



Nanoscale carbon materials from hydrocarbons pyrolysis: Structure, chemical behavior, utilisation for non-aqueous supercapacitors



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ABSTRACT

This work systematically studies adsorption properties of carbon nanomaterials that are synthesized through hydrocarbons that is a powerful technique to fabricate different kinds of carbon materials, e.g., nanotubes, nanoshells, onions, including nitrogen substituted. The adsorption properties of the as-synthesized carbons are achieved by low temperature nitrogen adsorption and organic vapors sorption. Heptane, acetonitrile, water, ethanol, benzene and 1-methylimidazole, which are of great importance for development of supercapacitors, are used as substrates. It is discovered that while nitrogen adsorption reveals a high specific surface area, this parameter for most of organic compounds is rather small depending not only on the size of its molecule but also on chemical interactions for a pair adsorbent–adsorbate. The experimental values of heat of adsorption for carbon and N-substituted structures, when Coulomb cross-coupling of nitrogen atoms in adsorbent and adsorbate takes place, confirms this supposition.

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1. Introduction

Due to their unique characteristics, carbon nanomaterials are suitable for different kinds of applications in various spheres of industry. They are also very promising as major component of electrode materials in most of electrochemical devices such as supercapacitors, Li-ion batteries, ionistors and solar cells [1–5]. Most of authors note that combination of high electric conductivity and specific surface area as well as correspondence between electrolyte ion size to pore size in material are responsible for their perspectives [2,6][2,6 (pp. 403–426,pp. 565–590,pp. 653–674)]. Present article is mostly devoted to media, suitable for supercapacitors. There are two main types of these devices: the former are based on water solutions of acids, bases or salts, the latter – on the use of organic electrolytes, which are quaternary ammonium or lithium salts (LiPF₆, LiBF₄) solutions in organic solvents such as acetonitrile, ethylene carbonate, propylene carbonate, acetone, etc. either ionic liquids [3,5,7,8]. Utilization of such systems allows to

expand operating voltage at least up to 2.7 V under temperature range –30 °C to +80 °C. Implementation of high voltage ionic liquids, which are the salts of high volume organic cations with different anions, can overcome even these limitations. Their solutions in appropriate organic solvents can also be used as electrolytes: one of the most common combinations is acetonitrile solution of imidazolium based ionic liquids with BF₄ or PF₆-anions [7]. The most promising results in such non-aqueous supercapacitors are revealed by carbon nanotubes, active carbon and carbon nanoshells [7,8].

In spite of some researches stressing the geometric correspondence between electrolyte and pores of electrode materials, the mechanism of interaction between them is still not clear from the point of weak chemical interactions. Present work describes the acetonitrile and 1-methylimidazole sorption on carbon nanoshells, nanotubes and active carbon. For the reference, interaction with water, which is the major impurity in supercapacitors electrolytes, ethanol, benzene and heptane was also studied. In all cases graphite powder was used as a non-porous substance for adsorption heat calculations. 1-Methylimidazole was used instead of imidazolium based ionic liquids since their vapor pressure is pretty negligible and the size of molecule is mostly determined by

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cation [8]. The results obtained might be very important for the future technological developments in supercapacitors and Li-ion industry as well as for other applications [9,10].

2. Experimental

Graphite (ash content less than 0.1 wt.%, water content less than 0.1 wt.%, NII “Graphite”), active carbon (ash content less than 0.1 wt.%, NII “Graphite”), purified cylindrical carbon nanotubes with 10–15 nm diameter (ash content less than 0.3 wt.%), carbon nanoshells (ash content less than 0.2 wt.%), N-doped carbon nanotubes (ash content less than 0.3 wt.%), N-doped carbon nanoshells (ash content less than 0.3 wt.%) from hydrocarbons pyrolysis were used in adsorption capacity measurements together with 1-methylimidazole (99.9%, Sigma), acetonitrile (99.99%, Merck), heptane (99.99%, Merck), ethanol (99.99%, Merck). Double distilled water was additionally purified by deionization until 18 Ω resistance.

Synthesis of carbon materials was carried by hydrocarbons pyrolysis apparatus by passing of benzene-based (99.9%, Reakhim) precursor mixture vapors over modified MgO template. Acetonitrile was added to the blend when obtaining N-doped materials. The experimental conditions are given in Table 1.

The as-synthesized carbon products containing amorphous carbon admixtures were further purified from metal oxide template by boiling in 10% solution of hydrochloric acid for 4 h with ultrasonication. After that the materials were washed with distilled water until neutral pH, annealed in the muffle furnace for 4 h at 330 °C and then dried in vacuum oven at 120 °C.

Low temperature nitrogen adsorption measurements were performed at 77.3 K using an automated surface area and pore structure analyzer Autosorb-1C/QMS (Quantachrome Inc., USA). Samples were degassed at 573 K for 3 h prior to adsorption analysis. BET surface area values for the samples were calculated from 5 points in a p/p^0 range of 0.1–0.3. The error of BET calculated surface area does not exceed 10%. For pore size distribution the experimental data were analyzed using a BJH and DFT approaches under cylindrical pore model.

The experiments on organic vapors adsorption were performed using DVS Advantage instrument (Surface Measurements Systems Inc., UK) operated at 20, 30 and 40 °C. The construction of device includes microbalances with sample cell placed in thermostatic chamber. The vapor of adsorbate carried by 100 ml/min purified nitrogen flow to sample cell with ca. 30 mg of adsorbent. Dry nitrogen provides the flow until given partial pressure will be reached at defined flowrate and temperature. The partial pressure raised by 5 p/p^0 step from 0 to 40%, then by 10% step from 40 to 90% and reduced back to 40% and finally from 40 to 0% by 5% step. The dew point was determined by precision optical sensor and then converted to the solvent partial pressure using the sample temperature and standard vapor pressure tables. 2 mkg/min mass change was used as equilibrium criteria. Experimental data were analyzed using DVS Analysis program package.

The heat of sorption is considered to be the amount of energy absorbed or released when the vapors sorbs by the sample. An adsorption isotherm describes a sample's equilibrium vapor uptake as a function of vapor partial pressure. If isotherms were measured at

different temperatures, assuming that heat of sorption is only exothermic and does not depend on temperature, it is possible to calculate the isotheric heat of sorption (ΔH_S) using Clausius–Clapeyron type equation:

$$\left(\frac{\partial \ln p}{\partial T}\right)_\theta = -\frac{\Delta H_S}{RT^2}. \quad (1)$$

Taking into account that $(d(1/T)/dT) = (-1/T^2)$, this equation can be written as

$$\left(\frac{\partial \ln p}{\partial (1/T)}\right)_\theta = \frac{\Delta H_S}{R}. \quad (2)$$

If the partial pressures (p_1 and p_2) at two temperatures (T_1 and T_2) under the same surface are obtained, then the heat of sorption can be calculated directly from

$$\Delta H_S = -R \frac{\ln(p_2/p_1)}{(1/T_2) - (1/T_1)}. \quad (3)$$

Simultaneous thermal analysis of the carbon materials was performed with STA 449 PC Jupiter thermal analyzer (Netzsch GmbH, Germany) connected with quadrupole mass spectrometer QMS 403C Aeolos (Netzsch GmbH, Germany) in the synthetic air atmosphere under 10 K/min heating rate.

Vario MicroCube elemental analyzer (Elementar GmbH, Germany) was used for elemental analysis (EA) of materials for C, H, N, S and O. Combustion products in it were analyzed by temperature-program adsorption–desorption technique with gas thermal conductivity and infra-red detectors.

XPS analysis was performed on Kratos Axis DLD spectrometer operated at monochromatic MgK α radiation under X-rays gun power 150 W at –120 °C. The spectra were recorded at a transmission energy of 160 eV for the general spectrum and at 40 eV for the spectra of separate lines. The preliminary calibration of the energy scale corresponded to the following reference peak values: Au 4f_{5/2} 83.96 eV, Cu 2p_{3/2} 932.62 eV, and Ag 3d_{5/2} 368.21 eV. To minimize the sample charging effect, a charge neutralizer was used. The spectra were calibrated against the C1s peak of carbon adsorbed on the sample surface, assuming the binding energy of the component corresponding to C–C/C–H bonds to be 285.0 eV. Spectrum decomposition into components was performed with Casa XPS program package.

Cyclic voltammetry measurements of supercapacitors assemblies made from prevacuumed components were performed using Biologic VSP-219 potentiostat–galvanostat in symmetrical cell option in 0–3.5 V potential range at sweep rate of 5, 20 and 30 mV/s up to 50 cycles. The integral capacitance under charging and discharge was calculated from:

$$C_{\text{int.charge}} = \frac{(Q_2 - Q_1)}{[m \times (E_2 - E_1)]}, \quad (4)$$

and

$$C_{\text{int.discharge}} = \frac{(Q_3 - Q_2)}{[m \times (E_3 - E_2)]}, \quad (5)$$

where Q_1 is initial charge, Q_2 , charge after charge, Q_3 , transferred charge during discharge, $E_2 - E_1$, voltage difference in charge (V),

Table 1
The conditions of carbon nanomaterials synthesis.

Catalyst/template	Precursor	Content/wt.% ^a : C _{am} /ash	Synthesis temperatures (°C)	Product
Co _{0.03} Mo _{0.01} MgO	C ₆ H ₆	1.4/1.1	750	Cylindrical CNT
Co _{0.03} Mo _{0.01} MgO	Acetonitrile	1.5/1.8	750	N-doped CNT
MgO	C ₆ H ₁₄	0.5/0.5	800	Carbon nanoshells
MgO	Acetonitrile	2.8/2.6	800	N-doped nanoshells

^a Amount given is on the basis of thermal analysis results.

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