transport together with acceptable electronic conductivity. As shown in Fig. 3c, LFP/GN demonstrates acceptable rate performances though partial graphene wrapping limits the ion diffusion to inside LFP to some extent. Fig. 3d shows the cyclic voltammetry curves of LFP@GN and LFP/GN (scanning rate: 0.1 mV s^{-1}). The lower and weaker redox peaks of LFP@GN than the LFP/GN cases indicate a lower electrochemical reactivity of LFP@GN which is resulted from the shower Li^+ diffusion, which is in accordance with the DSC results. Based on the electrochemical impedance spectroscopy (EIS) profiles (Fig. 3e), it is found that the charge-transfer resistance of LFP@GN is much larger than that of LFP/GN, which is related to the Li^+ extraction and insertion reactions. This result further suggest that partial graphene wrapping is beneficial to the performance of LFP, while the full and tight graphene wrapping is resistive to the Li^+ transport, resulting in the large charge transfer resistance.

In this study, we use graphene as an ideal model to probe how carbon coating works in the enhancement of the electrochemical performance of LIB. The results indicate that a partial graphene coating provides a balance between increased electron transport and fast ion diffusion which shows an improved electrochemical performance, while full and tight graphene wrapping totally isolates active materials from the electrolyte and retards ion diffusion. Generally, an ideal carbon coating for LIB cathode should be characterized by highly graphitic structure guaranteeing excellent electron transport property together with the unimpeded path for fast ion diffusion.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2013.01.070.

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Charge carrier transport control in activated carbon fibers

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ABSTRACT

We present the results of measurements of electronic transport in an activated carbon fiber performed over a wide temperature range. The fiber had been subjected to the adsorption of various molecules, one type at a time. The presence of guest molecules inside the fiber's pores causes significant changes in the electronic transport which has been observed to depend on the molecules' dipole moment. Results show the possibility of controlling the charge carrier transport through the fiber by using specific adsorbents.

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Nanosized carbon systems, including the low-dimensional structures, are of current interest due to their unconventional properties and potential applications in nanotechnology and nanoelectronics (molecular electronics or spintronics). A single sheet of graphite called graphene has peculiar electronic and magnetic properties resulting from quantum effects [1]. Due to that the systems built of carbon nanoparticles connected by single graphene fragments can exhibit specific electrical transport properties.

Activated carbon fibers (ACFs) are mostly composed of graphite-like fragments which create the so-called nanographitic units (NGUs) [2]. NGUs are turbostratic stacks of 3–6 graphene sheets and a single ACF can be described as a texture of NGUs due to their random arrangement. The mechanical linkages (connections) between the NGUs are considered to form potential barriers for electron transport. Thus the NGUs create a system of electrically separated conducting particles, where conditions for existence of hopping, tunneling or Coulomb repulsion (at the edges of NGU) mechanisms are fulfilled according to the specific nanoparticle arrangement. ACF exhibits peculiar electronic transport behavior where effects characteristic of systems of quantum wells are controlled by the level of localization of carriers within the NGUs.

In our previous work we have suggested that the NGU system can be treated as a quantum-dot matrix [2,3], where it is possible to control the charge carrier transport by introduction of various molecules (adsorption) inside the porous texture of ACF. Presented results allow us to discuss the problem from the point of view of dielectric properties, with the dielectric constant as an important parameter used in different models.

Due to the host–guest interactions between the adsorbed molecules and the NGU system, parameters of quantum wells are modified [4] and a strong change in the localization of electrons within the system appears. This effect has been observed with electron paramagnetic resonance (EPR) [2]. We have shown that dipolar guest molecules cause the strongest changes of the EPR signal of ACF [2–4]. The changes of localization of electrons with lowering of the temperature have also been observed in the electrical transport measurements (and agreed with the EPR results), but so far experiments have been carried out only for ACF with empty pores.

In this letter we present the results of resistivity measurements performed for the ACF system described in our previous papers [2–4] with various guest molecules adsorbed within the pores. Pores were filled by injection of liquid guest molecules into the carefully pre-evacuated quartz tube containing the sample. This ensures that all accessible pores are filled with guest molecules. Similar method has been used in our dielectric spectroscopy and X-ray diffraction studies of phase transitions and high-pressure effects inside the pores [5]. To avoid evaporation of the guest molecules during the measurement procedure, samples were quickly cooled down to 4.2 K and the measurements were performed in the heating regime. Fig. 1 shows the rapid decrease of electrical resistivity ρ with the temperature T increase. Temperature-dependent localization is shifted towards the higher T values when the dipole moment of the guest molecules increases. The shift is the result of the stronger localization generated by guest molecules with larger dipole moment.

ρ versus T behavior shown in Fig. 1 is usually described in the frame of granular metal model [6] where electrical resistivity ρ follows the equation: $\rho = \rho_0 \exp(T_0/T)^{1/2}$; ρ_0 is a proportionality constant. T_0 parameter is defined by the slope of the line when plotting ρ in the logarithmic scale against $T^{-1/2}$. According to the different models presented in Ref. [7] the linear behavior over a wide temperature range (Fig. 2) evidences the charge-energy-limited tunneling conduction (CELTC), used also to describe the granular metallic systems [6]. Similar behavior with carrier hopping between the localized states

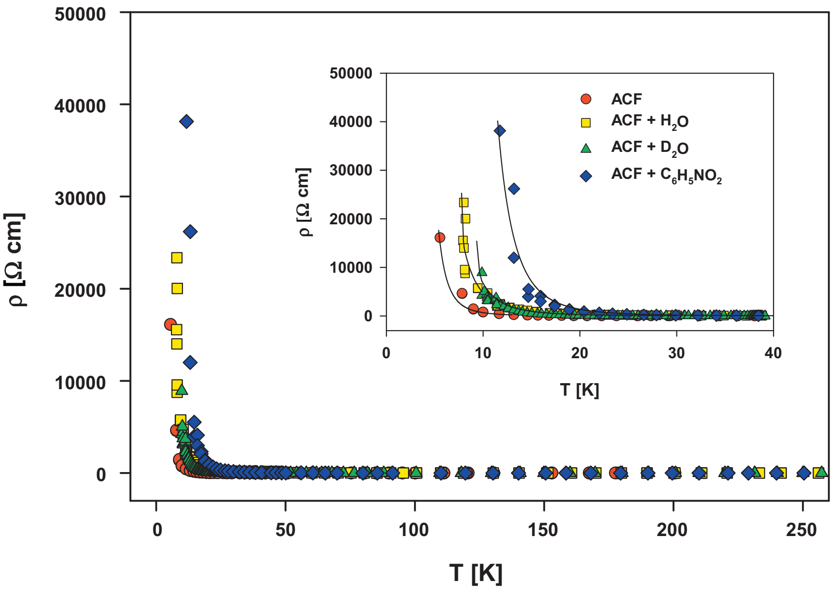

Fig. 1 – Resistivity versus temperature. Main figure shows the whole measured temperature range and presents the strong changes of ρ over the low temperature region. The inset zooms in low temperature region to clearly show that the strong change of resistivity shifts towards the higher temperatures with increasing dipole moment (lines are guides for eyes). It evidences that localization is an increasing function of dipole moment.

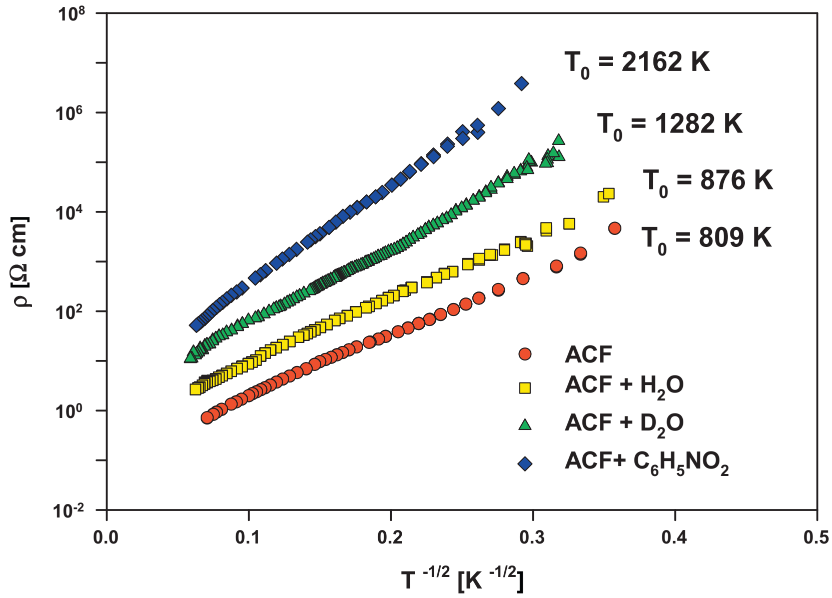

Fig. 2 – The logarithm of resistivity versus reciprocal square root of pure ACF and ACF filled with dipolar molecules. For clarity values of resistivity have been vertically shifted up by the factors of 30 Ω cm for ACF + D_2O and 100 Ω cm for ACF + $C_6H_5NO_2$.

has been observed in low temperatures for various temperature-treated carbon materials [8].

In general, when talking about granular systems with the hopping conduction, the T_0 parameter describes the energy which is needed to overcome the barrier separating the nanogranules (which, in our case are the NGUs). In the CELTC model T_0 is proportional to the charging energy E_c which is given by $E_c = 2e^2/Kd$ [6] where e is the electronic charge and K is the dielectric constant of the medium separating the nanogranules of diameter d. This way the T_0 parameter should decrease when K increases. Such tendency is shown in Fig. 2 where $K = 78.4$, 78.06 and 34,8 for H_2O, D_2O and $C_6H_5NO_2$ respectively (dipolar moments μ are as follows: 1.855 D, 1.852 D and 3.98 D).

Results from Fig. 2, especially for H_2O and D_2O, which have similar K and μ values, together with the above definitions of T_0 and E_c implicate that dielectric constant K in CELTC model is a parameter which is not connected with the medium located in pores, but rather characterizes the connections between the NGUs (that may be considered as insulating gaps) which are modified by local electric fields generated by dipoles (the guest molecules). These gaps can be as small as one carbon atom vacancy [7] what makes them fit to the tunneling model.

The reported change of T_0 seems to appear also due to the ionization of the molecules inside the pores what is clearly visible if to compare the results on adsorption of H_2O and D_2O in Fig. 2. Both, normal and heavy water have almost the same K and μ values but different dissociation ability pK_w ("*potentio*" of ionic product K_w): 13.9965 and 14.869 for H_2O and D_2O respectively[1]. It means that the easier dissociating normal water gives less number of dipoles responsible for the T_0 increase. Also new (ionic) transport path between the NGUs could be created by excess ions, what could additionally reduce the T_0 value.

Presence of guest molecules in ACF's porous system could also influence the behavior of nanographitic system in a different way, e.g. paramagnetism could be suppressed as a result of structural changes [9] resulting from the so-called high-pressure effect [5]. Such changes are also discussed in our earlier papers, e.g. [3].

Presented results are in good agreement with our previous EPR measurements and show that electronic transport in disordered carbon-based systems is very sensitive to the adsorption of guest molecules, with dipole moment playing an important role. Further research on the electronic transport in nanocarbons should aim at the better understanding of the properties of the single NGUs (for example by means of the scanning tunneling spectroscopy which can give insight into the local density of states of NGU) and the potential barriers between them in order to propose more exact model of controlled charge transport in nanocarbons and hopefully some application solutions.

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