Advanced nanostructured carbon materials for electrical double layer capacitors

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Abstract. Thermodynamical and electrochemical characteristics for the non-aqueous electrolyte | nanostructured carbide-derived carbon (CDC), activated carbon cloth (ACC) or commercial activated nanoporous carbon RP-20 (from Kuraray Chemical Co.) interface have been established by XRD, Raman spectroscopy, BET, cyclic voltammetry and electrochemical impedance spectroscopy. The gas adsorption measurement data have been used for the obtaining the specific surface area, pore size distribution, nanopore volume and other characteristics, dependent on the nanostructured carbon used (nanopores are pores in the range of 2 nm and below — i.e. micropores according to IUPAC classification).

1. Introduction
Nanostructured carbons are attractive electrode materials with the unique nanoporous structure, narrow pore size distribution and possibility to fine-tune the pore size [1-4] for electrodes of electrical double layer capacitors (EDLC), commonly called supercapacitors [5-12]. EDLCs are the very important energy storage and conversation systems, which can be used in the various pulse energy generation instruments. The charge storage in EDLC is based mainly on the electrostatic interactions i.e. physical Gibbs adsorption of ions at/inside porous electrodes, determining the very good reversibility and cyclability of EDLC systems. However for the optimal energy density — power density regime the nanoporous carbide material characteristics have to be optimised [5-11]. This paper reports the results of the systematic studies of the interface non-aqueous electrolyte | activated nanoporous carbide-derived carbon (CDC), activated carbon cloth (ACC) AUVM and commercial nanoporous carbon RP-20 additionally activated by us at different temperatures from 950 to 1150°C [13].

2. Measurement methods and experimental data
XRD analysis was carried out on powder samples to investigate the structural changes at different chlorination or activation temperatures of carbon by using CuKα radiation with a step size of 0.05° glancing angle θ and with the holding time of 1s at fixed θ. The 1mm thick powder sample was placed on a plastic holder and the diffraction spectra were recorded at 25°C. Raman spectroscopic analysis was carried out using Nd:YAG laser excitation (λ = 532 nm). The first-order Raman spectra for graphite show one peak at 1582 cm⁻¹, whereas disordered amorphous carbon generally demonstrates two peaks [14,15]: the so-called graphite (G) peak at 1582 cm⁻¹ and the so-called disorder-induced (D) peak at 1350 cm⁻¹ and it was found that the nanostructured carbons studied in this work have mainly amorphous structure.
Porosity analysis was carried out at temperature of liquid nitrogen using the Quantachrome Nova 1200 System. Specific surface area ($S_a$) (Table 1), pore size distribution, micropore volume ($V_m$), micropore area ($S_m$) and other parameters were calculated according to the non-local density functional theory (NLDFT) [16] and Brunauer-Emmett-Teller (BET) [17,18] approximations.

Table 1. Pore characteristics of selected nanostructured carbon materials.

| Nanostructured carbon | C(α-SiC) | C(TiC) | C(Mo₂C) | C(B₄C) | C(Al₄C₃) | AUVM   | RP-20  |
|-----------------------|----------|--------|---------|--------|----------|--------|--------|
| $S_a$                 | 1085     | 1505   | 1490    | 1525   | 1470     | 1495   | 1358   |
| $S_m$                 | 1030     | 1205   | 0       | 930    | 1130     | 1284   | 1056   |
| $V_m$                 | 0.46     | 0.60   | 0       | 0.43   | 0.57     | 0.56   | 0.48   |
| $V_{tot}$             | 0.49     | 0.75   | 1.50    | 0.99   | 0.74     | 0.80   | 0.79   |
| $D_{NLDFT}$           | ~0.7     | ~0.8   | ~4.0    | ~1.3   | ~0.8     | ~1.1   | ~1.1   |

$S_a$ — BET specific surface area (m$^2$g$^{-1}$), $S_m$ — micropore surface area (m$^2$g$^{-1}$), $V_m$ — micropore volume (cm$^3$g$^{-1}$), $V_{tot}$ — total pore volume (cm$^3$g$^{-1}$), $D_{NLDFT}$ — peak pore diameter calculated according to NLDFT method (nm).

According to the data in Table 1 the BET specific surface area, micropore surface area, micropore and total pore volume, NLDFT median pore diameter (Fig. 1) and the nanopore size distribution depend noticeably on the nanoporous carbon material synthesised and investigated. For C(α-SiC) there are practically only nanopores at the surface of carbon electrode but for C(Mo₂C) there are no nanopores on the surface at all. Thus, the total pore volume $V_{tot}$ and micropore volume $V_m$ values depend noticeably on the raw material (crystallographic structure and electron configuration of the central element in binary carbide) used for the synthesis of the nanoporous carbon material. These results obtained are in a good agreement with the data of Refs [1-7]. The EDLC electrodes were constituted from an aluminium foil current collector and the active material layer, consisting of nanoporous carbon prepared from TiC, Mo₂C, α-SiC, Al₄C₃ and B₄C (noted as C(TiC), C(Mo₂C), C(α-SiC), C(Al₄C₃) and C(B₄C), respectively) by the chlorination method [2,3,6,8-11].

Figure 1. Pore size distribution for nanostructured carbon prepared from different precursor carbides [2,3].

The mixture of nanoporous carbon, binder (polytetra-fluoroethylene PTFE, 60 % solution in H$_2$O) and of the carbon black was laminated on the Ni foil and pressed together to form a very flexible layer of the active electrode material (thickness 60-250 μm). After drying and plating under vacuum, the pure Al layer ($3±1$ μm) has been vacuum-spray evaporated onto the one side of the carbon material.
using plasma activated physical vapour deposition [2,3,6,8-11]. After that the Al-covered nanoporous carbon layer was spot-welded in the Ar atmosphere to the Al foil current collector.

The three electrode standard glass cell with a large counter electrode (apparent area ~30 cm$^2$), prepared from the carbon cloth (AUVM) was used for the investigation of various carbon material electrochemical fundamental characteristics. The reference electrode was an aqueous saturated calomel electrode (SCE) connected through the electrolytic salt bridge with the measurement system. Pure Ar (99.9999%) was used for saturating of the solutions.

The cyclic voltammetry ($j,E-$) curves for C(TiC), C(Al$_4$C$_3$), C(Mo$_2$C) and C(B$_4$C) electrodes in 1 M (C$_2$H$_5$)$_3$CH$_3$NBF$_4$ solution (Fig. 2), obtained at small scan rates of potential $v = dE/dt \leq 5$ mV s$^{-1}$, have nearly mirror image symmetry of the current responses about the zero current line ($j$ – current density, obtained using the flat cross section (geometrical) surface area). The current density values at $E > 0.5$V (SCE) increase in the order of materials C(B$_4$C)< C(Mo$_2$C)< C(Al$_4$C$_3$)< C(TiC)< C(α-SiC). The current densities obtained for C(α-SiC) are very small at $E < -0.3$V (SCE) and there are very well expressed distortion effects caused by the very small micropore diameter $D_{NLDFT}$ values for this electrode material (Table 1). Thus, it can be concluded that the micropores with medium diameter $D_{NLDFT} \leq 0.7$ nm are to small for the effective adsorption of big (C$_2$H$_5$)$_3$CH$_3$N$^+$ cations into the nanopores (Fig. 2) at negatively charged electrode surface. The cyclic voltammograms show that the so-called ideal capacitive behaviour for nanostructured carbons has been established at potential scan rates $v \leq 10$ mV s$^{-1}$ and $\Delta E \leq 3.2$ V. There is a very well detectable minimum in $j,E-$curves, corresponding to the total zero charge potential for the non-aqueous electrolyte | nanostructured carbon interface, depending on the carbon and electrolyte used. At higher scan rates the so-called distortion effects [6,10,11,19-23] were observed in the region of the potential switch-over.

![Figure 2](image_url). Current density vs. potential curves for nanostructured carbon materials: 1-C(α-SiC), 2-C(TiC), 3-C(Al$_4$C$_3$), 4-C(Mo$_2$C) and 5-C(B$_4$C)) in 1M (C$_2$H$_5$)$_3$CH$_3$NBF$_4$ + AN solution at potential scan rate 50 /mV s$^{-1}$.

The electrochemical characteristics of the electrical double layer capacitor (EDLC) single cell (two-electrode system) based on the nanoporous carbon electrode in 1M (C$_2$H$_5$)$_3$CH$_3$NBF$_4$ solution in various non-aqueous electrolytes [8,9] using the cyclic voltammetry (CV) and the electrochemical impedance spectroscopy (EIS) methods.

The values of total capacitance of the two-electrode cell, C, can be calculated from the cyclic voltammetry data ($j,E-$curves) according to Eq. (1)
if we assume that total capacitance of cell is constant and if the series resistance $R_s \rightarrow 0$ or if the current $I \rightarrow 0$. In a symmetrical two-electrode system, specific gravimetric capacitance $C_g$ (farads per gram) for one activated carbon electrode, to a first approximation, can be obtained from the total capacitance of the cell by Eq. (2):

$$C_g = \frac{2C}{m}$$

where $m$ is the weight in grams of activated carbon. It should be noted that Eq.(2) is correct only if the capacitance of positively and negatively charged electrodes is the same. Electrochemical characteristics of some selected nanoporous carbon materials in various non-aqueous electrolytes are presented in Table 2.

**Table 2.** Electrochemical characteristics for selected nanostructured carbon materials in various 1M non-aqueous electrolyte solutions [2,3,6,8,9,13].

| Nanostructured carbon | $d_{cl}$ ($\mu$m) | Solvent | Salt                  | $C_s$ (F cm$^{-2}$) | $C_s$ (F g$^{-1}$) |
|-----------------------|-------------------|---------|-----------------------|---------------------|-------------------|
| C(TiC)                | 60                | AN      | (C$_2$H$_5$)$_4$NBF$_4$ | 0.34                | 99.1              |
| C(TiC)                | 100               | AN      | (C$_2$H$_5$)$_4$NBF$_4$ | 0.60                | 85.5              |
| C(TiC)                | 150               | AN      | (C$_2$H$_5$)$_4$NBF$_4$ | 0.94                | 79.7              |
| C(TiC)                | 200               | AN      | (C$_2$H$_5$)$_4$NBF$_4$ | 1.06                | 75.5              |
| C(TiC)                | 250               | AN      | (C$_2$H$_5$)$_4$NBF$_4$ | 1.30                | 74.1              |
| C(α-SiC)              | 100               | AN      | (C$_2$H$_3$)$_3$CH$_3$NBF$_4$ | 0.14                | 16.3              |
| C(Mo$_2$C)            | 100               | AN      | (C$_2$H$_3$)$_3$CH$_3$NBF$_4$ | 0.63                | 120.0             |
| C(Al$_4$C$_3$)        | 100               | AN      | (C$_2$H$_3$)$_3$CH$_3$NBF$_4$ | 0.60                | 82.3              |
| C(B$_2$C)             | 100               | AN      | (C$_2$H$_3$)$_3$CH$_3$NBF$_4$ | 0.47                | 70.9              |
| C(TiC)                | 100               | AN      | (C$_2$H$_3$)$_3$CH$_3$NBF$_4$ | 0.69                | 98.3              |
| C(TiC)                | 100               | AC      | (C$_2$H$_3$)$_3$CH$_3$NBF$_4$ | 0.61                | 86.9              |
| C(TiC)                | 100               | GBL     | (C$_2$H$_3$)$_3$CH$_3$NBF$_4$ | 0.65                | 92.6              |
| C(TiC)                | 100               | PC      | (C$_2$H$_3$)$_3$CH$_3$NBF$_4$ | 0.61                | 86.9              |
| ACC AUVM              | 250               | AN      | (C$_2$H$_3$)$_3$CH$_3$NBF$_4$ | 1.18                | 51.3              |
| ACC AUVM              | 250               | EC+DMC+EA (1:1:1) | (C$_2$H$_3$)$_3$CH$_3$NBF$_4$ | 1.26                | 54.8              |
| ACC AUVM              | 250               | PC+DMC+EA (1:1:1) | (C$_2$H$_3$)$_3$CH$_3$NBF$_4$ | 1.21                | 52.6              |

$d_{cl}$ — thickness of the nanoporous carbon layer, $C_s$ — series differential and specific capacitances at $E$= -1.4 V vs SCE and at $f$= 5 mHz.

It should be noted that the specific capacitance of the monocrystalline carbon plane depends highly on the crystallographic structure $(h:k:l:m)$ of the surface exposed at the carbon electrode surface [8-11,21,24]. However the specific surface double layer capacitance of the high surface area activated carbons for double layer capacitors is dominated by the space-charge surface layer capacitance [2,3,6,8,9], and the very thin pore walls may result in capacitance saturation [25]. However, this effect was not seen in our experiments and thus the carbon layer capacitance seems to remain constant during activation of RP-20, but the increasing pore volume leads to a decrease in the mean thickness of pore walls [26]. Assuming a slit-shaped pores model [27] for nanostructured carbon studied, we can
estimate the mean pore wall thickness ($\delta_w$) by using the relation $\delta_w = 2/(\rho \beta_{BET})$, where $\rho = 2.2 \text{ g cm}^{-3}$ is the density of the carbon walls equaling to the density of pure graphite (Table 3). According to these data, the value of $\delta_w$ are maximal for C($\alpha$-SiC) carbon. Thus, the mean pore wall thickness $\delta_w$ depends on the median pore diameter calculated according to NLDFT method (Table 1).

Table 3. Average pore wall thickness $\delta_w$ for different nanostructured carbon materials studied.

| Nanostructured carbon | $\delta_w$ (nm) |
|-----------------------|-----------------|
| C(TiC)                | 0.60            |
| C($\alpha$-SiC)       | 0.84            |
| C(Mo$_2$C)            | 0.61            |
| C(Al$_4$C$_3$)        | 0.62            |
| C(B$_4$C)             | 0.60            |
| ACC AUVM              | 0.61            |
| RP-20                 | 0.67            |

For the detailed analysis of adsorption processes (charge accumulation, mass transfer) of ions at nanoporous carbon electrodes the various model approximations have been tested including classical Frumkin—Melik-Gaikazyan [28], Randles [29], Paasch et al. [30] and Meyer et al. [31] models.

Results of non-linear regression analysis of the Nyqu ist (complex impedance) plots show that, to a first very rough approximation, these plots can be formally simulated using the modified Frumkin—Melik-Gaikazyan—Randles (or Ershler-like) equivalent circuit with the chi-square function $\chi^2 \geq 1.8 \times 10^{-3}$ and weighted sum of squares $\Delta^2 \geq 0.25$ for the 1.0 M (C$_2$H$_5$)$_4$NBF$_4$ solution (Fig. 3; scheme I), where the generalised finite length Warburg element (GFW) with the reflective boundary condition (finite length transmission line terminated with an open circuit) is expressed as

$$Z_{GFW} = \frac{R_D \coth[(iT\omega)^{\alpha_W}]}{(iT\omega)^{\alpha_W}}$$

(3)

where $R_D$ is the so-called limiting diffusion resistance, the frequency parameter $T$ is expressed as $T = L^2 / D$, where $L$ is the effective diffusion layer thickness and $D$ is the effective diffusion coefficient of a particle, $\alpha_W$ is a fractional exponent varying from 0 to 1. The values of $\alpha_W$ higher than 0.5 indicate to the deviation of nanoporous carbon electrode | AN + 1 M (C$_2$H$_5$)$_4$NBF$_4$ system from the classical semi-infinite diffusion model [28-30], increasing with dilution of the electrolyte and with the increase of the active nanoporous carbon layer thickness and negative polarization of nanoporous carbon electrode [6]. The parallel charge transfer (or adsorption) resistance $R_{ad}$, as well as diffusion resistance $R_D$ increase with increasing the negative electrode potential, and with decreasing the electrolyte concentration and thickness of the nanoporous carbon electrode active layer [6]. The frequency parameter $T$ has minimal values in the region of $E_{\sigma,0}$ and $T$ increases with $d_{el}$. 

![Diagram](image-url)
Figure 3. Equivalent circuits used for fitting the experimental Nyquist plots: I – combined Frumkin-Melik-Gaikazyan and Randles (so-called Ho [29] circuit, where $R_1$ is the high frequency series resistance ($R_1 = Z'(\omega \to \infty)$), CPE – constant phase element, $R_{ad}$ – the charge transfer resistance, $Z_W$ is the Warburg-like diffusion impedance and $C_{ad}$ is adsorption capacitance; II – Paasch et al. circuit, where $dY$ is the complex admittance of the hindered charge transfer reaction (involving the hindrance factor $y(\omega)$ of the charge transfer reaction with the charge transfer conductance $g_{ct}$), $dC_{dl}$ is the double layer capacitance, $dR_1$ and $dR_2$ are the ohmic resistances of the porous electrode material and of the electrolyte in the pores, in the volume element $A_dx$ [30], respectively.

Figure 4. Nyquist plots ($-Z', Z'$) for nanostructured carbon electrode material C(TiC) (thickness of nanoporous carbon layer $d_{el} = 100 \mu m$) | acetonitrile + 1 M (1) and 0.1 M (2) (C$_2$H$_5$)$_4$NBF$_4$ interfaces at -1.4V vs SCE, (symbols – experimental data; solid lines – simulation according to Paasch et al. model [30]. However, a better agreement between simulations and experimental data for nanoporous carbon electrode | 1 M (C$_2$H$_5$)$_4$NBF$_4$ + AN interface with the chi-squared function $\chi^2$ ($\chi^2 \leq 6 \times 10^{-4}$) has been established if the Paasch et al. model I [30] (circuit II in Fig. 3 and Fig. 4) has been used. According to results of simulations, the values of characteristic frequencies $\omega_2; \omega_3 \ll \omega_0$, and thereby the relative magnitudes of $\omega_1, \omega_2$ and $\omega_0$ determine the low-frequency behaviour of the Nyquist plots ($\omega_0, \omega_1, \omega_2$ and $\omega_0$ are characteristics frequencies, discussed in more detail in Refs. [2,3,6]). For that reason at very low frequency $f \leq 5 \times 10^{-2}$ Hz, there is a transition to a pure capacitive behaviour, since both the field diffusion and the species diffusion are finite. In the region of frequencies $0.2 < f < 10$ Hz, the absolute value of the slope equal to $\pi/4$ at $E = E_{red}$ for Nyquist plot was observed around $\omega_2$, where the diffusion of the species in the solution phase dominates. At higher frequency ($f \geq 40$ Hz), the shape of the the impedance spectra is determined mainly by the ratio of the $\omega_0$ and $\omega_1$ values, i.e. by high frequency processes without regard to the diffusion of ions inside the pores.

The dependence of the function $X_B = d_{el}[(\rho_1\rho_2)/(\rho_1+\rho_2)]$ on $E$ as well as on $d_{el}$ indicates that the value of the electrolyte resistance per unit length $\rho_2$ inside a porous material depends very noticeably on the electrolyte concentration, solvent viscosity as well as on the electrode potential. The obtained value of resistivity of the electrode material per unit length $\rho_1$ is independent of the electrolyte concentration studied [6]. It should be noted that the simplified Meyer et al. model [31] where the intercalation of ions into the nanoporous carbon material has not been taken into account can be used for the fitting of the impedance data for nanoporous carbon | non-aqueous electrolyte systems with very good fitting parameters.
3. Conclusions
The micro-, meso- and macropore characteristics have been obtained using gas adsorption, X-ray diffraction and Raman spectroscopy methods.

The nanoporous carbide-derived carbon (CDC), activated carbon cloth AUVM and commercial nanoporous carbon RP-20 additionally activated at $950^\circ C < T < 1150^\circ C$ were investigated in 1M (C$_2$H$_5$)$_3$CH$_3$NBF$_4$ acetonitrile, propylene carbonate, $\gamma$-butyrolactone and mixed solvent systems solutions, using two and three electrode test cells and different electrochemical (cyclic voltammetry, impedance) methods. The results of the cyclic voltammetry and impedance studies indicate that the measured capacitance depend noticeably on the nanostructured carbon used, on the thickness of active carbon layer and electrolyte composition as well as on the electrode potential applied. Some systematic trends of the influence of pore size distribution and pore volume on the electrochemical parameters have been established and discussed.

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