NITROGEN CONTAINING COMPOSITES AS ATTRACTIVE CAPACITOR ELECTRODES

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INTRODUCTION

Carbon nanotubes are of great interest for electrochemical use because of their extraordinary physical characteristics. Especially, their electrical conductivity and mechanical properties (high resiliency) as well as mesoporous character are profitable for formation of various electrode composites with polymers, conducting polymers and transition metal oxides. Such composites appear to be interesting materials for supercapacitors. High power supercapacitor is able to supply or collect a charge in a short time, e.g. for starting vehicle or recovery energy from braking. It is an attractive power source of long-durability mainly for hybrid application. Hence, for this application, the electrode materials with a quick charge propagation and a good cyclability is demanded.

It has been already proved that the capacitance values of pure nanotubes are moderate from 10 to 40 F/g (per electrode material) because of poor microporosity, i.e. low surface area. Enhancement of capacitance values can be realized through pseudocapacitance effects, i.e. quick faradaic reactions (Frackowiak, E. 2000.) In this case, instead of developing the specific surface area, pseudo-faradaic properties can be used. One of the most interesting routes based on pseudoeffects is doping of carbon through foreign elements, e.g. nitrogen (Jurewicz, K. 2003, Kodama, M. 2004, Hulicova, D. 2005, Beguin, F. 2005, Lota, G. 2005, Hulicova, D. 2006, Frackowiak, E. 2006, Lota, K. 2007). Presence of nitrogen in carbon material can enhance capacitance due to the following effects: faradaic redox reactions, increase an electron donor capability and improvement of electrode wettability. Our target is to investigate this beneficial effect of nitrogen in the composite with incorporated nanotubular bacbone.

EXPERIMENTAL

For preparation of Nt-rich composites, a polymerisation of melamine (Fluka purity > 99%) with formaldehyde (Chempur 36-38% p.a.) in the presence of controlled amount of nanotubes was performed. Polymerisation was done without any catalyst. The polymerised blend was subjected to carbonisation at 750 ^{0}C for one hour under nitrogen flow. The final carbonisation product was named M+F (i.e. melamine with formaldehyde) whereas Nt+M+F means composite with carbon nanotubes. 2M and 3M stands for a twofold and threefold melamine proportion in the blend.

Transmission electron microscopy (TEM) observations of composites were performed using JEM3010 apparatus. The elemental analysis on CHNS VARIO EL3 and XPS data (VSW Ltd England) allowed to estimate a chemical nature of bulk and surface, respectively. For nitrogen sorption/desorption at 77K an ASAP 2010 apparatus was used. The micropore volume and surface were estimated from t-plot analysis.

The electrodes for supercapacitor investigation contained 85 wt.% of NTs composite, 10 wt% of polyvinylidene fluoride (PVDF Kynar Flex 2801) and 5 wt% of acetylene black. Electrodes were prepared in the form of pressed pellets (8-14 mg) with geometric surface area of one electrode 0.8 cm^2. 1 mol.l^{-1} H_2SO_4 aqueous solution served as electrolyte. The capacitance properties of the composite materials (expressed per mass of one electrode) were studied by galvanostatic (50 mA/g – 50 A/g) and potentiodynamic cycling at voltage scan rates from 1 mV/s to 1000 mV/s and by impedance spectroscopy (100 kHz -1 mHz) using ARBIN Instruments BT2000 – USA, VMP2/Z Biologic - France and AUTOLAB 30 FRA2-Netherlands potentiostat-galvanostats.

RESULTS AND DISCUSSION

Preparation of Nt-composites rich in nitrogen was realized by carbonisation of melamine/formaldehyde polymer blend in the presence of well dispersed nanotubes. It is noteworthy to stress that the carbonisation was performed without any activation process. Composites were carefully characterized physicochemically and correlated with electrochemical data measured in a two-electrode and three-electrode capacitor.
Nt-composites were observed by TEM and selected images are shown in Fig. 1a, b, c, d. It is perfectly seen that nanotubes play a template effect, composites reflect entangled morphology of nanotubes preserving presence of mesopores. A simple carbonisation product of melamine and formaldehyde blend without nanotubes is shown in Fig. 1a for comparison. An example of composite with a ~7 wt% of nitrogen (Nt+M+F) and with a higher N amount (~12 wt%), i.e. Nt+2M+F are presented in Fig. 1b and 1c, respectively. A moderate amount of melamine in composite Nt+M+F gives a partly distributed polymer on the NTs backbone which plays the role of a three-dimensional support for carbon. Increasing the melamine content, in the case of Nt+2M+F (Fig. 1c), a gradual change in composite morphology takes place. A good adhesion of well distributed polymer to Nts is demonstrated whereas a compact texture of composite with an excess of polymer (Nt+3M+F) is visible in Fig. 1 d. For NTs composite with the biggest amount of melamine as a nitrogen source, material starts to form some aggregates often in the shape of irregular chains (Fig. 1d).

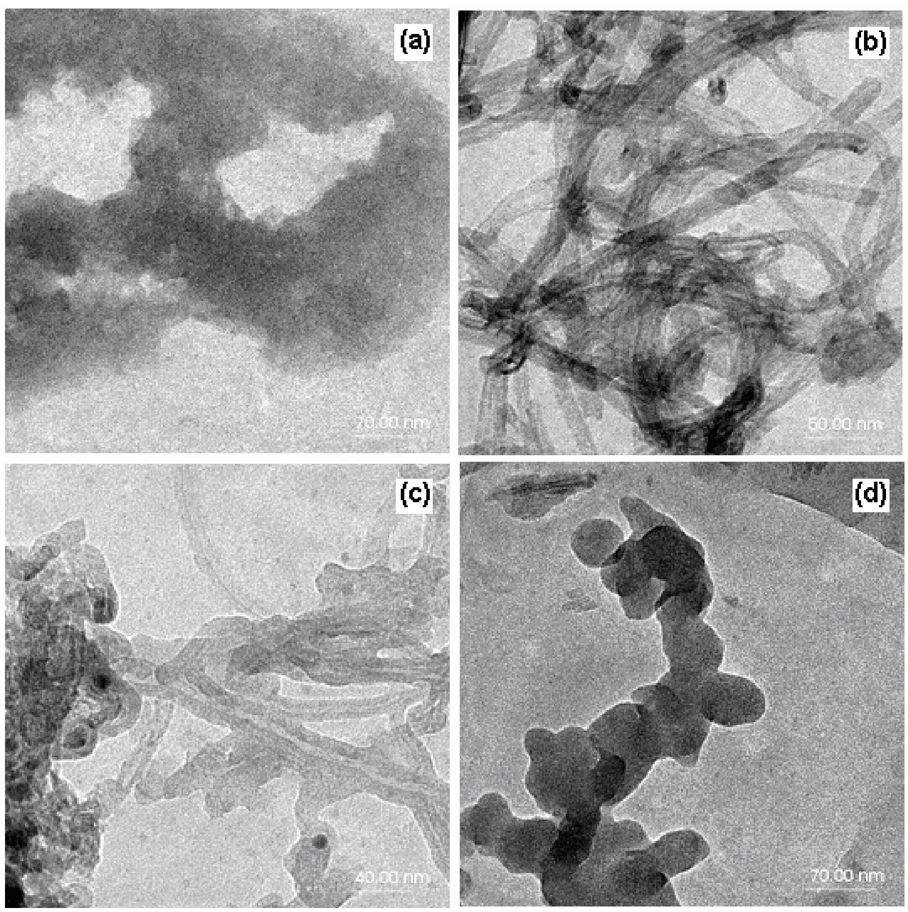


Figure 1. TEM images of composites with a variable N content (a, b, c, d)

Nitrogen sorption/desorption data (Fig. 2) allow to estimate the specific BET surface area, pore size distribution as well as micro/meso ratio. It is clearly seen that carbon materials are entirely mesoporous, the amount of micropores is comparable varying from 0.152 to 0.174 cm^3/g (Table 1), similarly to micropore surface area (287 m^2/g – 352 m^2/g).

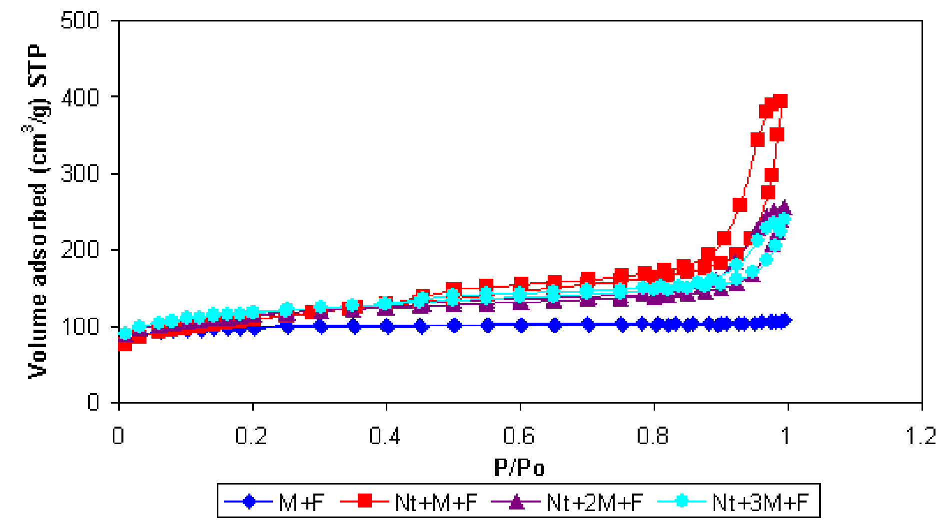


Figure 2. Nitrogen sorption/desorption isotherms at 77 K for NTs-composites.

The elemental analysis performed on CHNS VARIO EL3 showed that nitrogen content in composites varied from 7.4 to 21.7 wt% (Table 1). The higher amount of nanotubes in composite, the lower nitrogen content. Obviously the highest N amount (21.7 wt%) was in the composite without nanotubes, i.e. M+F. On the other hand, the amount of oxygen was almost the same in all the samples giving values from 5.9 to 7.8 wt%. The proportion of all the elements in composites is presented in the bar graph (Fig. 3).

Table 1. Physicochemical and electrochemical characteristics of Nt composites rich in nitrogen (C* stands for capacitance estimated at 5 A/g current load)

Sample	N [wt. %]	S_{BET} [m²/g]	V_{total} [cm³/g]	V_{micro} [cm³/g]	C^* [F/g]	C^* [µF/cm²]	C^* [F/cm³]
M+F	21.7	329	0.162	0.152	4	1.2	3
Nt+3M+F	14.0	403	0.291	0.174	100	24.8	64
Nt+2M+F	11.7	393	0.321	0.167	126	32.1	73
Nt+M+F	7.4	381	0.424	0.156	83	21.8	45

X-ray Photoelectron Spectroscopy (XPS) technique was used to analyse the surface chemistry of samples (Table 2). Three main peaks N1s are observed, however, pyridinic with binding energy of 398.7 eV and quaternary (400.9 eV) are dominant. It is important to stress that values from elemental analysis and XPS are very comparable that is a proof of the same perfect distribution of nitrogen in the bulk of carbon network as well as on the surface.

Table 2. XPS analysis of composites rich in nitrogen

Sample	Pyridinic (N-6) [at. %]	Quaternary (N-Q) [at. %]	Oxidized nitrogen (N-X) [at. %]	Total (N) [at. %]
M+F	10.2	13.4	1.2	24.8
Nt+3M+F	4.9	7.9	0.8	13.6
Nt+2M+F	4.9	7.3	0.5	12.7
Nt+M+F	2.7	4.8	0.4	7.9

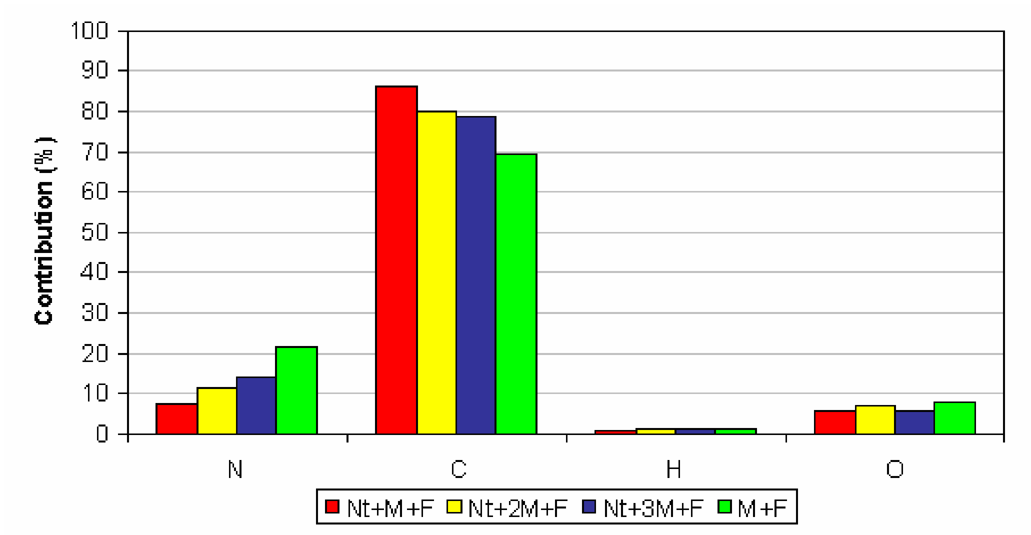


Figure 3. Elemental composition of NTs composites

For practical applications of materials obtained, the effect of nitrogen functionalities on electrochemical properties of composites was carefully investigated. The electrochemical characterization was performed mainly in a two-electrode cell, however, three electrode cell measurements were also performed to observe the performance of positive and negative electrode, separately. Electrochemical tests proved a beneficial conducting and supporting role of nanotubes in carbon composite. A very well interconnected mesoporous network of carbon composite gives a good access of electrolyte to electrode bulk. Even if lately a great interest of nitrogenated carbons for capacitor application is observed, the available data on such carbon materials are mainly devoted to three electrode cell quite often using moderate discharge load. Often the samples investigated contained a limited amount of nitrogen.

In this paper, for the first time composites with a various amount of nitrogen (from 7.4 to 21.7 %) have been presented whereas porous characteristic (BET surface area, micropore and mesopore volume) were comparable. It is also noteworthy that constant amount of oxygen in composites gives a possibility to investigate systematically almost a pure effect of nitrogen. The main question was what is an optimal amount of nitrogen in carbon composite. What is the limit which gives a loss of material conductivity if excess of heteroatoms is introduced?

Electrochemical data from three techniques could try to give an answer for that. The reliable capacitance values were obtained from galvanostatic charge/discharge characteristics. Capacitance values were obviously compared with voltammetry experiments in 1 mol.l^{-1} H_2SO_4 solution at different scan rates (from 1 to 1000 mV/s). For a low current regime (50 mA/g) the capacitance values of all composites varied from 113 to 167 F/g. However, for practical application only the heavy regimes are interesting. The higher scan rate, the moderately lower response from faradaic reactions can be expected revealing that some diffusion limitations take place. Table 1 shows a drastic difference in capacitance values for composites with a different N content at 5 A/g current load, sample with ca. 12% of N looks to be optimal. A quite good shape of the voltammetry curves performed in acidic medium at extremely high scan rate of 1V/s also proves that a capacitor built with an optimal composite electrodes (Nt+2M+F) can easily operate and still supply capacitance of 60 F/g at the scan rate of 1V/s and current density of 50 A/g. Good capacitive properties have been confirmed by impedance spectroscopy measurements. A Nyquist plot for Nt-based electrodes at frequency from 100 kHz to 1 mHz in acidic electrolyte showed a perpendicular dependence of the imaginary part versus real one. The values from Nyquist plots were taken to present dependence of capacitance versus frequency. An exceptional dependence is shown for optimal composite with ~12 wt% of nitrogen, i.e. Nt+2M+F (Fig. 4a). A capacitance value of 50 F/g is even observed at 10 Hz frequency, which is extraordinary. It is noteworthy that for composite with ~14 wt% of nitrogen an aggravation of characteristics has been already observed. An interesting capacitance response on current load for all composites is also presented in Fig. 4b. It is again confirmed that composite with ~12 wt% of nitrogen is the most promising. Apart of capacitance values another important characteristic is cyclability. Cycling tests at 500 mA/g was performed at the voltage range (0-0.8 V) and the values dropped only from 150 F/g at first cycles to 140 F/g after 5000 cycles.

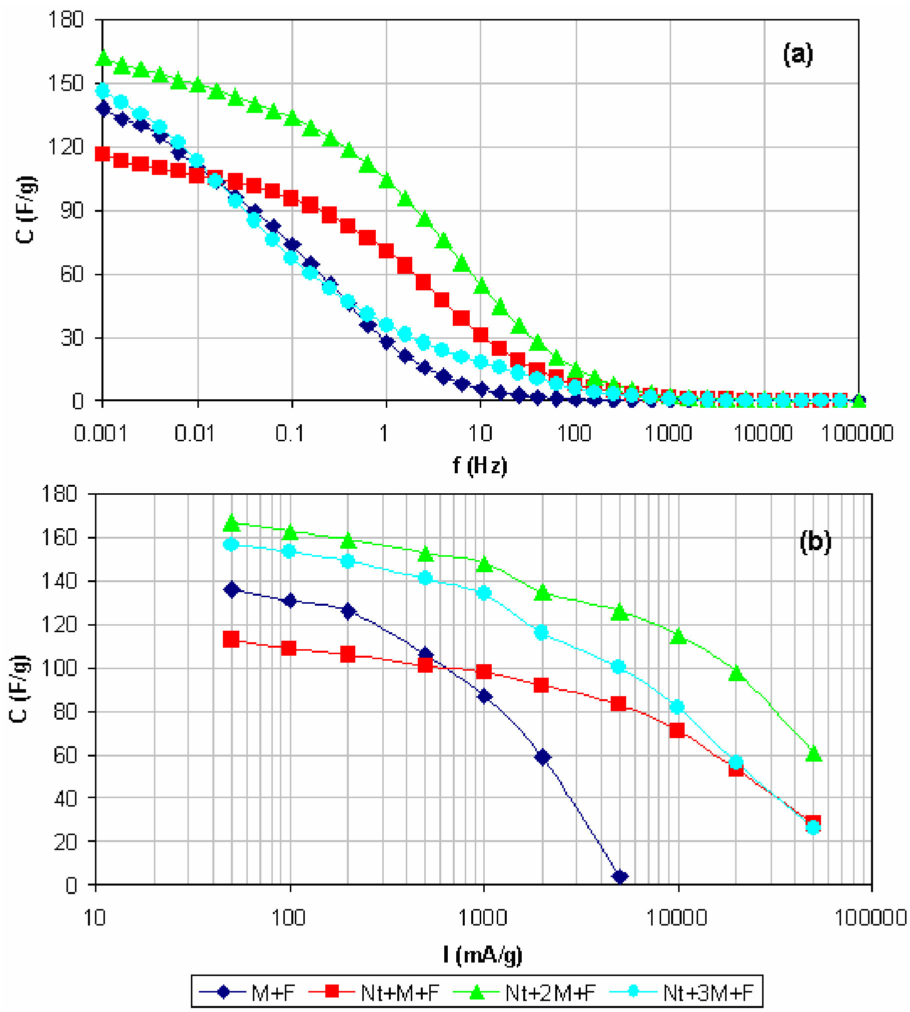
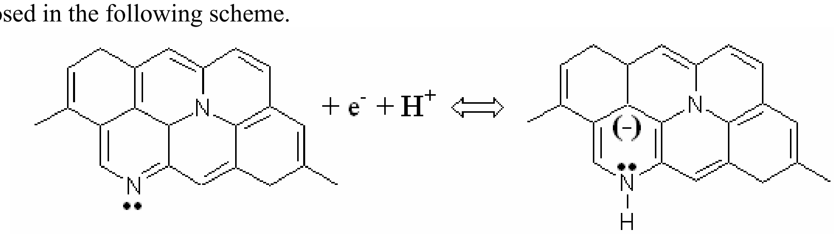


Figure 4. Capacitance versus frequency dependence (a) and different current loads (b) for NTs-composites

The main contribution of beneficial profit on capacitance values as well as for good cyclability is a nitrogen presence. The following question should be answered: Which nitrogen groups are profitable?

Surely not only the total quantity of nitrogen heteroatoms in the carbon matrix is relevant, but first of all, the form in which N participates in carbon network. It seems that effect of NH_2- groups being outside of matrix where N is chemically bound to organic molecules ("chemical nitrogen") will be negligible. Substituted to carbon ("lattice nitrogen") in the peripheral pyridinic groups could play some useful role according to redox reaction proposed in the following scheme.



Obviously, a great difference between a "top" and a "valley" N position is expected, the latter being more profitable because of stronger donor electron character. On the other hand, quaternary nitrogen seems to be the most beneficial position having a significant effect on the carbon electronic structure through decreasing an energy gap between lowest unoccupied molecular orbitals (LUMO) and the highest occupied molecular orbitals (HOMO). Donor properties are responsible for filling a conduction band by electrons, in turn, more ions can be sorbed in electrical double layer, especially for composites where carbon is optimally substituted by nitrogen.

However, it was observed that the higher amount of nitrogen (over 12%) could be at the origin of significant aggravation of conductivity.
It should be also stressed that these composite do not need any activation process, hence, their moderate surface area give profitable values of specific surface capacitance (30-42 $\mu F/cm^2$) as well as attractive volumetric capacity from 61 to 100 F/cm^3 in the case of low current load (50 mA/g). The great discrepancy in capacitance values is observed for higher regimes (5A/g, Table 1).

CONCLUSIONS

Exceptional conducting and mechanical properties of multiwalled carbon nanotubes used for carbonisation of a polymer blend, without any activation process, enabled to prepare a unique Nt-composites with a comparable texture (surface area of ca. 400 m^2/g) but variable N content ranging from ca. 7 to 20 wt%. Pseudocapacitance effects related to the nitrogen presence in carbon composite, where NTs played a role of a three dimensional conducting support, have been efficiently used in electrodes of supercapacitor. The beneficial role of nitrogen is connected with faradaic reactions partly due to the presence of pyridinic groups but also because of presence of quaternary nitrogen which is obviously responsible for drastic modification of electronic structure. Extremely good charge propagation was obtained especially for composite with ~12 wt% of N. The capacitance values of 160 F/g at 1mHz frequency diminish only to 120 F/g at 1 Hz and being still equal to 55 F/g at 10 Hz. This composite could be loaded at high current density of 50 A/g because mesoporous network allowed a pseudocapacitance effect of nitrogen to be efficiently used.

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