ANOMALOUS CAPACITANCE PROPERTIES OF NITROGEN DOPED CARBONS PREPARED BY REPLICATION

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INTRODUCTION

The performance of electrical double layer (EDL) capacitors is typically associated with the accumulation of charges in the electrode/electrolyte interface by electrostatic forces. Hence, pure EDL capacitance depends on the extent of this accessible interface. Quite often the capacitance values do not correlate proportionally with the BET specific surface area of activated carbons which are the most often used electrode materials. A better proportionality has been found between capacitance and the amount of ultramicropores for a series of nanoporous carbons (Vix, C. et al. 2005; Chmiola, J. et al. 2006). Lately, a great attention is devoted to enhance capacitance values by combining the EDL capacitance with pseudocapacitive effects connected with quick faradic reactions in aqueous medium. Pseudocapacitance can be originated from such materials as conducting polymers, transition metal oxides, but also from the presence of heteroatoms in activated carbons. It has been already proved that oxygen and/or nitrogen present in the carbon network can be very profitable elements for capacitance enhancement (Frackowiak et al. 2000; Jurewicz et al. 2003; Kodama et al. 2004; Hulicova et al. 2005; Lota et al. 2005; Hulicova et al. 2006; Frackowiak et al. 2006; Raymundo-Pinero et al. 2006; Lota et al. 2007).

In the present work, the interesting properties of template carbons with an interconnected micro/mesoporosity have been combined with pseudocapacitance effects related with the presence of nitrogen and oxygen in the carbon network. The behavior of capacitors as well as single electrodes has been correlated with the physicochemical properties of template carbons. Different precursors such as glucose, sucrose and amino-glucose have been selected to induce the pseudocapacitance effect of nitrogen and oxygen functionalities.

EXPERIMENTAL

The nanostructured porous carbons have been synthesized by a templating procedure using two ordered mesoporous silica (SBA15 and MCM48) scaffolds. Silica was infiltrated with a carbon precursor, e.g., a solution of sugar and sulfuric acid, and the composite was dried at 100°C and subsequently pre-calcinated at 150°C during 6h. A second infiltration was done in order to obtain a good carbon yield. Then, calcination was carried out at 900°C in vacuum during 5h. The carbon/silica nanocomposite was treated by hydrofluoric acid in order to remove silica. The carbon replica was then washed with distilled water and dried.

The nanotexture of templated carbons has been analyzed in detail by Transmission Electron Microscopy (TEM) and gas adsorption (nitrogen and carbon dioxide). The nitrogen and oxygen amounts were determined by elemental analysis. The data are summarized in table 1. The total content of nitrogen in the template samples varied from 0 to ca. 5 wt%, whereas the oxygen content ranged from 6 to 18 wt%.

Table 1. Textural parameters and nitrogen content of the templated carbons

Material reference	Silica scaffold	Carbon precursor	Nitrogen wt%	S_{BET} m^2/g	V_p cc/g	V_{DRN2} cc/g	V_{DRCO2} cc/g
V15AG	SBA15	Glucose	0	1270	1.11	0.48	0.31
V15AGn	SBA15	Amino-Glucose	4.1	1070	1.09	0.40	0.27
V15AGnS	SBA15	Amino-Glucose+Sucrose	2.7	1200	1.14	0.47	0.29
V48BG	MCM48	Glucose	0	1447	1.01	0.56	0.27
V48BS	MCM48	Sucrose	0	1680	1.14	0.50	0.27
V48AGn	MCM48	Amino-Glucose	4.7	624	0.43	0.26	0.22
V48AGnS	MCM48	Amino-Glucose+Sucrose	2.0	1024	0.71	0.4	0.25

The capacitance properties of the templated carbons were estimated in 1 mol.L^{-1} sulfuric acid by voltammetry, galvanostatic charge/discharge and impedance spectroscopy, using multichannel potentiostat-galvanostats ARBIN Instruments BT2000 (USA), VMP-Biologic (France) and an AUTOLAB FRA2 (The Netherlands).

RESULTS AND DISCUSSION

The capacitance properties strongly depend on the nanoporous texture, however, a suitable surface functionality plays also a crucial role. For the carbons preparation, three types of precursors (glucose, sucrose and amino-glucose) have been used, supplying materials with different elemental composition and slightly different nanotexture. As it is shown in Table 1, the ultramicropore Dubinin-Raduskevitch volume (V_{DR}) measured by carbon dioxide adsorption at 0°C (pores less than 0.7 nm) is almost the same for all the samples, varying from 0.22 to 0.31 cc/g, whereas the micropore volume estimated by nitrogen adsorption (V_{DRN2}) ranges from 0.4 to 0.56 cc/g, being smaller (0.26 cc/g) only for one sample, V48AGn. By contrast, the total pore volume changes more significantly, from 0.7 to 1.1 cc/g, being again the lowest (0.43 cc/g) for the sample V48AGn. In sum, the samples are characterized by the same amount of ultramicropores, slightly different amount of supermicropores, but a noticeably different mesoporosity. The microporosity developed in all these carbons is due to their autoactivation by the evolved carbon dioxide during carbonization.

It is well accepted that ions are more efficiently accumulated in the smallest pores, i.e., ultramicropores, which are the closest to their dimensions. In 1 mol.L^{-1} sulfuric acid, a good attraction of solvated hydronium and HSO_4^- ions (with a dimension ca. 0.53 nm) is expected. Obviously, to preserve a good charge propagation for higher charge/discharge regimes, some amount of small mesopores is demanded. In the case of templated carbons, the interconnectivity of micro and mesopores is especially useful, allowing all micropores as well as the oxygen and nitrogen functionalities to be efficiently used.

It is noteworthy that in this research a great attention has been devoted to the capacitance behavior depending on the polarity of both electrodes, quite often ignored by most authors. Generally, either two electrode capacitors are investigated without controlling the potential of single electrodes, or three electrode cells are considered being very far from a real capacitor (great excess of electrolyte, different nature of counter electrode, etc..).

In table 2, the capacitance values (F/g) are presented for a full capacitor as well as for the two electrodes separately. It is observed that, especially in the case of the samples prepared by double infiltration of amino-glucose into the silica host, the capacitance of the two electrodes differs significantly. For instance, the sample V48AGn gives 127 F/g for the positive electrode and 171 F/g for the negative one. Similarly in the case of V15AGn the negative electrode pointed out a higher capacitance 179 F/g than the positive one (150 F/g).

Table 2. Capacitance properties of templated carbons. Capacitance measured by galvanostatic charge/discharge at 2 A/g current load.

Material	Capacitance of two electrode cell (F/g)	Capacitance of el. + (F/g)	Capacitance of el. - (F/g)
V15AG	157	164	148
V15AGn	164	150	179
V15AGnS	162	160	171
V48BG	210	198	208
V48BS	185	187	185
V48AGn	145	127	171
V48AGnS	165	156	176

An important information has been obtained by studying the capacitance values of the two electrodes versus frequency from 1 mHz to 100 kHz. Examples are shown in Figs. 1-4 for template carbons using SBA-15 and MCM48 as matrix and glucose, amino-glucose, amino-glucose together with sucrose as carbon precursor. The values measured at 1 mHz reflect almost the capacitance characteristics obtained during the galvanostatic charge/discharge regime. Generally, in the typical EDL capacitors, the capacitance values gradually diminish especially for frequencies higher than 1 Hz. However, the materials rich in heteroatoms can supply un-typical spectra.

Striking anomalous dependences are observed depending on the polarity and elemental composition of the materials. Surely the type of oxygen and nitrogen surface functionality has a dominant role. A detailed analysis by XPS is under progress, and some data already proved the existence of mainly pyridinic and quaternary bonded nitrogen, however, nitrogen bonded to oxygen is also significant. The synergetic contribution of both elements in the electronic structure of the carbon network is very complex, and further investigation is needed.

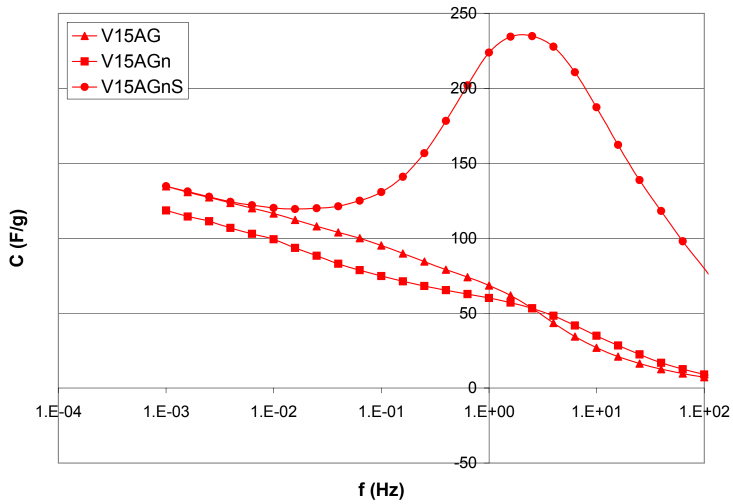

Figure 1. Capacitance vs frequency for positive electrodes of capacitors built from templated carbons based on SBA15.

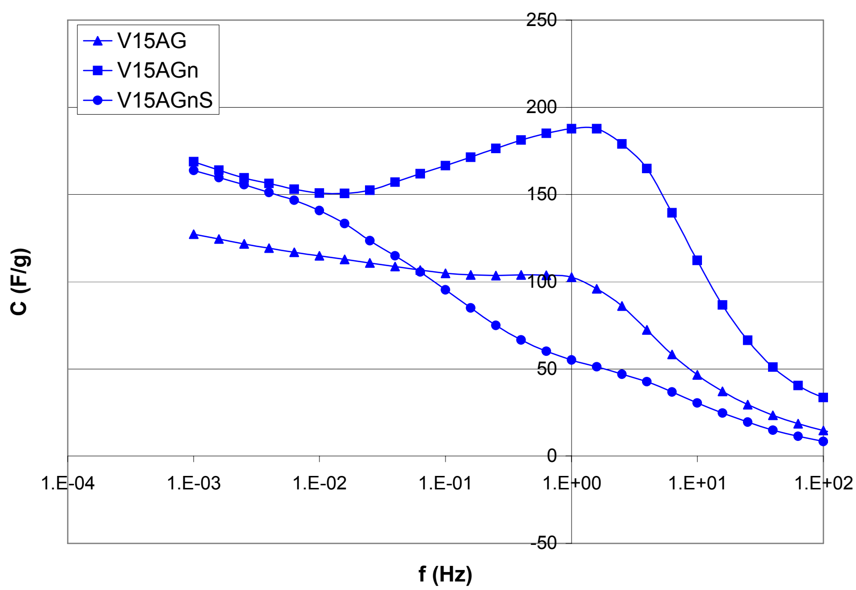

Figure 2. Capacitance vs frequency for negative electrodes of capacitors built from templated carbons based on SBA15.

Our investigations clearly prove that the electrode polarity must be considered for the selection of optimal materials. From a first observation, it seems that the oxygen-rich materials will serve better for the positive electrode, whereas the nitrogen-rich ones could be better for the negative electrode. For amino-glucose which is a source of both nitrogen and oxygen, the functionalities related with these two elements can be concurrent to each other.

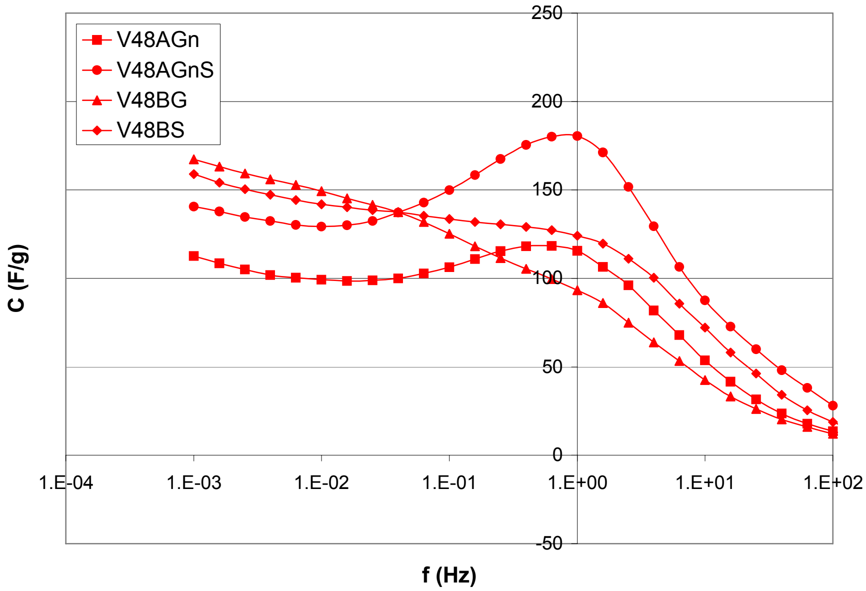

Figure 3. Capacitance vs frequency for positive electrodes of capacitors built from templated carbons based on MCM48.

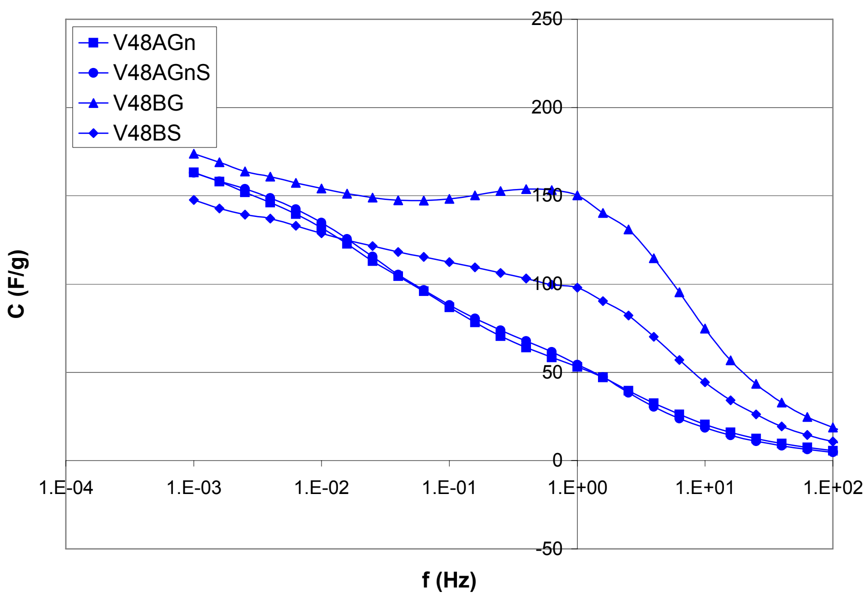

Figure 4. Capacitance vs frequency for negative electrodes of capacitors built from templated carbons based on MCM48.

An example of voltammetry characteristics of both electrodes (+) and (-) is presented in Fig. 5 for the sample V15AGn rich in nitrogen (ca. 4 wt%). It is clearly seen that this material is better adapted for the negative electrode. The voltammogram of the two electrode capacitor presented in Fig. 6 is some kind of average of the previous characteristics. Therefore, for practical application, single electrode measurements are very useful.

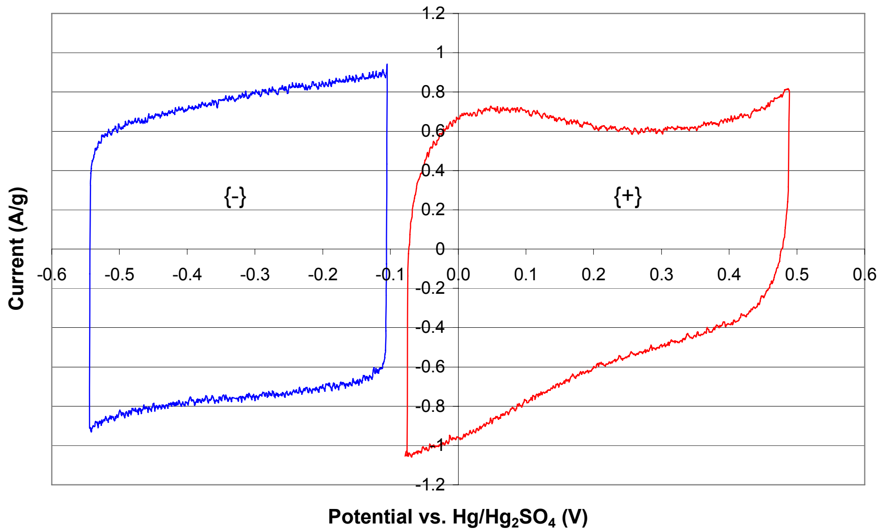

Figure 5. Voltammetry characteristics for the negative and positive electrodes of a capacitor built from the templated carbon V15AGn

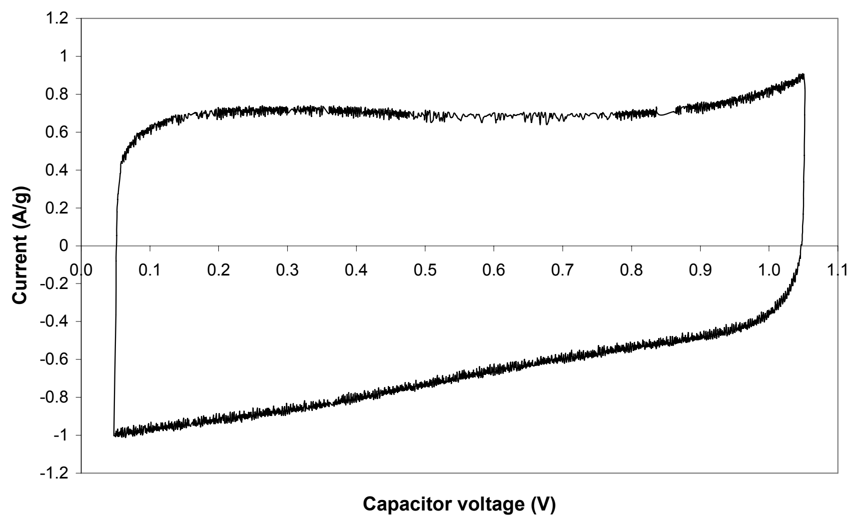

Figure 6. Voltammetry characteristics of a capacitor built from the templated carbon V15AGn

CONCLUSIONS

In the present work, it has been proved that templated carbons with an interconnected network of micro/mesopores are perfect reference carbons for a detailed study of capacitance properties in aqueous medium. A series of carbons with almost identical ultramicroporosity has been produced. These carbons differ only by the content of supermicropores and small mesopores. Such a well sized nanotexture allows the narrow micropores, where ions with a distorted solvation shell closely approach the electrode surface, to be efficiently used.

It has been shown that the presence of heteroatoms in the carbon network can greatly affect the electrochemical performance of the electrodes through pseudo-faradic reactions of nitrogenated and oxygenated groups as well as an accelerated sorption of ions in the regions of locally modified electronic structure.

Capacitance values of total capacitors vary from 145 F/g to 210 F/g, however, a great difference can be observed for single electrodes. Generally, the negative electrodes supply higher values of capacitance. It is anticipated that asymmetric systems with a negative electrode preferably from nitrogen-rich carbon and a positive electrode from a material with oxygen in-built in the carbon network would be an optimal solution.

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