

WELL-SIZED POROUS MATERIALS FOR SUPERCAPACITORS PREPARED BY A TEMPLATING PROCEDURE

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Introduction

The novel class of nanostructured carbons with a highly ordered porosity prepared by a template technique [1-4] is considered as electrode materials for supercapacitors [5-7]. The pores are characterized by a well-defined size determined by the wall thickness of the silica used as substrate for carbon infiltration; they can be also interconnected, that is very useful for the charges diffusion in the electrodes. The application of these well-sized porous materials in supercapacitors allows an exact screening of the pores adapted for an efficient charging of the electrical double layer.

Experimental

Two types of organized mesoporous silica, MCM-48 and SBA-15, which display different crystallographic structure, size and shape of the pores, were selected as a template for carbons. The pores of the silica template can be filled by carbon from a gas or a liquid phase. In the first case, pyrolytic carbon is inserted into the pores of these silica matrices by chemical vapor infiltration (CVI). The silica template is contacted with a flow of propylene Pr, (2.5 vol%) diluted in argon at 750 °C during 15 hours. A quite uniform pore filling can be obtained by CVI. At the end, the carbon represents about 50 wt% of the C/SiO₂ material. Since the deposition time is the same for the two silica precursors, the fraction of the pore volume filled with carbon is function of the template. The C/SiO₂ material is then treated with hydrofluoric acid (HF) to remove the silica template and the carbons obtained are designed CPr48 and CPr15.

The second type of template carbon is formed by liquid impregnation of the pores of MCM-48 and SBA-15 silica by a sucrose (S) solution, followed by a carbonization treatment at 900°C under vacuum. After a second impregnation step, the amount of carbon introduced in the silica matrix represents 33 wt% which is not far of the theoretical amount expected taking into account the pore volume of the silica matrix and the concentration of the sucrose solution, i.e. 36 wt% of the total mass of the C/SiO₂ composite. The silica template is eliminated by dissolution in HF to recover the carbon

material denominated here as CS48 and CS15. Carbons obtained by replica method are characterized by nitrogen adsorption at 77K and X-ray diffraction (Table 1). The electrochemical performance of the capacitor electrodes prepared from the various template carbons have been determined by galvanostatic charge/discharge, cyclic voltammetry (ARBIN B 2000), impedance spectroscopy (AUTOLAB-ECOCHÉMIE BV) and are tentatively correlated with their structural and microtextural characteristics.

Results and Discussion

Figure 1 presents the general principle of the carbon preparation by a template technique, where the silica matrix can be for example MCM-48 or SBA-15. Schematic representations of the porous network organization in MCM-48 and SBA-15 are given in Fig. 2. The mesoporous silica material referred as MCM-48 displays a cubic structure which consists of two independent and intricately interwoven networks of mesoporous channels. The structure of the material named SBA-15 is composed of a hexagonal arrangement of 1-D silica rods forming cylindrical pores interconnected through smaller pores randomly located perpendicular to the 1-D channels. Both silica materials exhibit a highly-ordered porous structure, a high specific surface area and a narrow pore size distribution centered at 2.6 nm and 5.2 nm for MCM-48 and SBA-15, respectively.

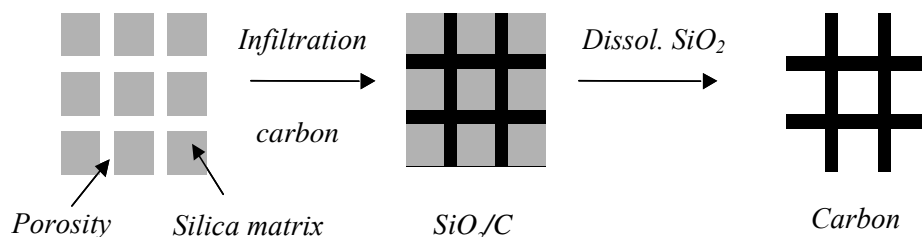


Figure 1. Schematic representation of carbon elaboration by a template technique



Figure 2. Two examples of silica matrices: (a) MCM-48 and (b) SBA-15

The total surface area of the template carbons prepared by sucrose impregnation is significantly higher than the surface area of the corresponding silica template (Table 1), that confirms the formation of micropores during the carbonization. Just an opposite tendency is observed when propylene is used as carbon precursor. In the latter case, the pore volume of the template carbon is consistent with an uniform pore filling, and the values of surface area are easily justified by different pores and walls diameters in the

pristine template. The higher pore volume and surface area of sucrose derived template carbons is attributed to the release of water and gases during the thermal treatment.

Materials	a (nm)	S_{BET} (m^2/g)	V_p (cm^3/g)	Pore size (nm)
MCM-48	8.6	1330	1.07	2.6
CPr48	8.4	850	0.56	-
CS48	7.6	2000	1.10	2.7
SBA-15	11.3	807	0.97	5.2
CPr15	10.5	713	0.60	3.4
CS 15	9.4	1470	1.11	3.1

Table 1. Characteristics of the silica templates and the corresponding carbon materials a: unit cell parameter; S_{BET} : specific surface area; V_p : total pore volume at $P/P_0=0.95$.

The capacitance values determined by the three techniques are reported in Table 2 for the different types of carbons (CS48, CS15, CPr48, CPr15) depending on the electrolytic medium (acidic, basic and organic). For each kind of capacitor, it can be seen that a satisfactory correlation is found between the three techniques. The various electrode materials give rise to different values of capacitance due to their different physico-chemical characteristics as seen in Table 1. The voltammograms of CS15 and CS48 for the acidic and organic media have a box-like shape which is characteristic for an ideal capacitor with quick charge propagation. As seen in Table 2, the two materials exhibit high values of capacitance both in aqueous and organic medium. Especially, CS48 reaches values which are promising compared to other reported in the literature for various activated carbons with comparable specific surface area. Hence, the additional porosity created during the carbonization step is profitable for the performance of these template carbons. Comparing the performance of the electrodes made from CS48 and CS15, the specific capacitance per surface unit in acidic medium is roughly the same for the two materials, ca. $10 \mu F/cm^2$ and $12 \mu F/cm^2$, respectively. This would lead to the conclusion that the main parameter controlling the electrochemical performance in these materials is the total surface area (Table 1). However, taking into account that the surface area determined by nitrogen adsorption and the electrochemically active surface area are different, other factors might explain the different capacitance values observed for CS48 and CS15, e.g. the different pore arrangement which affects the diffusion of the solvated ions, the presence of a more marked secondary microporosity ($1.5 \text{ nm} < D < 1.8 \text{ nm}$) for CS48 and consequently smaller pore size compared to CS15.

The electrochemical performance of CS15 looks to be similar in basic and acidic medium, while smaller values are observed for CS48 in basic medium (Table 2). Such a difference might be related to the different surface functionality of the two materials, the latter controlling the wettability of the materials. In the case of CS48, surface oxygenated groups, which dissociate differently depending on the electrolyte pH, could be responsible of different adsorption of the ions on the carbon surface in both media. On the other hand, CS15 behaves rather as a material which has a poor surface

functionality. A careful analysis of the surface properties of these carbons is necessary to support these hypotheses.

Material : CS48	C (F/g) 1M H ₂ SO ₄	C (F/g) 6M KOH	C (F/g) TEABF ₄ in CH ₃ CN
G (2mA)	206	184	115
G (5mA)	188	170	116
P (2mV/s)	193	181	118
P (10mV/s)	170	159	114
I (1mHz)	210	177	96

Material: CS15	C (F/g) 1M H ₂ SO ₄	C (F/g) 6M KOH	C (F/g) TEABF ₄ in CH ₃ CN
G (2mA)	169	174	93
G (5mA)	158	161	90
P (2mV/s)	162	170	98
P (10mV/s)	144	156	94
I (1mHz)	171	172	78

Material: CPr48	C (F/g) 1M H ₂ SO ₄	C (F/g) 6M KOH	C (F/g) TEABF ₄ in CH ₃ CN
G (2mA)	101	74	65
G (5mA)	99	87	62
P (2mV/s)	113	82	64
P (10mV/s)	99	75	62
I (1mHz)	113	81	57

Material: CPr15	C (F/g) 1M H ₂ SO ₄	C (F/g) 6M KOH	C (F/g) TEABF ₄ in CH ₃ CN
G (2mA)	62	58	48
G (5mA)	61	55	46
P (2mV/s)	62	56	50
P (10mV/s)	58	51	49
I (1mHz)	78	59	42

Table 2. Capacitance values in F/g in three electrolytes. G, P, I stand for measurements by galvanostatic, potentiodynamic and impedance spectroscopy, respectively.

Conclusions

Interesting carbon materials were prepared by a templating procedure from MCM-48 or SBA-15 highly ordered mesoporous silica. The perfectly controlled texture of the template carbons allows a better understanding of the electrochemical performance in supercapacitors. Capacitance values as high as 200 F/g and 110 F/g in aqueous and organic media are reached with the carbons CS from sucrose presenting secondary

micropores. Taking into account these high values, it is obvious that the presence of interconnected mesopores and secondary micropores makes the active surface more available for charging the electrical double layer than in a strictly microporous material. An improved capacitance-frequency dependence has been also found for the essentially mesoporous carbons. It is the first time that the beneficial effect of mesopores on the diffusion of ions to the active surface is so clearly demonstrated. The template carbons, with a well-tailored pore size and pore distribution are of prime interest for designing high performance supercapacitors.

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