessarily electrically good. Adsorption process, which causes structural changes, also modifies conductive properties of ACF observed by EPR. Similar changes were detected for purified ACF in electrical conductivity measurements. Electrical properties evolve with decreasing temperature from half-metallic to nearly-insulating [8] consistently with granular metal model [9]. Modification of Coulomb gaps between ACF nanoparticles (by adsorption or

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temperature as well) causes entrapment of charge carriers at localized states. As a result, there is a strong increase in number of localized spins detected by EPR. For materials with constant number of non-interacting localized spins, integral intensity *I* of the EPR signal is described by Curie law resulting from Langevin paramagnetism. In ACF the spin number increases due to Coulomb-gap modification, causing additional increase of *I*. The model, which is a fusion of two approaches – Langevin paramagnetism and granular metal behavior, is proposed to describe *I(T)* dependence [10].

Potential wells system in which carriers are trapped, besides guest molecules, can also be modified by temperature. As a result spectroscopic splitting factor *g* changes. Applying the theory of EPR of small metal particles [11,12] the attempt of the mean grain size estimation of ACF's nanoparticles is made. Comparison between two systems: ACF + $C_6H_5NO_2$ and ACF + H_2O is discussed in order to present *g*-shift interpretation.

2. EXPERIMENTAL

EPR spectra of ACFs were acquired with Radiopan ES/X spectrometer, equipped with Oxford Instruments gas flow helium cryostat, in the temperature range 4.2÷300K. Observed EPR signal becomes well visible below 100K. Microwave frequency was measured by microwave frequency counter with an accuracy of 5 kHz. The magnetic field was calibrated by tracking NMR magnetometer with an accuracy of 0.005 mT.

Electric resistivity measurements were performed by the four-probe method with Picowatt RV-Elektronikka OY AVS-47 resistance bridge, equipped with helium-flow cryostat, in the temperature range of 20÷295K.

Fibers were acquired from Osaka Gas Chemicals Co. Ltd, Japan.

ACF samples were evacuated at 200 °C by pumping with turbomolecular pump at 10^{-4} mbar for 1 hour, to assure the pores are empty. Some samples were consecutively saturated with $C_6H_5NO_2$, H_2O, CCl_4 or CH_3OH guest molecules.

3. RESULTS AND DISCUSSION

3.1. Pure ACF

EPR

EPR spectrum, consisting of single Lorentzian line as shown in Fig. 1a, becomes observable only below 50K. Its spectroscopic splitting factor $g = 2.0031$ is equal to $g_\perp$ characteristic of graphite [13]. Peak to peak line width ΔB_{pp} is approximately 0.4 mT. Both, *g* and ΔB_{pp} are temperature independent. Integral intensity *I* of the signal increases with temperature lowering but it was difficult to prove the Curie-like behavior from the weak signal at narrow temperature range.

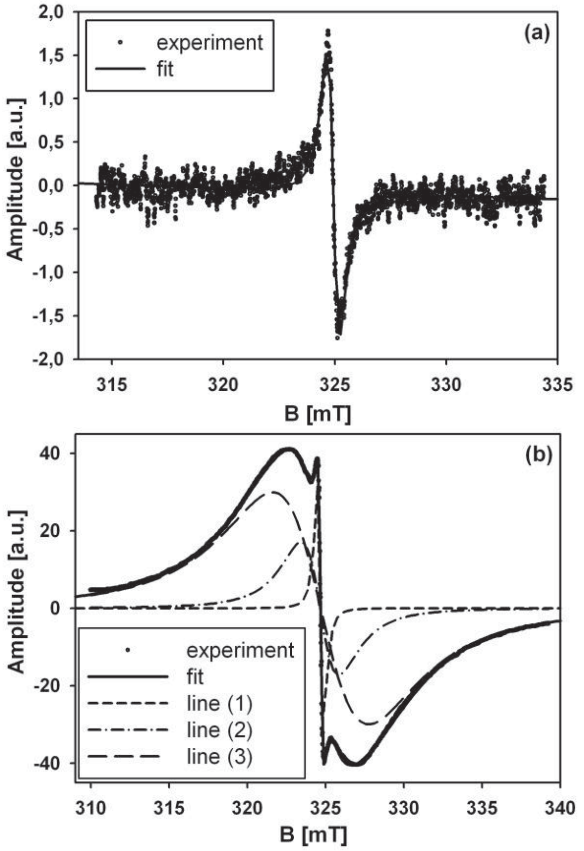

Fig. 1. EPR spectra of ACF recorded at 20K. (a) spectrum of pure ACF fitted with single Lorentzian line; (b) deconvoluted spectrum of ACF with adsorbed $C_6H_5NO_2$. Fit in (b) consists of three Lorentzian lines. Adsorption of guest molecules strongly influences nanographite electronic properties – signal gain in (b) is ten times lower than in (a).

Resistivity

In resistivity ρ measurements of a single fiber, temperature dependence $\rho(T)$ is consistent with the granular metal model with metal-insulator phase transition at low temperature region [1,9]. Fig. 2 shows

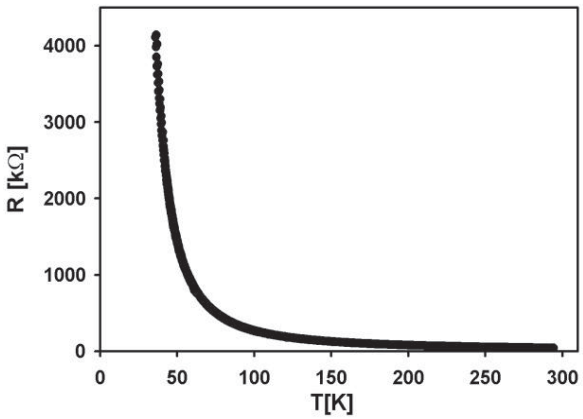

Fig. 2. Temperature dependence of ACF's resistance. Strong increase of resistance results from localization of charge carriers from conducting band.

characteristic behavior which confirms the model [10].

This behavior explains the only low-temperature existence of ACF's EPR signal, as EPR is hard to detect in case of delocalized spins from conducting band.

3.2. ACF + guest molecules

Strong changes appear in EPR spectra of ACF after adsorption of chosen substances. There is only physisorption case of examined substances, as can be seen on example of H_2O and CCl_4 adsorption/desorption experiment – Fig. 3. After desorption procedure, EPR signal is the same as the initial one.

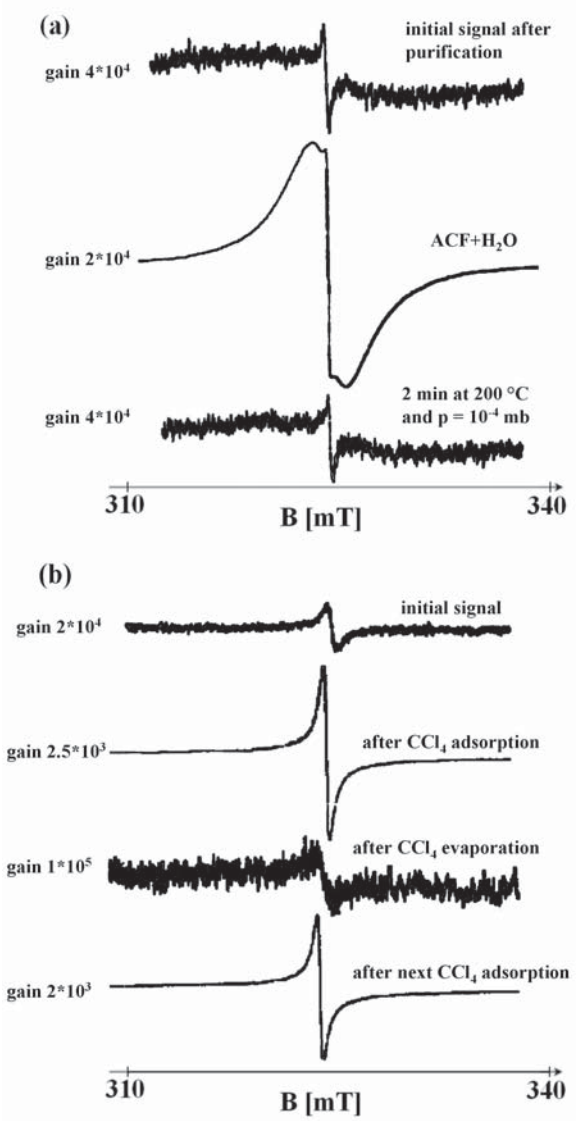

Fig. 3. Adsorption of different guest molecules: (a) H_2O and (b) CCl_4. Both substances cause strong modification of amplitude and shape of EPR spectrum of ACF. The process is fully reversible.

ACF + $C_6H_5NO_2$

EPR spectrum of such system is observable in higher temperature (about 120K) than the one of pure ACF. It means that conducting properties of ACF with filled nanopores are changed – the number of delocalized centers decreases. Also, the shape of the observed EPR line is changed. Result of the deconvolution procedure is shown in Fig. 1b. Line (1) is the same as for pure ACF, but its amplitude is much greater – it is the result of structural changes that may occur in ACF after adsorption [6]. These changes lead to localization of some part of carriers from conducting band. Line width and *g*-factor of line (1) are temperature independent (see Fig. 4 and 5a respectively), similarly as for pure ACF.

The additional, broader component of EPR spectrum consists of two Lorentzian lines. Both of them are related to the nanographite structure of ACF. Line (2) originates from nanographite particles (host) tightly surrounded by guest molecules captured in nanopores. Broadening of line (2), compared to (1), is caused by the shorter relaxation time of the more dense system. Line width and *g*-factor of line (2) are temperature independent, whereas both, line width and *g*-factor of line (3) strongly depend on temperature, as shown in Fig. 4 and 5a. Such a behav-

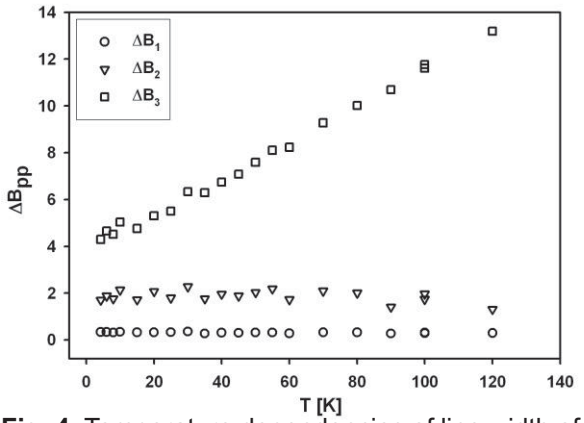

Fig. 4. Temperature dependencies of line width of three components of EPR spectrum of ACF. Strong instabilities of paramagnetic centers at the fiber's surface or in its large pores cause changes of the width of line (3) as a function of temperature.

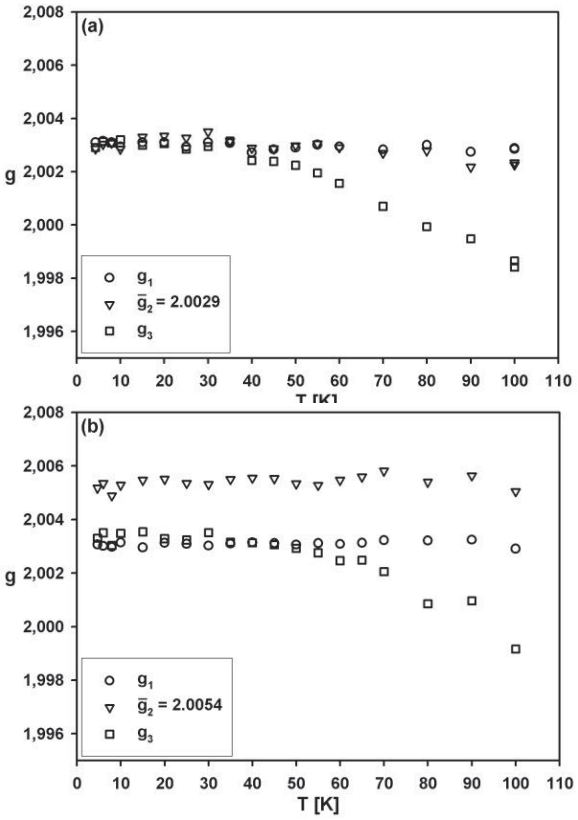

Fig. 5. Temperature dependencies of spectroscopic splitting factor *g*: (a) ACF + $C_6H_5NO_2$ and (b) ACF + H_2O. Increase of the *g* value of line (3) with lowering temperature confirms $\Delta B_{pp}(T)$ changes – compare with Fig. 4. Line (2) weak *g*-shift in (a) is a size effect, while in (b) there is a spin-orbit coupling, caused by shrinkage of lattice constant.

ior one can explain as a surface effect in ACF. Strong instabilities of paramagnetic centers at the fiber's surface or in its large pores give the temperature dependence.

Integral intensities of all three lines, constituting the EPR spectrum of ACF with guest molecules, increase with lowering temperature. *I(T)* dependencies of lines (2) and (3) are described by Langevin paramagnetism and hold the Curie law [10].

In case of line (1) the *I(T)* dependence is well described by the model which includes Langevin paramagnetism together with granular-metal character of ACF [10].

Curie-like behavior, as well as no visible hyperfine splitting arising from the interaction of unpaired electron spins with nuclear spins of H or N, ensures us that ACF can be considered as a system of nanographite particles, with paramagnetic centers strongly localized within the each single particle in low temperature region. For EPR centers localized at small conducting particles, quantum effect of trapped electrons in potential well is introduced – it is so called EPR theory of small conducting particles [11,12]. Such approach were proposed for fullerenes [14] and UDD (ultra dispersed diamond) [15] to estimate the size of described particles.

There are two effects modifying electronic properties of small particles (nanoparticles) – surface effects and quantum size effects [11]. It is due to the fact that nanoparticles have discrete structure of energy levels [11,12]. There is a strong influence of the size of a nanoparticle on the *g*-factor value.

General conclusion from papers [11,12] is that the absolute value of *g*-shift ($\Delta g = g - g_e$; $g_e = 2.0023$ is the value for free electron) should decrease with decreasing size of nanoparticle. The shift is described by following equation:

$$\Delta g(L) = \left[1 - \alpha \frac{a}{L}\right] \Delta g(\infty), \qquad (1)$$

$\Delta g(L)$ – *g*-shift of nanoparticle, *a* – lattice constant 0.335 nm, $\Delta g(\infty)$ – *g*-shift of a bulk material, *L* – radius of a spherical particle, α - parameter of the order of unity.

EPR measurements of paramagnetic centers localized on ACF nanocrystallites in the nitrobenzene-filled ACF show *g*-factor shift to lower values:

g_{bulk}=2.0031 [13],
$\bar{g}_{nanoparticle}$=2.0029 =$\bar{g}_{(2)}$,
where $\bar{g}_{nanoparticle} = \bar{g}_{(2)}$ is the mean value of *g*-factor of the line (2) (see Fig. 5a). Strong temperature dependence of the width of the line (3) (Fig. 4) suggests that the line originates from the instabilities that may occur in large pores or the fibers' surface. So, only the *g* value of line (2) have been taken into account. Substituting $\bar{g}_{(2)}$ to Eq. (1) we get the radius of spherical particles on which paramagnetic centers are localized. This radius is approximately 1.35 nm, what is in quite good agreement with the size of graphite nanocrystallites of ACF given in paper [1]. Obtained radius value shows that in case of $C_6H_5NO_2$ guest molecules, EPR centers are trapped at the edges of particles and are quantum delocalized in a potential well. Particle's surface play role of a potential barrier that prevents carriers from splitting out of the particle. $C_6H_5NO_2$ guest molecules can change the parameters of the potential wells which define *g*-factor value. Similar results were obtained in case of CCl_4 and CH_3OH adsorption where only drastic changes of spin number are registered after adsorption.

ACF + H_2O

EPR of ACF + H_2O system is similar to EPR of described above ACF + $C_6H_5NO_2$ with one important difference - *g*-factor of line (2) is shifted to higher values in comparison to *g* of line (1), see Fig 5b. This is due to the spin-orbit interaction caused by shrinkage of lattice constant in graphite nanoparticles, what is suggested in paper [6]. Spin-orbit interaction detected in strongly hydrophobic system of ACF + H_2O makes the use of the theory of EPR of small particles impossible. In this theory *g*-value changes with the particle's size. This size defines the potential well for paramagnetic centers. Additional effects can appear when guest molecules modify also the parameters of the potential well. In case of H_2O guest molecules, this modification leads to spin-orbit coupling.

4. CONCLUSIONS

There is a significant influence of guest molecules adsorption on electronic properties of ACFs. Two, new broader lines appear in the EPR spectrum of ACF after the adsorption. Each of them is connected with graphite nanoparticles that build ACF's structure. Guest molecules influence electrical contacts between nanoparticles – charge carriers from conducting band become trapped at localized states. After adsorption process resistivity of ACF decreases, while integral intensity of EPR signal increases, making EPR signal observable in higher temperature than before adsorption. As guest molecules modify potential wells in which spins are localized, *g*-factor value changes. In case of nitrobenzene adsorption *g* value decreases. It enables us to use theory of EPR of small particles and estimate the size of graphite nanoparticles that build ACF's structure. Water adsorption causes even more changes in the nanographitic system. Its molecules cause shrinkage of lattice constant. In this case spin-orbit interaction becomes significant and *g* value strongly increases for line which describe nanographite particles tightly surrounded by guest molecules. It means that the theory of EPR of small particles cannot be used because spin-orbit coupling veils size effects, which are visible when nitrobenzene molecules are adsorbed in ACF.

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