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Graphene-doped carbon xerogel combining high electrical conductivity and surface area for optimized aqueous supercapacitors

María Canal-Rodríguez [a], Ana Arenillas [a], Natalia Rey-Raap [a], Gloria Ramos-Fernández [b], Ignacio Martín-Gullón [b], J. Angel Menéndez [a, *]

[a] Instituto Nacional del Carbón, CSIC, Apartado 73, 33080, Oviedo, Spain
[b] Chemical Engineering Department, University of Alicante, Alicante, 03690, Spain

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ABSTRACT

A graphene doped carbon xerogel was synthesized by simply replacing the water (solvent) by an aqueous well-dispersed graphene oxide stable suspension in the precursor mixture used for the synthesis of the organic xerogel. During the carbonization of the organic xerogel, the graphene oxide sheets are reduced to graphene, which is embedded and well dispersed within the carbon xerogel matrix. Only a small minimum amount of graphene oxide is necessary to interconnect the graphene sheets throughout the carbon xerogel. This material has both a high porosity and an excellent electrical conductivity so that, when used as electrode in aqueous supercapacitors at high current density, it provides them with 25% more capacitance and 100% more power than the undoped carbon xerogels. The synthesis conditions, characteristics of the carbons and how these affect the electrical conductivity and performance of the materials in the supercapacitors are discussed.

1. Introduction

Energy storage and power delivery are currently acquiring increasing importance as society becomes more concerned with the supply of clean energy and its sustainability. As a consequence, special attention is paid to the development of renewable energy sources and the need to store the energy generated for future supply or demand. Thus, to overcome the fluctuations in the grid, not only a system that stores energy is needed but also one able to supply it as a quick response, i.e. a high power density device. On the other hand, devices which can store large amounts of energy and have long cycle life are also preferred [1]. Unfortunately, at the moment there is no single device capable of dealing with the main both requirements, i.e. the supply of a large amount of energy and a high power density [2]. Batteries are generally preferred for high energy density applications. However their power density is low and their charge-discharge processes often involve irreversibility in the short-medium term, and so the cycle-life of batteries is usually limited. By contrast, in supercapacitors (or electrochemical capacitors) the energy storage mechanism is a reversible process, enabling them to offer a long durability (over 10^6 cycles). Moreover, supercapacitors are capable of supplying high power densities, i.e. more than 10 kW kg^{-1} [3]. Nevertheless, their capacitances are still lower than those of batteries, and therefore R&D in this field is focused on finding new materials for supercapacitors that improve its current performance [4–14].

The ideal active material for use in electrodes of supercapacitors would be a material with a large surface area (i.e. a high volume of micropores for storing the ions of the dissociated electrolyte), with a sufficient amount of transport pores (i.e. mesopores for the electrolyte to pass through and reach the entire micropore structure), and a high electrical conductivity to ensure an easy and fast transportation of electrons. Typically, carbon materials do not have both a high electrical conductivity and at the same time a high specific surface area (see Table 1). This is because a good electrical conductivity requires an ordered and crystalline carbon structure, like that of graphite, which implies a poor porous structure. On the other hand, a high surface area carbon with a large pore volume implies, in general, a disordered amorphous carbon structure with a low electrical conductivity. Nevertheless, there are some exceptions to this general rule as can be seen in Table 1.

A possible solution to overcome this problem might be to embed a highly conductive ordered carbon, like nanotubes or graphene [5–11], inside a porous carbon in such a way that the conductive

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* Corresponding author.
E-mail address: angelmd@incar.csic.es (J.A. Menéndez).

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Table 1
BET specific surface areas and electrical conductivities of selected carbon materials.

Carbon Material	Reference	S_{BET} ($m^2 g^{-1}$)	K-FPP ($S m^{-1}$)	K-COM $\times 10^2$ ($S m^{-1}$)
Biomass derived activated carbon	[15]	2800	13	3
Graphene doped carbon xerogel	This work	1556	310	125
Polimer derived activated carbon	[16]	836	30	10
Graphene/carbon composite aerogel	[6]	763	528	216
Comercial (biomass) activated carbon	[17]	711	12	2
CNT aerogel	[18]	635	150	59
Chemically treated carbon black	[19]	559	249	100
Graphene aerogel	[7]	244	133	52
Graphite (= to basal plane)	[20]	<100	6057	2500
Graphite (⊥ to basal plane)	[20]	<100	15	3

K-FPP: Electric conductivity measured using four point probing. K-COM: Electric conductivity measured using the compression method. Note that the values obtained by these two methods are not directly comparable. However, they can be converted each other using the equations from Ref. [21].

carbon creates a network that facilitates electron transportation, while retaining the porosity of the material that acts as matrix. However, the synthesis of such a carbon is not straightforward. Ling et al. [9] attempted to dope a porous carbon directly with graphene using an ionic liquid template approach, but with difficulties for a good dispersion of the conductive material along the amorphous carbon matrix. Other authors [5,6,8], doped the porous carbonaceous materials with different quantities of graphene oxide and obtained the final graphene-doped carbon by subjecting the material to subsequent thermal treatment. However, either these doped materials do not have a large pore volume, which is the key to the performance of supercapacitors, or the amount of doping is extremely high (i.e. up to 10 wt% in the precursor solution), being in some cases considered as carbon composites by the authors [5,6], and resulting in less cost-effective carbons.

The solution proposed in this work consists in obtaining a carbon xerogel, with the appropriate porous structure in terms of micro and mesoporosity by using a suspension (in water) of graphene oxide (GO) as solvent, instead of just water which is the usual method. This is not only a simple process but it is also relatively cheap (compared to some of those described above) since it uses GO (cheaper than graphene), that is then converted into graphene by carbothermal reduction. The process is fast and simple, and in addition, it might open up a new market for GO, thereby redressing the, until now, low commercialization of this product.

2. Experimental

2.1. Materials

An organic xerogel (MWOX) was synthesized by the polycondensation of resorcinol (R) with formaldehyde (F) in water (W) using a 1 M solution of NaOH to adjust the pH. Firstly, the resorcinol was dissolved in deionized water in a flask under magnetic stirring. Then, formaldehyde (37 wt%) was added to the mixture and kept under stirring until a homogeneous solution was obtained. The gel was synthesized using a molar ratio (R/F) of 0.5, a dilution ratio (D) of 5.7 and a pH of 6.5. Finally, the solution was placed inside a microwave oven at 85 °C for 5 h to undergo gelation, ageing and drying [12–14,22,23]. It is worth noting that this process is much shorter than the other processes reported in the bibliography that usually take several days [24,25].

Two organic xerogels were doped with Graphene Oxide (GO). The synthesis procedure was identical to that used for MWOX except that 50 wt% and 100 wt% of the solvent (W) were replaced with an aqueous 5 mg/ml GO suspension, so that the GO concentrations in the precursor solutions were of 0.11 wt% and 0.22 wt% respectively. Given that no GO was lost during the gelation, ageing and drying steps (maximum temperature of 85 °C), the resulting doped organic xerogels had GO contents of 0.23 wt% (MWOX-0.23) and 0.46 wt% (MWOX-0.46) respectively.

GO suspension was produced by liquid phase exfoliation by ultrasonication of graphite oxide. Graphite oxide was synthetized by modified Hummers-Offeman method starting of natural graphite (NG) flakes BNB90, purchased to Imerys Graphite and Carbon (Bodio, Switzerland) [26]. Basically, 1 g of graphite, 200 ml of H_2SO_4 and 1 g of $NaNO_3$ were mixed and stirred at room temperature. After 3 h, 4 g of $KMnO_4$ were added and the suspension was stirred for 2 h. Subsequently, the temperature was increased to 60 °C and kept for 1 h. Once the reaction was completed, it was cooled down to room temperature, and poured into 400 ml of cold water with 40 ml of H_2O_2, in order to prevent MnO_2 precipitation. After several water washing/filtration procedures, the solid graphite oxide product was dried overnight at 65 °C. Finally, graphite oxide powder (1 g) was introduced in deionized water (200 mL) and exfoliated into GO by high-energy sonication (QSonica Ultrasonic Q500) at 30 W for 2 h, alternating cycles of 60 s in ON mode and 30 s in OFF mode.

The organic xerogels were then subjected to a one-step carbonization/activation process in a horizontal tubular reactor under a CO_2 flow of 100 ml/min. The heating rate used was 50 ºC/min up to 1000° C. This temperature was then kept constant for the time necessary to obtain a surface area of ca. 1600 m^2/g. The overall yields attained in these processes were: 13 wt%, 18 wt% and 15 wt% for MWOX, MWOX-0.23 and MWOX-0.46, respectively. It has to be noted that the yields are relatively low because the former organic xerogel have more than 50 wt% of volatiles, moisture and residual reagents that simple evolve during the thermal heating.

In order to estimate the amount of reduced GO (which from now on will be referred to simply as “graphene”) contained in the resulting carbon xerogels, it was assumed that (i) GO is completely reduced to graphene during the carbonization/activation process. Therefore, all its oxygen content (27 wt %, according to its elemental analysis by means of a LECO TRUSPEC Micro-O analyzer) is gone during the pyrolysis and (ii) the CO_2 does not gasify the graphene but the more amorphous carbon structures instead. On the basis of these assumptions, the final percentages of graphene in the activated xerogels were ca. 1 wt% (MWAX-1) and 2 wt% (MWAX-2) respectively. Since this assumption is the only way to obtain an estimation of the wt% of graphene present in the doped carbon xerogels it should be noted that these values are only approximate.

Apart from the above mentioned samples, a commercial activated carbon (YP-50F by Kuraray) specifically recommended for use in supercapacitor electrodes (and one of the most widely used currently in commercial ultracapacitors), was also included in this study for comparative proposes.