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Performance of mesoporous carbons derived from poly(vinyl alcohol) in electrochemical capacitors

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Abstract

The present work shows that mesoporous materials obtained by the carbonization of mixtures of poly(vinyl alcohol) with magnesium citrate are very promising candidates for electrodes in supercapacitors. Their high performance arises essentially from a double-layer mechanism through the extent of the total surface area and one obtains at low current density (1 mA cm^{-2}) values as high as 180 F g^{-1} in aqueous 2 M H_2SO_4 electrolyte and around 100 F g^{-1} in 1 M $(C_2H_5)_4NBF_4$ in acetonitrile. Moreover, in most cases the specific capacitance is reduced only by 15% at 100 mA cm^{-2}, as opposed to many other types of carbons which display much higher reductions.

This study suggests that these novel carbons could be potentially more advantageous as electrodes in electrochemical capacitors than templated mesoporous carbons.

Keywords: Electrochemical capacitor; Carbon; Mesoporosity; Surface area

1. Introduction

Carbon in electrochemical capacitors stores charge by ion attraction on the surface of porous carbon at the electrode/electrolyte interface. It has been recently reported [1] that ion–carbon distance is significantly decreased in highly microporous materials with pores smaller than the size of solvated electrolyte ions, thus allowing more ions to cover the carbon surface and leading to increase the electric energy storage.

On the other hand, several studies have reported that high-surface-area carbons with a porosity formed essentially by mesopores could be potentially more advantageous than microporous carbons [2–4] to provide high power density. At the present time, research on alternative procedures to the conventional activation process for manufacturing mesoporous carbons with well-defined structural characteristics is being intensive [5]. Following the so-called templating technique [6–10], carbons with high specific surface areas and with narrow pore size distributions centered in the mesopores range have been obtained by filling the pore system of an inorganic template matrix with a carbon precursor and the subsequent carbonization of the composite. The inorganic template is finally removed by acid treatment. Previous studies showed that templated mesoporous carbons (TMCs) are well adapted for high charge/discharge loads [2–4,10], but the high production costs are a major obstacle to their commercial use [11].

Recently, carbons with high surface areas were successfully prepared from mixtures of thermoplastic precursors with MgO precursors. The carbons obtained were rich in mesopores with sizes close to those of the original MgO particles [12–15].

The aim of the present study is to show that the electrochemical behaviour of low-cost materials obtained by the carbonization of mixtures of poly(vinyl alcohol) with magnesium citrate is practically the same as that observed for templated mesoporous carbons. They essentially perform as electrochem-

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ical double-layer capacitors through the extent of their total surface area.

2. Experimental

The synthesis of the carbons has been reported in detail elsewhere [12,15]. Briefly, powder mixtures of Mg citrate ($Mg_3(C_6H_5O_7)_2$, reagent grade) with poly(vinyl alcohol), PVA, were heat-treated ($5\,°C\,min^{-1}$) at 900 °C for 1 h in a flow of Ar gas ($60\,ml\,min^{-1}$). After carbonization, carbon-coated MgO particles were obtained and the carbon was isolated by removing MgO with 1 M H_2SO_4 at room temperature. The carbon content of carbon-coated MgO was around 35 wt.% [15]. The majority of particles seem to be below 50 μm in diameter.

The mixing ratio was defined as the mass ratio of MgO which was expected to be formed from Mg citrate, to the carbon precursor PVA. Carbons are designated as MPXY (Table 1), which indicates that the materials were prepared by using a mixture made of X parts of MgO and Y parts of PVA (in mass). MP100 means the carbon prepared from Mg citrate only.

Different and complementary techniques were used to determine the specific surface area of the carbons, such as N_2 adsorption at −195 °C (*Micromeritics ASAP 2010*) and immersion calorimetry (Clavet-type calorimeter) into benzene and 0.4 M phenol aqueous solutions at 20 °C [16].

Sandwich-type capacitors were prepared with two carbon pellets (8 mm in diameter) separated by a glass fibre sheet and placed inside a Swagelok-cell. The electrodes were obtained by pressing a mixture of carbon (75 wt.%), polyvinylidene fluoride (20 wt.%) and carbon black (Super P, 5 wt.%). The electrolytes were 2 M H_2SO_4 aqueous solution and 1 M $(C_2H_5)_4NBF_4$ in acetonitrile. The properties for charge storage were tested by galvanostatic charge–discharge voltage cycles (potentiostat–galvanostat *Autolab-Ecochimie PGSTAT 30*) at current density ranging between 1 and $100\,mA\,cm^{-2}$. The specific capacitance ($F\,g^{-1}$) is relative to the carbon mass in a single electrode.

3. Results and discussion

In a first step, the analysis of the adsorption isotherms by a comparison plot based on the reference nitrogen isotherm for *Vulcan 3G* led to total surface areas S_{comp} (Table 1). It is in good agreement with the values obtained from immersion calorimetry into aqueous solutions of phenol (S_{phenol}) and into benzene ($S_{benzene}$). On the other hand, the BET equation frequently overrates the surface area of the carbons (S_{BET}). Fig. 1 shows the evolution of the average specific surface area $S_{av} = (S_{comp} + S_{phenol} + S_{benzene})/3$ of the carbons with the MgO/PVA ratio in the pristine mixture. It appears that the addition up to approximately 40% of MgO to the raw mixture gradually increases the specific surface area of the resulting carbons to approximately $1300\,m^2\,g^{-1}$. For higher MgO contents, S_{total} visibly levels off at this value.

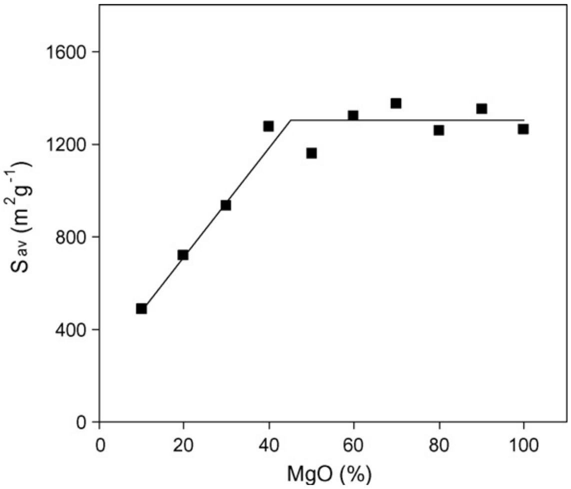

Fig. 1. Evolution of the average specific surface area of the carbons with the percentage of MgO in the raw mixture.

In a second step, the analysis of the low pressure data with the Dubinin equation [16] led to values of E_0 below $16\,kJ\,mol^{-1}$ (Table 1) which practically exclude the presence of classical micropores (carbons MP19, MP28 and MP37 are limiting cases). The pore size distributions (PSD) of the mesopores were obtained by applying the Kruk–Jaroniec–Sayari (KJS) method to the adsorption branch [17]. Fig. 2 shows a large variety of PSDs, strongly dependent on the MgO/PVA ratio. Thus, the increase in MgO content up to 50% gradually shifts the carbon porosity to narrow pore size distributions around 5 nm. No significant changes in PSD are observed for carbons derived from higher MgO/PVA mixing ratios.

The analysis of the textural properties of materials obtained by the carbonization of mixtures of MgO and PVA shows that

Table 1
Textural parameters for the materials obtained by carbonization of Mg citrate/PVA mixtures

Carbon	MgO/PVA ratio	S_{comp} ($m^2\,g^{-1}$)	S_{phenol} ($m^2\,g^{-1}$)	$S_{benzene}$ ($m^2\,g^{-1}$)	S_{BET} ($m^2\,g^{-1}$)	E_0 ($kJ\,mol^{-1}$)
MP19	1/9	442	505	512	590	17.0
MP28	2/8	755	700	691	867	16.8
MP37	3/7	967	932	889	1197	16.0
MP46	4/6	1230	1249	1348	1464	15.6
MP55	5/5	1305	1085	1089	1727	15.5
MP64	6/4	1264	1235	1455	1736	15.4
MP73	7/3	1263	1375	1470	1792	15.5
MP82	8/2	1160	1154	1456	1579	15.8
MP91	9/1	1332	1147	1574	1838	15.4
MP100	10/0	1208	1215	1368	1810	15.9

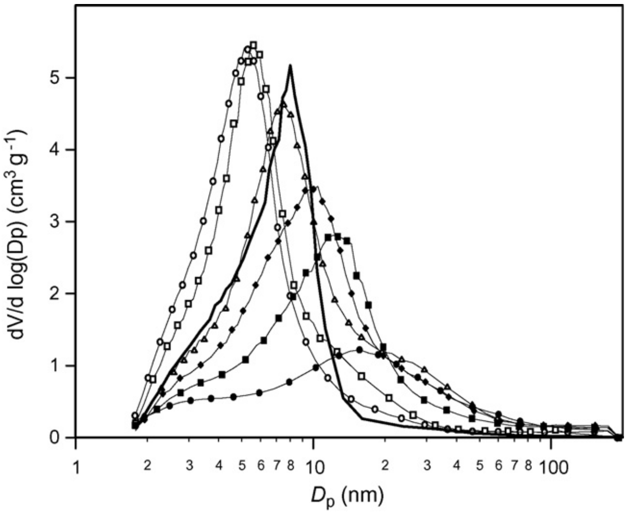

Fig. 2. Pore size distributions for mesoporous carbons obtained from Mg citrate/PVA mixtures: (●) MP19, (■) MP28, (♦) MP37, (△) MP46, (□) MP55, (○) MP100 and for a mesoporous carbon obtained by templating method C2 (▬) [3]. D_p is the pore diameter.

they are comparable to those reported for mesoporous carbons obtained by the templating method [2,3,10]. As an example, Fig. 2 also includes the pore size distribution for a mesoporous carbon (C2), templated from SBA-16-type silica by using polyfurfuryl alcohol as carbon precursor. Sample C2 displayed a total specific surface area of approximately 1500 m^2 g^{-1} and a porosity around 8 nm in diameter [3].

Fig. 3 illustrates the linear increase of the limiting specific capacitance at low current density (1 mA cm^{-2}), C_0, with the total surface area of the carbons obtained by the heat treatment of Mg citrate/PVA mixtures. It leads to average surface-capacitances of 0.14 F m^{-2} in aqueous 2 M H_2SO_4 solution and of 0.07 F m^{-2} in the aprotic electrolyte 1 M $(C_2H_5)_4NBF_4/CH_3CN$. From a practical point of view, it should be pointed out that the high mesoporous volume of these carbons results in volumetric capacitances (referred to the electrode volume) of around 50 F cm^{-3}, which are significantly lower than those found for microporous carbons.

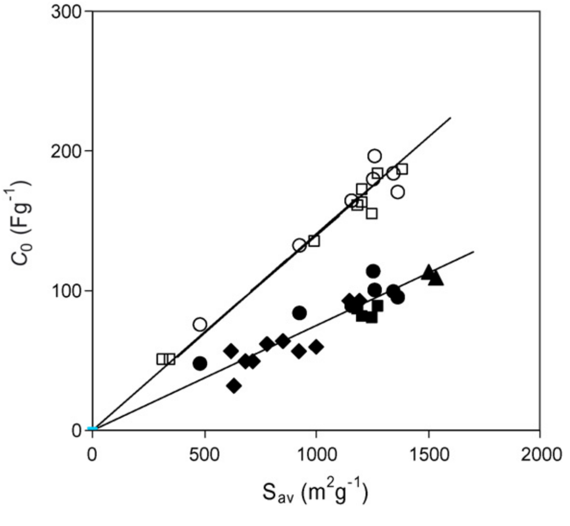

Fig. 3. Variation of C_0, the specific capacitance at 1 mA cm^{-2}, with the total surface area for different mesoporous carbons. In 2 M H_2SO_4: carbons derived from Mg citrate/PVA mixtures (○) and templated carbons from Ref. [10] (□). In 1 M $(C_2H_5)_4NBF_4/CH_3CN$: carbons derived from Mg citrate/PVA mixtures (●) and templated carbons from Ref. [2] (▲), [3] (♦) and [10] (■). The lines through the origin correspond to 0.14 F m^{-2} (2 M H_2SO_4) and 0.075 F m^{-2} ($(C_2H_5)_4NBF_4/CH_3CN$).

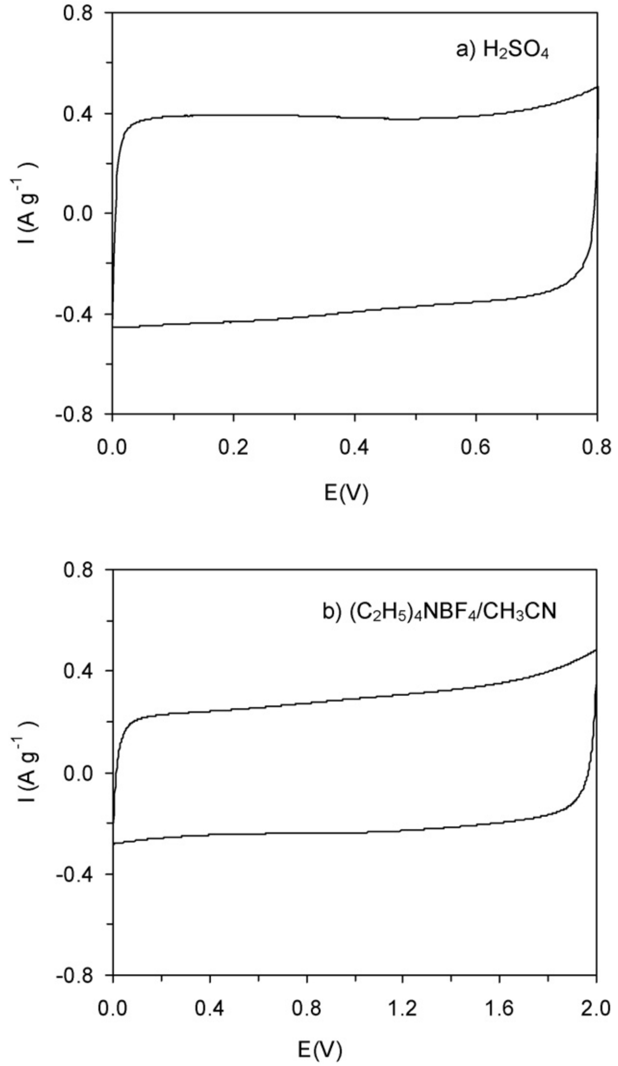

Fig. 4. Cyclic voltammograms for the carbon MP37 at 5 mV s^{-1} in 2 M H_2SO_4 (a) and $(C_2H_5)_4NBF_4/CH_3CN$ (b).

The good fit to the general pattern reported for a large variety of templated mesoporous carbons [10,18] suggests that the performance of the present carbons is comparable to that of TMCs and they behave in both aqueous and aprotic electrolytes as electrical double-layer capacitors through the extent of their total surface area. As already observed for TMCs [10], cyclic voltammograms present a rectangular shape (Fig. 4) and the contribution from redox processes involving oxygen-containing surface species does not seem to be significant due to the relatively low content of surface functionalities in materials obtained by only carbonization around 900–1000 °C. The measurement of the enthalpy of immersion into water [16] led to a surface density of oxygen-containing functionalities around 2 μmol m^{-2} for the present carbons. In the case of the aprotic electrolyte

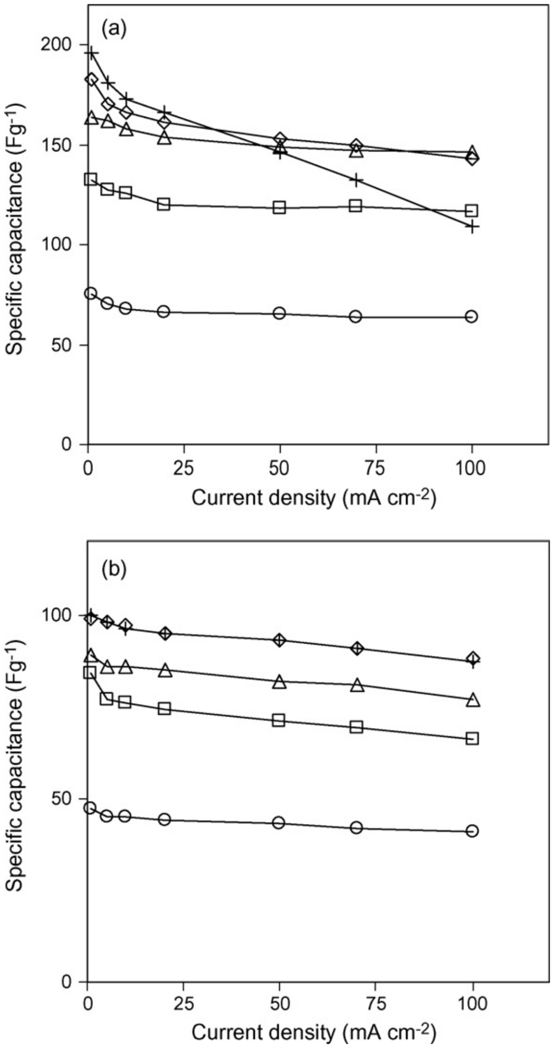

Fig. 5. Evolution of the specific capacitance of the carbons derived from Mg citrate/PVA mixtures with the current density in 2 M H_2SO_4 (a) and 1 M $(C_2H_5)_4NBF_4/CH_3CN$ (b): (○) MP19, (□) MP37, (△) MP55, (◇) MP91 and (+) MP100.

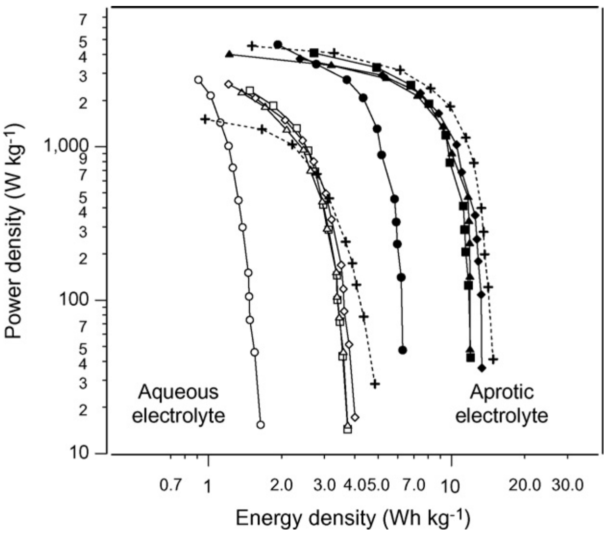

Fig. 6. Ragone-type plots for carbons derived from Mg citrate/PVA mixtures: (○, ●) MP19, (□, ■) MP55, (△, ▲) MP73, (◇, ◆) MP91 and (+) a templated mesoporous carbon C-65-HT [10]. Open symbols for 2 M H_2SO_4 aqueous solution. Closed symbols for 1 M $(C_2H_5)_4NBF_4/CH_3CN$.

$(C_2H_5)_4NBF_4/CH_3CN$, the presence of oxygen surface groups has no significant effects on the performance of carbon materials [19].

It is also interesting to point out that the ratio of the limiting capacitances in the aprotic electrolyte and in the acidic medium for the present carbons, $C_0(\text{aprotic})/C_0(\text{acidic}) = 0.57 \pm 0.05$ confirms an earlier correlation of 0.54 ± 0.09 obtained for a variety of carbons [10,19].

The evolution of the electrical capacitance with the current density is of prime importance to evaluate the potential of carbons for high power applications. Fig. 5 reports the slight decrease of the specific capacitance with current density for carbons of series MP in 2 M H_2SO_4 (Fig. 5a) and in 1 M $(C_2H_5)_4NBF_4/CH_3CN$ (Fig. 5b) electrolytes. Thus, the change from 1 to 100 mA cm^{-2} reduces their specific capacitance approximately 15% in both electrolytes. This is a great advantage over templated mesoporous carbons, which usually display, under similar experimental conditions, a loss in capacitance of around 35% [14]. According to previous studies [10,12,16,19], their improved EDLCs-performance at high current density may be due to a low proportion of acidic groups on the surface of MP-carbons.

As illustrated by Fig. 6, carbons derived from Mg citrate/PVA appear to have a reliability at high power similar to that of the best TMCs performers [10]. MP-capacitors provide about 3 Wh kg^{-1}at power 4000 W kg^{-1} (based on active mass of carbon in the capacitor) for 2 V-$(C_2H_5)_4NBF_4/CH_3CN$ devices, whereas 0.8 V-H_2SO_4 systems achieve power densities around 2600 W kg^{-1} at 1 Wh kg^{-1}.

4. Conclusions

Porous carbons with specific surface areas up to 1300 m^2 g^{-1} were successfully prepared by the carbonization at 900 °C of mixtures of poly(vinyl alcohol) with magnesium citrate. The porosity of the resulting materials corresponded almost exclusively to mesopores centered between 5 and 15 nm.

Their performance in electrochemical capacitors is essentially based on a double-layer mechanism through the extent of their total surface area. Average values of surface-capacitance around 0.140 and 0.075 F m^{-2} for 2 M H_2SO_4 aqueous solution and 1 M $(C_2H_5)_4NBF_4$ in acetonitrile, respectively, have been observed at low current density (1 mA cm^{-2}). Moreover, the behaviour at high current density of these novel carbons appears to be very promising, since the specific capacitance measured at 1 mA cm^{-2} in the aprotic electrolyte is only reduced, on average, by approximately 15% at 100 mA cm^{-2}. With the exceptions of carbons MP91 and MP100, a similar behaviour is observed for the 2 M H_2SO_4 electrolyte. In comparison, in the case of typical activated carbons and templated mesoporous carbons, the decrease in capacitance between 1 and 100 mA cm^{-2} often exceeds 35%. This clearly illustrates the advantage of the present type of carbons.

As far as the correlation between the unit cost and the specific capacitance is concerned, the carbons obtained by the carbonization of mixtures of poly(vinyl alcohol) with magnesium citrate seems to be potentially more advantageous as electrodes in electrochemical capacitors than templated mesoporous carbons and many types of activated carbons.

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