Templated mesoporous carbons for supercapacitor application

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Abstract

Mesoporous carbons prepared by an inverse replica technique have been used as electrodes for electrochemical capacitors. Such well sized carbons were prepared from mesostructured SBA-16 silica materials that served as templates whereas polyfurfuryl alcohol was the carbon precursor. Two highly mesoporous carbons characterized by 3 and 8 nm average pore diameter were tested in various electrolytic solutions (acidic, alkaline and aprotic).

It can be concluded that templated mesoporous carbons with tailored pore size distribution are very promising materials to be used as electrodes in supercapacitors. The design of their pore size allows suiting the dimensions of electrolyte ions and efficient charging of the electrical double layer is achieved especially at high current load. Definitively better capacitance performance has been found for carbon with 3 nm pores range, however, cycling performance depends not only on the pore size.

Keywords: Supercapacitor; Charge/discharge; Template carbon; Mesopores

1. Introduction

Electric double-layer capacitors (EDLCs) have been extensively developed due to the increasing demand for a new kind of accumulators of electrical energy with a high maximum specific power of more than 10 kW kg^{-1} for the best devices and a long durability (over 10^6 cycles). The main advantage of this storage device is the ability of a high dynamic of charge propagation (short-term pulse) that can be useful in the hybrid

power sources for electrical vehicles, digital telecommunication systems, UPS (uninterruptible power supply) for computers and pulse laser technique.

EDLCs utilize the electric double layer formed at the electrode/electrolyte interface where charges are accumulated on the electrode surfaces and ions of opposite charge compensate them [1-3]. EDLC electrode materials should, thus, have a large surface area for charge accumulation with an appropriate pore structure for electrolyte wetting and rapid ionic motion. At present, mainly activated carbons are used as the EDLC electrode materials because of their low cost and a wide variety of carbon precursors. Even if these conventional carbons have a large surface area, their EDLC application can be limited because they contain an abundant proportion of micropores (diameter <2 nm) not always fully accessible to ions. The micropores are not easily wetted by the electrolyte and the exposed surface in micropores may not be utilized for charge storage. Moreover, even in the situation wherein the micropores are wetted by the electrolyte, the ionic motion in such small pores may be so slow that the high rate capability, which is one of the advantages of EDLCs may not be realized. Both charge storage and rate capability are further limited if the pores are randomly connected. Therefore, high surface area carbon materials containing regularly interconnected mesopores (> 2 nm) are highly desirable for the EDLCs electrodes. Obviously, some compromise must be found in the meso/micro ratio because a too high amount of mesopores can diminish the volumetric capacitance due to a lower density of the carbon material.

Recently, many groups have synthesized ordered mesoporous silica which could be used afterwards for the preparation of carbons with well controlled pores [4-15]. Well sized carbons could meet the above mentioned capacitor requirements. Such mesoporous carbons were prepared via the replica route, in which mesostructured silica

materials were utilized as templates whereas the carbon source was a liquid phase, e.g. sucrose solution [14, 15], polyfurfuryl alcohol [8-10], gas such as propene [14, 15] or solid phase, e.g. pitch [14]. After deposition of the carbon precursor inside the pores of the template, the carbonization process was performed. In such a way, mesoporous carbons with three dimensionally interconnected pores were obtained after removing the inorganic template with a hydrofluoric acid treatment. Due to the ordered pore arrangement of such templates, the new advanced carbons preserved well defined and controllable pore diameters [4-16]. Such novel carbons were tested as supercapacitor materials [11-16], however a full optimization of these interesting materials for high power devices is still missing. It has been recently proved that templated mesoporous carbons are especially adapted for high current loads [16].

The main objective of this paper is to correlate the pore size of mesoporous carbons obtained by the replica method with the capacitor performance, i.e. capacitance values, charge propagation, cycleability, self-discharge and leakage current. Trials were also undertaken to select the optimal electrolyte solution (acidic, alkaline and aprotic) for the investigated carbons and to estimate the advantages as well as some drawbacks of the template carbons in capacitor application.

2. Experimental technique

2.1. Preparation of silica templates and mesoporous carbons

The preparation of the SBA-16 silica materials used as templates was carried out through a two-step process following the procedure reported by Zhao et al. [17]. Depending on the temperature used in the second step (100°C or 150°C) two SBA-16 samples possessing different pore sizes were obtained, i.e. 4.1 nm at 100°C and 13 nm

at 150°C. These samples were used as templates to prepare the mesoporous carbons. The synthesis of the carbons was performed with furfuryl alcohol as carbon source and by using a technique reported elsewhere [8]. Briefly, the mesostructured silica was impregnated with furfuryl alcohol up to incipient wetness. The impregnated sample was cured in air for 2 hours at 80°C to polymerise the furfuryl alcohol and to convert it into polyfurfuryl alcohol, which was then carbonised under N₂ at 800°C (2°Cmin⁻¹). The sample was held for 1h at this temperature. The treatment of the silica-carbon composites with hydrofluoric acid to remove the inorganic skeleton led to carbon materials with a well-defined porous structure. Subsequent heat treatment at temperatures around 1000°C in inert atmosphere was carried out in order to increase the electrical conductivity of the carbons. This heat treatment induces a loss of volatile surface groups together with a better organization of the graphitic-like layers. Such prepared templated carbons (Fig. 1) were denoted as C-1 (obtained from the SBA-16 prepared at 100°C) and C-2 (obtained from the SBA-16 prepared at 150°C).

2.2. Analysis of the porous structure of the mesoporous carbons

The BET-specific surface area was determined from N₂ physisorption at 77 K (Micromeritics ASAP 2010 volumetric adsorption system). The total pore volume was calculated from the amount adsorbed at a relative pressure of 0.99 whereas the mesopore volume and external surface were estimated by using the α_s -plot method. The pore size distributions were obtained by applying the Kruk-Jaroniec-Sayari (KJS) method to the adsorption branch [18]. The micropore volume was estimated from the CO₂ adsorption isotherm (gravimetric system CI Electronics) at 293 K by using the Dubinin-Radushkevich equation.

2.3. Electrochemical characterization

The electrodes in the form of pellets were obtained from a composite consisting of the mesoporous carbon (85 wt%), acetylene black (5 wt%) and a binder Kynar Flex 2801 Atochem (10 wt%). The geometric surface area of the electrodes was 0.79 cm². The mass of the electrodes ranged from 9 to 12 mg and their typical thickness was from 0.22 mm to 0.25 mm. Two-electrode capacitor cells were assembled in a teflon Swagelok[®] system with gold or stainless steel collectors depending on the electrolyte used. The electrolytic solutions were aqueous 6 mol l⁻¹ KOH, 1 mol l⁻¹ H₂SO₄ and organic 1 mol l⁻¹ TEABF₄ in CH₃CN. Stainless steel cylindrical collectors were used in the case of organic medium and alkaline solution. The cells were tested by galvanostatic charge/discharge with a current load from 100 mA g⁻¹ to 1000 mA g⁻¹ (that corresponds to a current density from ca. 1 to 10 mA cm⁻²), voltammetry cycling at scan rates from 1 mV s⁻¹ to 20 mV s⁻¹ and impedance spectroscopy in a wide frequency range (100 kHz -1 mHz). The impedance measurements were performed at open circuit voltage with a ±10 mV voltage amplitude. The capacitance values from impedance spectroscopy were obtained using the following formula:

$$C = -\frac{1}{2\pi fZ''}$$

(1)

A potentiostat-galvanostat BT2000 ARBIN Instruments and AUTOLAB-ECOCHÉMIE FRA2 BV were used for the electrochemical measurements.

3. Results and discussion

3.1. Porous structure of the templated carbons

SEM images of the two investigated mesoporous carbons C-1 and C-2 are presented in Fig. 1. The carbon particles possess almost a perfectly spherical shape that replicates the morphology of the silica used as template. The N₂ adsorption/desorption isotherms and the pore size distributions displayed in Fig. 2 show the highly mesoporous character of the templated carbons. Both materials present large equivalent BET-surface areas, 1880 m² g⁻¹ for C-1 and 1510 m² g⁻¹ for C-2 (Table 1) and strictly controlled pore size diameters (Fig. 2, inset). The more significant difference in the porous structure of the templated carbons is reflected in Fig. 2, where a unimodal pore size distribution centred at 3 nm is observed for C-1 whereas in the case of the carbon C-2 the average pore diameter is around 8 nm. The C-2 carbon exhibits a wider pore size distribution than C-1 being the values for the full width at half maximum (FWHM) of 5 nm for C-2 and 2.5 for C-1. Additionally, for C-1 a remarkable presence of micropores below 2 nm is also observed. The CO₂ adsorption method, which is adapted for monitoring the pores below 0.7 nm, detected for both carbons a small amount of narrow micropores (~0.3 cm³ g⁻¹), which corresponds to the intrinsic porosity of the carbon skeleton. It does not contribute significantly to the total pore volume of the materials (1.2 cm³ g⁻¹ for C-1 and 2.0 cm³ g⁻¹ for C-2), however, it plays an important role in the formation of the electrical double layer taking into account the size of solvated and/or non-solvated ions.

3.2. Electrochemical properties

Both types of mesoporous carbons were investigated as electrodes for supercapacitors. They present significant differences in electrochemical behaviour which reflect the different pore size distribution. The values of capacitance were estimated from the equation

$$C = dq dE^{-1}$$

(2)

and expressed per mass of mesoporous active material of one electrode. For the calculation of specific capacitance ($F g^{-1}$) from the galvanostatic experiments, the values of current is multiplied by the discharge time. Then, the charge obtained is divided by the voltage range in which the capacitor is discharged. In the case of cyclic voltammetry the average capacitive current is divided by the scan rate. Because of the two-electrode system, the result is multiplied by two and divided by the active mass of one electrode to obtain the specific capacitance in $F g^{-1}$.

Table 2 presents the capacitance values for both samples C-1 and C-2 in acidic, alkaline and aprotic media estimated from impedance spectroscopy at 1 mHz, galvanostatic discharge at a current load from 100 mA g^{-1} to 1000 mA g^{-1} and voltammetry cycling at scan rates from 1 mV s^{-1} to 20 mV s^{-1} . The behavior of both samples in acidic media fits in the pattern previously reported for templated mesoporous carbons [16]. In particular, the slighter decrease of specific capacitance for sample C-1 compared to that observed for a similar material with a narrower pore size distribution indicates that such novel carbon presents an accessible pores structure for efficient charging of electrical double layer even at high current density. Independently on the regime used (Table 2), the carbon C-1 presents higher capacitance values than C-2 in all the electrolytic solutions that correlates with a more developed surface area (1880 m²/g in comparison to 1510 m²/g) [16]. Slightly higher values have been found for C-1 and

C-2 in acidic ($1\text{ mol l}^{-1} \text{ H}_2\text{SO}_4$) than in alkaline medium ranging from 200 F g^{-1} to 140 F g^{-1} depending on the regime used. Quite amazing is the fact that the carbon C-2 dramatically loose the ability for charge accumulation at higher current load in KOH medium, e.g. at 500 mA g^{-1} it supplies only 87 F g^{-1} whereas the capacitance of C-1 in the same conditions is 145 F g^{-1} . Such capacitance aggravation for C-2 could be interpreted by a worse connectivity between pores than in C-1. Contrarily, in the acidic electrolyte as well as in aprotic medium only a very moderate decrease of capacitance was observed for both carbon samples with the increase of scan rate or current density. In aprotic medium ($1\text{ mol l}^{-1} \text{ TEABF}_4$ in acetonitrile), values close to 100 F g^{-1} were estimated that represents a high capacitance for an organic solution.

Among the three methods used for the capacitance estimation each one supplies a different information, e.g. the most correct values are given by the galvanostatic technique, impedance spectroscopy supplies too low values due to the hindrance of alternating current penetration, on the other hand, voltammetry can be very useful for the estimation of accompanying redox phenomena. An example of voltammetry experiments (from 2 mV s^{-1} to 20 mV s^{-1}) for the carbon C-1 in acidic electrolytic solution is shown in Fig. 3. A good charge propagation is observed with a quite regular box-like shape without drastic changes of characteristics at higher scan rates. However, the slight tilt of the voltammetry characteristics can be interpreted by some parasitic reactions, probably due to remaining oxygen in the carbon material originated from its polyfurfuryl precursor. A lack of this tilt in the organic and alkaline media supports such an assumption because the eventual redox reactions of the oxygenated groups are definitively more pronounced in the acidic than in the aprotic electrolyte. For comparison in Fig. 4a, a perfect capacitor behaviour is shown for C-1 in organic electrolyte with square shape characteristics in a wide range of scan rates from 2 to 20

mV s⁻¹. The same observation is obtained from the galvanostatic mode, at high current load of 1A g⁻¹, showing a symmetric charge/discharge characteristic of triangular shape typical for ideal capacitor behaviour, that proves a quick charge propagation with a very limited ohmic drop (Fig. 4b).

Electrochemical impedance spectroscopy (EIS) supplies additional information about the capacitor performance such as frequency dependence and equivalent series resistance (ESR). All the samples were investigated by EIS in the three electrolytes before and after cycling. Very similar behaviour has been found for the acidic and organic solution independently of the sample. Fig. 5 presents an impedance Nyquist plot of a supercapacitor built from the carbon C-1 before and after 3000 cycles performed at 500 mA g⁻¹ in acidic solution. Only a slight increase of ESR is found after cycling, however, an opposite situation appears in alkaline solution where the ESR increases significantly. The capacitance-frequency dependence for the carbon C-1 in acidic electrolyte is shown in Fig. 6. It can be observed that after 3000 cycles performed at 500 mA g⁻¹ current load, the ability of penetration for alternating current into the pores remains almost the same at high frequencies but the capacitance is slightly smaller at low frequencies. The moderate decrease of capacitance in the low frequency range (1mHz - 10mHz) observed before cycling could indicate the contribution of pseudocapacitance effects which gradually disappear with cycling. Such an assumption is very coherent with the remarks drawn from Fig. 3 to interpret the tilt of the voltammetry characteristics. On the other hand, for organic solution the better frequency dependence was found than for acidic medium.

Some trials were also undertaken to find a possible correlation of the cycling ability of both mesoporous carbons with such parameters as leakage currents (L_c) and self-discharge (S_d). L_c reflects the flow of residual current when the capacitor is charged

potentiostatically to 1V in aqueous medium and to 2V in organic solution. This current represents to some extent all the parasitic reactions which in the equivalent circuit are expressed as a resistor connected in parallel. From a practical point of view, it seems that the lower leakage current, the better capacitor performance. The capacitor is charged for 2 h and the flowing current (L_c) is measured at this time. After 2 h, the potentiostatic mode is stopped, hence, a gradual loss of capacitor voltage with time, i.e. self-discharge is measured. L_c and S_d were estimated for both carbons in all the electrolytes and the lowest L_c values were found for carbon C-2 in organic electrolyte. For example, in organic medium L_c was equal to 3.8 mA g⁻¹ for C-2 and 6.5 mA g⁻¹ for C-1, whereas after 20 h S_d was 54 % for C-2 and 40% for C-1. The comparison of these parameters for the carbon C-1 in acidic and organic solution is given in Fig. 7. One of the most important parameters of a capacitor is its durability. Only in some cases we found a strict correlation between the lower value of L_c and the good ability for cycling. Capacitors based on the carbon C-2 cycled over 3000 galvanostatic cycles with a high load of 500 mA/g (ca. 5 mA cm⁻²) preserved capacitance values of 135 F/g in acidic medium (before cycling 144 F/g). Moderate aggravation of cyclic behaviour was found for carbon C-1 from 147 F/g to 114 F/g even if L_c was smaller (L_c = 5.1 mA g⁻¹ for C-1 and 8.9 mA g⁻¹ for C-2). The lack of strict correlation proves that the leakage current can be affected by many other parameters. Systematic studies of capacitance values during cycling at 500 mA g⁻¹ are shown in Table 3. Quite comparable behaviour is observed for such regime in the case of both carbons. However, a careful analysis shows that cyclability for organic medium is comparable for both carbons but contrarily carbon C-2 maintains higher capacitance values with cycling in acidic medium. Taking into account that templated carbons are especially adapted for a high charge/discharge rate the sample C-1 was loaded until 20 A g⁻¹ (ca. 20 mA cm⁻²) in acidic electrolyte. A

gradual decrease of capacitance was observed with a higher load and at 20 A g⁻¹ a remarkable loss of capacitance was observed ($C = 44 \text{ F g}^{-1}$) and the energy diminished significantly.

Another important parameter of capacitor is the time constant RC which determines the performance. It is important to mention that capacitors built from both carbons were characterized by a small time constant RC of the order of 0.6-3 s calculated from impedance spectroscopy.

The novel carbon materials seem to be especially adapted for performance in the organic medium (TEABF₄ in AN) where the diffusion of large-size ions (cation ca. 7.4 Å and anion ca. 4.9 Å) can proceed more easily. A significant profit of organic electrolyte is especially expressed in enhanced energy due to the wider operating voltage of minimum 2 V.

4. Conclusions

The nanostructured carbons prepared from silica templates are certainly a good issue for providing useful information on pore size effects. Electrochemical measurements on the two types of mesoporous carbons used as capacitor electrodes proved that the carbon with a smaller average pore centred at 3 nm presents definitively a better capacitor performance than carbon with 8 nm average pore size. It is generally accepted that mainly micropores play an essential role for charging the electrical double layer and they determine the values of capacitance, however, a good charge propagation and ability for high current loads is strongly affected by the presence of small mesopores (2-4 nm). Since both investigated carbons have the same amount of narrow micropores below 0.7 nm, the values of capacitance are quite comparable in the two

cases. However, the carbon C-1 has additional supermicropores which improve the capacitors performance. We proved that a 3 nm size of pores is sufficient and the most useful for a perfect ions motion. It seems that pores with a size over 4 nm have a limited use for efficient charging of EDL. Well balanced micro/meso porosity is crucial for a good capacitor operation. It is well known that very high mesopores content is even harmful for optimal capacitor operation [19]. Moreover, the higher mesopore volume, the lower density of material that diminishes the volumetric energy of these advanced carbons. However, it is also necessary to mention the high cost of template carbons which are perfect for fundamental research, but cannot practically replace activated carbons.

Our experiments proved that templated mesoporous carbons are well adapted for high charge/discharge load especially in acidic as well as in organic electrolytic solutions.

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CAPTIONS TO TABLES

Table 1. Characteristics of the porous structure of the templated carbons

Table 2. Capacitance values (F g^{-1}) of the mesoporous carbons C-1 and C-2 prepared through the template technique. The capacitance was measured by impedance spectroscopy at 1 mHz, galvanostatic discharge and voltammetry techniques.

Table 3. Capacitance values during cycling of capacitors built from mesoporous carbon C-1 and C-2 in three electrolytic solutions. Current load of 500 mA g^{-1} .

Table 1. Characteristics of the porous structure of the templated carbons

Carbon	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Total pore volume ($\text{cm}^3 \text{g}^{-1}$)	α -analysis		Maximum of pore size distribution (nm)	FWHM (nm) ^a
			Mesopore volume ($\text{cm}^3 \text{g}^{-1}$)	Sext ($\text{m}^2 \text{g}^{-1}$)		
C-1	1880	1.22	1.08	20	2.8	2.5
C-2	1510	1.96	1.79	50	8.0	5.0

^a Full width at half maximum

Table 2. Capacitance values (F g^{-1}) of the mesoporous carbons C-1 and C-2 prepared through the template technique. The capacitance was measured by impedance spectroscopy at 1 mHz, galvanostatic discharge and voltammetry techniques.

	1 mol l^{-1} H_2SO_4 (F g^{-1})		6 mol l^{-1} KOH (F g^{-1})		Aprotic medium (F g^{-1})	
	C-1	C-2	C-1	C-2	C-1	C-2
Impedance-1 mHz	145	127	137	115	91	83
100 mA g^{-1}	191	161	184	134	97	93
200 mA g^{-1}	172	154	169	121	96	89
500 mA g^{-1}	155	144	145	87	90	86
1000 mA g^{-1}	143	132	133	67	86	80
1 mV s^{-1}	199	164	205	160	113	109
2 mV s^{-1}	178	158	186	143	108	99
5 mV s^{-1}	163	156	156	136	100	97
10 mV s^{-1}	154	143	148	69	98	96
20 mV s^{-1}	144	134	132	47	94	95

Table 3. Capacitance values during cycling of capacitors built from mesoporous carbon C-1 and C-2 in three electrolytic solutions. Current load of 500 mA g⁻¹.

cycles	C – 1			C – 2		
	1 mol ⁻¹ H ₂ SO ₄ (F g ⁻¹)	6 mol ⁻¹ KOH (F g ⁻¹)	Aprotic (F g ⁻¹)	1 mol ⁻¹ H ₂ SO ₄ (F g ⁻¹)	6 mol ⁻¹ KOH (F g ⁻¹)	Aprotic (F g ⁻¹)
20	147	144	92	144	90	90
500	141	140	92	142	87	87
1000	132	137	91	137	87	89
1500	128	133	90	139	84	89
2000	122	131	88	136	84	92
2500	119	126	89	135	80	90
3000	114	125	88	135	75	87

Fig. 1 SEM images of the mesoporous carbons C-1 and C-2

Fig. 2 Nitrogen adsorption/desorption isotherms at 77K. Inset: pore size distributions of the templated carbons

Fig. 3 Capacitor behaviour of the carbon C-1 at different voltage scan rates.

Electrolyte: $1 \text{ mol l}^{-1} \text{ H}_2\text{SO}_4$

Fig. 4 Capacitor performance of the carbon C-1 in 1mol l⁻¹ TEABF₄ in CH₃CN: a) voltammetry at three voltage scan rates; b) galvanostatic charge/discharge cycling at 1 A g⁻¹ current load.

Fig. 5 Impedance spectroscopy of the carbon C-1 before and after 3000 cycles in the organic medium.

Fig. 6 Capacitance-frequency dependence for the carbon C-1 in 1 mol l⁻¹ H₂SO₄ solution before and after cycling with 500 mA g⁻¹ current load.

Fig. 7 Self-discharge and leakage current for carbon sample C-1 in organic (1mol l^{-1} TEABF₄ in CH₃CN) and acidic (1mol l^{-1} H₂SO₄) medium.