



Performance of carbon xerogel-graphene hybrids as electrodes in aqueous supercapacitors

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ABSTRACT

A pristine carbon xerogel (AX) and two hybrid samples (AX-3% and AX-9%), with different graphene percentages (3 and 9 wt%), were synthesized using a fast and economical process. It was observed that graphene produces less shrinkage of the xerogel structure during synthesis. Moreover, the electrical conductivity of the materials increases linearly with the percentage of graphene added. Thus, AX-9% presents an electrical conductivity 135 and 321% greater than that of AX-3% and AX, respectively. As a result of the good pore size distribution and high electrical conductivity of AX-9%, when this material is used as electrode in supercapacitors, the resistance of the cell is reduced; therefore, better power densities are obtained. However, its capacitance values are the same as those of AX-3%. The performances of these materials as electrodes in supercapacitors were evaluated taking into account the influence of their porosity and electrical conductivity. Moreover, AX and AX-9% were subjected to mild oxidation with air to study the effect of air on the porosity, electrical conductivity, and performance of these treated samples as electrodes in supercapacitors.

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1. Introduction

Supercapacitors are energy storage devices that are attracting a lot of attention because, unlike batteries, they are able to supply high power densities of up to 10 kW kg^{-1} and offer long durability (over 10^6 cycles) [1]. Since their main drawback is the inability to store large energy densities, a lot of research and development projects are investigating new active carbon electrodes in an effort to overcome this [2–9]. Supercapacitors store energy mainly through two mechanisms: (i) the formation of an electrochemical double layer and (ii) faradaic reactions known as pseudocapacitance [10]. Many authors believe that the best option is the electrochemical double layer formation mechanism, as it is a quick and reversible process [11]. The performance of supercapacitors (i.e., the energy, which is directly proportional to their capacitance [12] and power values), depends on both the porosity and electrical conductivity of the active materials used as electrodes. The higher their microporosity, the greater is the charge that can be stored [11–14]. Whilst the mesoporosity and high electrical conductivity allow the ions to move faster [11,12,15–17], thereby favouring a

greater power density. On the one hand, ions move through mesopores to get to micropores, therefore the more mesopores there are, the more space there is for the ions to move through. On the other hand, a high electrical conductivity facilitates the movement of the ions through the structure of the material. Therefore, a combination of both properties in a single material would enable the supercapacitor to not only achieve greater capacitances, and therefore energies, but also obtain the same in a much shorter time.

The presence of mesopores and electrical conductivity not only affect the charge of the supercapacitor; but also the discharge, i.e., the power delivered. If the active material has an appropriate pore size distribution (PSD) and a high electrical conductivity, the equivalent series resistance (ESR) of the cell is reduced. As the power of the supercapacitors is inversely proportional to the ESR, when materials with these characteristics are used as electrodes, the resistance of the cell is lower and more power is delivered [5,6,11,12].

Accordingly, active carbons with both high porosity and optimal electrical conductivity for the easy and fast movement of ions must be obtained. However, this is not an easy task as these are opposite characteristics. Typically, materials with high electrical conductivity, such as graphene or graphite, have greatly ordered and crystalline structures, while large surface structures imply discontinuities that are not favourable for the transport of

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electrons. One way to overcome this problem would be to synthesize a mixture of porous carbons with highly conductive ordered carbons like nanotubes or graphene [2,3,6–8,18,19] in order to promote the transport of electrons while retaining the porosity of the matrix. Some scientists have attempted to use graphene [6], but have encountered difficulties that impede a good dispersion of the conductive material through the amorphous carbon matrix. Others have combined the carbonaceous material with different amounts of graphene oxide (GO) suspension [3,8,19], thus obtaining the desired graphene-carbon mixture by subjecting the material to subsequent thermal treatment. However, they were either unable to obtain highly porous materials or the amount of graphene used was too high that they obtained unprofitable composite-materials.

Another possibility would be to combine both storage mechanisms. For this, it is necessary to use active materials that have not only large surface areas and high electrical conductivities but also a large number of functional groups such as oxygen in their structure. The oxidation is normally carried out after the synthesis and can use different oxidizing agents such as HNO_3 , H_2SO_4 , or air. Several authors have demonstrated that the presence of oxygen in carbonaceous structures improves the energy storage capacity of supercapacitors [20,21]. However, this solution is not without drawbacks since the grafting of oxygen into the carbonaceous structure decreases the electrical conductivity; therefore, a balance must be sought. Lee et al. [9] oxidized an activated carbon aerogel with HNO_3 , varying the time of oxidation to analyse its effect on the performance of supercapacitors. They found that the supercapacitor showed the best capacitance values after 6 h of treatment. However, after 12 h, the capacitance values decreased due to an increase in cell resistance.

Moreover, a large content of functional groups results in the energy being stored mainly by pseudocapacitance mechanisms, which shorten the durability of the device. Thus, one of the main advantages of supercapacitor devices (i.e., long cycle life) is lost.

In the present study, a pristine carbon xerogel with a porous structure appropriate for use in supercapacitors was mixed during synthesis with different percentages of GO using a fast and affordable mechanism. The hybrid materials obtained showed that graphene was widely dispersed and integrated throughout the carbon xerogel structure, thus combining high surface area with good electrical conductivity. It is also worth noting that in the present work the graphene structures did not physically interact within the polymeric structure nor were they grafted onto the surface of the carbon xerogels, as reported in other studies. On the contrary graphene became an integral part of the polymeric structure of the samples. The performance of the hybrids as electrodes in supercapacitors was evaluated considering the influence of the graphene incorporated into their porosity, their electrical conductivity, and interaction with the electrolyte (i.e. wettability). Furthermore, we investigated the optimum amount of GO to be introduced into the carbon structure. Surface modification using mild oxidation was carried out to improve the interaction between the electrode and electrolyte. The effect of these oxygenated surface groups on the porosity, electrical conductivity, and performance of the oxidized hybrid samples as active materials in supercapacitors, was also evaluated.

2. Experimental

2.1. Synthesis of the studied materials

Three organic xerogels OX, OX-0.46%, and OX-0.92% (where the numbers represent the percentages of GO) were synthesized using microwave heating [22,23]. The reagents used were resorcinol (R), formaldehyde (F) (37 wt%), water (W), two suspensions with

different concentrations of GO (5 and 15 mg/mL respectively), and 1 M NaOH to adjust the pH of the precursor solution. The conditions used for all the cases were as follows: molar ratio (R/F) of 0.5, dilution ratio (D) of 5.7, and pH of 6.5. The synthesis of OX and OX-0.46% is described in detail elsewhere [12]. To obtain OX-0.92%, 70 wt% of the solvent was replaced by a 15 mg/mL aqueous GO suspension, thus the initial solution contained 0.5 wt% of GO. The subsequent steps were the same as those followed for the preparation of OX and OX-0.46%. After the synthesis (i.e., gelation, ageing, and drying), the concentration of GO in the organic xerogel was found to be approximately 0.92 wt%. It should be noted that because microwave heating was used, only 5 h was required to obtain the organic xerogel, unlike the conventional method of synthesis, which requires several days [4,24].

The GO suspension was produced by liquid phase exfoliation through the ultrasonication of graphite oxide in accordance with the modified Hummers-Offeman method employing natural graphite (NG) flakes BNB90 purchased from Imerys Graphite and Carbon (Bodio, Switzerland) [25]. Further details about the synthesis process have been reported in previous studies [12].

Their respective carbon xerogels (AX, AX-3%, AX-9%) were obtained by means of a one-step activation/carbonization process. Approximately 8 g of each organic xerogel was introduced into a horizontal furnace, through which 200 mL min^{-1} of CO_2 was passed (prior to heating, the furnace was swept with CO_2). The programmed heating conditions selected were $50^\circ\text{C min}^{-1}$ up to 1000°C . This temperature was maintained constant until specific areas of approximately $2500 \text{ m}^2 \text{ g}^{-1}$ were obtained for each material. It was assumed that all the oxygen contained in the GO (27 wt %) was removed during this stage. According to this assumption the final hybrid samples were labelled AX-3% and AX-9% in order to show the different graphene contents integrated in the chemical structure of the carbon xerogel.

Subsequently, AX and AX-9% were exposed to mild oxidation with air (100 mL min^{-1}), thus obtaining AXO and AXO-9%. The samples were then introduced into a horizontal furnace and heated at 350°C for 8 h; the heating rate was $10^\circ\text{C min}^{-1}$.

Apart from these in-lab samples, a commercial activated carbon sample (YP-80F from Kuraray) was also used for comparative purposes.

To study their electrochemical behaviour, disc-shaped electrodes of all the samples (i.e. carbon xerogel, xerogel-graphene hybrid samples, oxidized samples, and the commercial carbon) were prepared by mixing 90 wt% of each of these materials with 10 wt% of polytetrafluoroethylene (PTFE) as a binder. It should also be mentioned that no additive was used to facilitate the evaluation of the electrical conductivity of the samples. The manufactured pellets were 100–200 μm thick and 1 cm wide, and weighed approximately 3–4 mg. A detailed description of their assembly is available in the literature [16,26].

2.2. Characterization

The textural characteristics of all the synthesized xerogels were estimated from N_2 adsorption-desorption isotherms at 77 K (Micromeritics Tristar 3020). The S_{BET} and V_{micro} parameters were determined from the Brunauer-Emmett-Teller (BET) and Dubinin-Raduskevich (DR) equations. The total pore volume (V_p) was calculated from the amount of nitrogen adsorbed at the saturation point ($p/p_0 = 0.99$). The samples were also examined using high-resolution transmission electron microscopy (HRTEM) with a JEOL JEM-2100F microscope operated at 200 kV accelerating voltage. The microscope was equipped with a field emission gun (FEG) and an ultra-high resolution pole-piece that provided a point-resolution higher than 0.19 nm. The samples were dispersed

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