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

María Canal-Rodríguez, J. Angel Menéndez, Ana Arenillas*

Instituto Nacional del Carbón, CSIC, Francisco Pintado Fe, 26, 33011 Oviedo, Spain

*Corresponding author: Tel. +34985119090, Fax: +34985297662, Email: aapuente@incar.csic.es

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.

Keywords: carbon xerogel, graphene, supercapacitor, power density, energy
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 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 HNO₃, H₂SO₄, 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 HNO₃, 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 CO₂ was passed (prior to heating, the furnace was swept with CO₂). The programmed heating conditions selected were 50 °C min⁻¹ up to 1000 °C. This temperature was maintained constant until specific areas of approximately 2500 m² 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 °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 $S_{\text{BET}}$ and $V_{\text{micro}}$ 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 in ethanol, sonicated, sprayed onto a carbon-coated copper grid, and then allowed to air-dry.

In order to estimate the percentage of oxygen in the samples, temperature-programmed desorption (TPD) experiments were performed in a Micromeritics AutoChem II analyser. The samples were heated up to 1000 °C at a 10 °C min$^{-1}$ heating rate under 50 cm$^3$ cm$^{-1}$ Ar flow. An OmniStar Pfeiffer mass spectrometer was used to monitor the amount of desorbed CO and CO$_2$. The X-ray photoelectron spectra (XPS) of the AXO and AXO-9% samples were recorded to determine whether oxidation had affected the bulk or surface of the materials. The measurements were performed in a SPCS Phoibos 100 analyser using Mg K$_\alpha$ X-rays (1254.6 eV) programmed to operate at a power of 100 W and in a residual vacuum of 10$^{-7}$ Pa. An analyser with 50 eV pass energy was used to collect the broad scan spectra (0–1100 eV). The atomic percentages (atom%) of the different elements present in the approximately 10 nm upper layer, recorded by
XPS, were calculated from the survey spectra by integrating the areas of the main XPS peaks.

The electrical conductivity of the disc-shape electrodes of each sample was evaluated by determining their electrical resistance using a four-point probe (FPP) (model SR-4-6L, Ever-being) based on the Van der Pauw equation [26]. The FPP procedure was performed by applying contact between the four points and the surface of the disc-shape electrodes. Once the four points were touching the surface of the electrodes, a constant current in the 9–10 mA range was applied between the four points (DC current source model 6220, Keithley), while the corresponding voltage drop was measured using a digital nanovoltmeter (model 2182A, Keithley).

The electrochemical performance of the materials was studied using a two-electrode testing cell (Teflon Swagelok®). Two electrodes of each sample were placed in contact with two stainless steel current collectors (anode and cathode). The electrodes were separated by a 400 µm thick fibre glass separator, on top of which we added several drops of an aqueous 1 M H₂SO₄ solution. To evaluate the behaviour of the materials as electrodes for supercapacitors several tests were performed: i) galvanostatic charge-discharge measurements (C-D) at several current densities in the 0.1–16 A g⁻¹ range with U= 1V, ii) cyclic voltammetry tests at a scan rate of 2 mV s⁻¹ and a voltage window from 0.6 to 1.2 V, and iii) electrochemical impedance spectroscopy (EIS) analysis at 0 V (i.e., open circuit) over a frequency range of 1 mHz-100 kHz and with an AC amplitude of 10 mV.

The specific capacitance (C in F g⁻¹), energy density (E, in Wh kg⁻¹) and power density (P, in W kg⁻¹) values obtained for each electrode were calculated from the C-D plots using expressions taken from the literature [12, 27].
3. Results and discussion

Comparing the porosities of AX, AX-3%, AX-9%, and YP-80F (Table 1) it can be seen that the four carbons present similar $V_{\text{micro}}$, and therefore similar $S_{\text{BET}}$ values. This is because the conditions for the activation/carbonization of the gels were selected so as to obtain microporosity volumes almost identical with those of YP-80F. The first point worth noting is that AX and YP-80F have practically the same $V_p$, thus they not only have similar microporosity volumes but also an analogous volume of mesopores. However, for the hybrid samples, $V_{\text{meso}}$ is higher and $D_{\text{meso}}$ is wider.

The pore size distributions (PSDs) of the organic xerogels (OX, OX-0.46% and OX-0.92%) included in the supplementary material (Figure S1) show that this widening occurs during the synthesis of the organic xerogels since OX has the narrowest PSD. Moreover, the greater the amount of GO added to the precursor solution, the wider is the mesopore size. According to Guo et al. [28], GO sheets help prevent the shrinkage of gel structures that normally takes place during the drying step, thereby helping in preserving their porosities.

Micropores are generated after the activation/carbonization stage, while mesopores experience a small contraction in all the samples [12, 29, 30], as can be seen in Figure S1.

The addition of graphene to the carbon xerogels structures caused changes not only in their porosities but also in their physical properties. Figure 1 shows that the electrical conductivity of the carbon xerogels increases in a practically linear manner with the addition of graphene. As a result, AX-9% shows $1010 \ \text{S} \ \text{m}^{-1}$ electrical conductivity, which represents 135 and 321% increases compared to those of AX-3% and AX
respectively, and a 742% improvement compared to that of YP-80F (Table 2). This remarkable increase in the electrical conductivity of the hybrid samples must be due to the total integration of the graphene structures into the polymeric matrix of the xerogels, as can be observed from the HRTEM images in Figure 2. As can be seen, the addition of GO to the precursor solution of the carbon xerogel leads to the homogeneous incorporation of graphene structures into the polymeric matrix. No agglomeration of the graphene structures occurs, even in the AX-9% sample (Figure 2c), and an increase in the number of ordered homogeneously distributed platelets is observed as the graphene content of the hybrid samples increases.

To assess the performance of these materials as electrodes in aqueous supercapacitors, EIS and galvanostatic C-D experiments were carried out in 1 M H₂SO₄ electrolyte. From the results of the C-D experiments (Figure 3) it can be seen that all samples show similar capacitances at low current densities. This may be due to the fact that at these intensities the charging of the supercapacitors occurs slowly, which means that the ions have enough time to reach the micropores [12] (all the carbons present the same micropore volume). Moreover, it can be observed that all the carbons are able to withstand current densities of up to 16 A g⁻¹. Nevertheless, YP-80F is the carbon that shows the smallest capacitance retention with a 63% capacitance drop, i.e., a capacitance of 62 F g⁻¹ at 16 A g⁻¹ (Table 2). Since AX and YP-80F have similar porosity properties (V_{micro} and V_{meso}), the differences in their capacitance values can be mainly attributed to the differences in their electrical conductivities. When working at high current densities, the charge time is very short (2–3 s) (Figure S2), therefore materials with low electrical resistance are required. Consequently, since the electrical conductivity of AX is 100% greater than that of YP-80F, its capacitance is 26% higher at 16 A g⁻¹. However, the reason xerogel-graphene hybrid carbons show a smaller
capacitance drop and a better capacitance under intensive work conditions, (i.e., high current densities) must be attributed not only to their better electrical conductivity but also to their porous characteristics. Although at low current densities the presence of mesopores does not seem to be of significant importance, at high intensities (the typical working conditions of most supercapacitors) their presence is important, since mesopores serve as transport pores. When working at high current densities, the charge time lasts only a few seconds; therefore, an appropriate mesopore distribution allows the ions to migrate more quickly. The carbon structures of AX-3% and AX-9% have more than twice the volume of mesopores compared to AX and YP-80F, therefore ions have more free space to move through and can arrive at the micropores in a shorter time. When comparing the behaviours of AX-3% and AX-9%, it can be seen that they have similar porous characteristics but different electrical conductivities due to the quantities of graphene added. However, this does not seem to be important for their capacitance performance. Even though the electrical conductivity of AX-9% is approximately 130% higher than AX-3% (Figure 1) their capacitance values are analogous. Since this result is not in agreement with the previously mentioned assumption (i.e. the higher the electrical conductivity, the better the capacitance under intensive work conditions) there must be other reason to explain the anomaly, as discussed below.

The Nyquist plots of the three carbon xerogels shown in Figure 4 shift on the real impedance axis. However, the Nyquist plot of AX-9% starts at lower values than AX and AX-3%. Accordingly, the ESR values of the samples (determined from the first intersection of the loop formed at high frequencies [31]) are 0.06, 0.12, and 0.1 Ω cm², respectively. Furthermore, AX shows a noticeable 45º Warburg zone. This zone is related to the equivalent distributed resistance (EDR) i.e. the resistance to the movement of ions through the structure of the material [31]. The EDR of the AX sample is 2 Ω cm²
as determined from the linear projection of the vertical portion at low frequencies on the real axis \([32, 33]\)). However, the Warburg zone for the two hybrid carbons is almost negligible, particularly for AX-9%. This can be attributed to both the improvement of the electrical conductivity of the materials and to the presence of a large volume of mesopores in their structure.

Taking all these factors into account, AX-9% registers a power density of 21000 W kg\(^{-1}\) at 16 A g\(^{-1}\) which represents a 24 and 854% improvement compared to AX and YP-80F, respectively (Table 2). However, the energy and capacitance values of AX-9% are more moderate; in fact, they are the same as those of AX-3% (see Table 2 and Figure 3) even though AX-3% has less graphene and its electrical conductivity is 130% lower (Figure 1).

Since this cannot be attributed to electrical conductivity or porosity, the reason must be sought in the surface chemistry of the materials. The hydrophobicity, i.e., the low wettability, of the hybrid carbons may be an influential factor. Graphene is known to be a hydrophobic material \([34, 35]\), thus the addition of graphene to the carbons will increase the hydrophobicity of the hybrid xerogel end products: the more the graphene added, the more hydrophobic will the hybrid carbons become. As a result, the interaction between the aqueous electrolyte and the electrode will worsen, since the electrolyte will not be able to wet the electrode. This will prevent the axial movement of ions through the mesopores and stop them from reaching the micropores. A possible solution to this problem might be to graft oxygen-containing functional groups onto the surface of the carbon xerogels by subjecting the materials to oxidation \([9, 10, 20, 21]\). Oxygen functional groups improve the hydrophilicity of carbons (i.e., their wettability) and consequently, increase the affinity of carbons for aqueous electrolytes \([10, 20, 21, 36, 37]\). Several treatments can be employed to incorporate oxygen functional groups
within the structure of carbons, the most common being: (i) electrochemical oxidation [38], (ii) chemical oxidation with HNO$_3$ or H$_2$SO$_4$ solutions [9, 10, 21, 39], and (iii) gaseous oxidation [20, 39] which is the most convenient method and the most respectful of the porosity of the original material [20]. In the present study AX-9% was subjected to mild oxidation with air to obtain its respective oxidized material (AXO-9%). Moreover, to compare the performance of the hybrid xerogel-graphene sample with the pristine one, AX was oxidized under the same conditions producing AXO. Figure 5 shows the increase in oxygen content in the samples with respect to the oxidation time. The percentage of oxygen in the samples was calculated from the TPD analysis data. As can be seen in Figure 5, the oxidizing process is more effective during the first 4 h of oxidation, then the reaction is more gradual. In fact, after 8 h, it seems that the evolution of the oxygen content has reached a plateau. Namely, there is a maximum quantity of oxygen that can be added to the carbon xerogels structure using this procedure, regardless of their graphene content. After the oxidation, both samples, i.e., AXO and AXO-9%, contained the same amount of oxygen (approximately 6 wt%). However, the oxidation was clearly more effective for the AXO sample since its oxygen content increased by 150%, while the increase was only 54% for the AXO-9%. This could be attributed to the fact that the oxidant agent mainly attacks the more amorphous structure (i.e. the more reactive structure). Therefore, since the hybrid sample has highly ordered graphitic planes embedded within its structure, there are less suitable places for oxygen to attach easily.

The physical characteristics of AXO and AXO-9% are recorded in Table 1 and show that after the oxidation treatment the respective S$_{BET}$ values of the samples decreased, and the decrease was more noticeable for AXO-9%. Furthermore, AXO-9% also underwent a decrease in its mesopore volume and a narrowing of its mean mesopore
size compared to the original AX-9% sample. Therefore, oxidation has greater repercussions on the porosity of the hybrid sample, since it plugs not only part of its microporosity, but also some of its mesoporosity. Despite this plugging, the structure of AXO-9% has a greater volume of pores (micro and mesopores) and its mesopores are also wider than those of AXO and YP-80F.

According to the XPS analysis (Figure 6), the oxygen content of AXO and AXO-9% is 13.5 and 10.9 at %, respectively. These values are higher than those obtained from the TPD analysis mentioned above (Figure 5). Therefore, it can be concluded that the performed oxidation introduces oxygen functionalities mainly onto the surface of the samples [40] and that AXO-9% is less oxidized than AXO, corroborating once again the results of the TPD analysis. Furthermore, it can be observed that the samples are oxidized in a different manner (Figure 6). The O1s spectra of both the samples presented three matching component peaks corresponding to C=O (531.2–531.6 eV, Peak I), C–OH (532.2–533.4 eV, Peak II), and chemisorbed oxygen (534.6–535.4 eV, Peak III) [41]. However, the O1s spectra of AXO-9% also presented an unusual peak with a maximum at approximately 538.5 eV (Figure 6b). This peak can be attributed to the oxygen bonded to the less conductive carbon. Some authors claim that oxidation can cause the exfoliation of graphene sheets as oxygen attempts to link itself to the carbon structure [10]. Therefore, during the oxidation of the AX-9% sample, part of the oxygen may destroy the ordered structured created during the synthesis. Furthermore, oxidation also managed to partially join the destroyed ordered-carbon structure, re-oxidizing the graphene sheets and leading a type of low conductive carbon like GO.

It is well-known that the presence of surface oxygen-containing groups not only enhances the wettability of carbons but also decreases their electrical conductivity due to the electronegative character of the oxygen groups [42]. This statement is supported
by Figure 7, where it can be seen that the electrical conductivities of both materials decrease as the percentages of oxygen in their structures increase.

During the first few hours of oxidation, a greater quantity of oxygen is linked to the structure of the carbon xerogels, and consequently, the drop in conductivity is more pronounced, while after 4 h, the increase in the amount of oxygen is less significant; therefore, the loss in conductivity observed is not as high. Once again, the oxidation effects are more noticeable for the hybrid xerogel-graphene sample because despite registering a minor increase in oxygen content the decrease in conductivity is more pronounced. This loss of conductivity may be due not only to the electron-withdrawal character of the oxygen-containing surface groups (TPD data in the supplementary information, Figure S3), but also to the appearance of some minor defects in the graphene sheets caused by the oxygen attack. This is corroborated by the HRTEM results in Figure 2 where it can be observed that the sample with a greater graphene content (AX-9%) presents abundant ordered structures that become less ordered after mild oxidation (Figure 2d). Nevertheless, it should be noted that the electrical conductivity of AXO-9% (870 S m$^{-1}$) is still greater than those of AXO (170 S m$^{-1}$) and YP-80F (120 S m$^{-1}$) (Table 2).

To test their electrochemical performance, AXO and AXO-9% were used as electrodes in supercapacitors. Figure 8a compares the evolution of the specific capacitance with respect to the current density for AX, AXO, and YP-80F.

As can be seen, AXO experienced an enhancement of its specific capacitance at low current density values. This can be attributed to the increase in oxygen-containing functional groups in the carbon xerogel structure. The almost rectangular shapes of the voltammograms for AX (Figure S4) indicate that it behaves very much like a double-layer capacitor. However, the presence of small humps at approximately 0.3 V
evidences a slight contribution by pseudocapacitance caused by oxygen groups [32]. The improvement in capacitance is reflected in an energy enhancement with values 10% greater at 0.2 A g⁻¹ compared to AX (Table 2). Nevertheless, from 8 A g⁻¹ the drop in capacitance is more pronounced, showing a 48% loss between 8 and 16 A g⁻¹ (Figure 8a). This pronounced drop in capacitance could be due to an increase in the resistance of the cell resulting from the loss of electrical conductivity. Moreover, the increase in resistance has a negative effect on the power values obtained, as the power density of AX at 16 A g⁻¹ is 86% higher than that of AXO (Table 2). The information provided by the Nyquist plot for the AXO sample (Figure 8c) supports these observations. On the one hand, the loop formed at high frequencies increases after the oxidation, i.e., oxidation produces an increase in the internal resistance of the cell related to the charge transfer between the electrode and electrolyte [9, 43, 44]. On the other hand, the 45° Warburg zone, which is related to the diffusive resistance of the electrolyte ions in the pores of the electrode [9, 31, 43, 44], is smaller, presenting a 1 Ω cm² EDR value and indicating improved contact between the electrode and electrolyte after oxidation. This is clearly due to the introduction of oxygen functionalities resulting from the mild oxidation with air, which improves the wettability of the samples, and in turn, the interaction between the electrode and electrolyte.

The electrochemical characterization of AXO-9% (Figures 8b and d) demonstrates that at low intensity working conditions, despite having a smaller S_BET and consequently a smaller volume of micropores for storing charges (Table 1), the capacitance of AXO-9% is almost the same as that of AX-9% (Table 2). However, as the work intensity increases, the capacitance curve experiences a steep drop exhibiting the smallest capacitance, therefore energy, of all the studied samples. This remarkable loss of capacitance in the performance of the supercapacitor indicates a radical increase in the
cell resistance that could be caused to some extent by the slight narrowing of the mesopores (Table 1) and, to a larger extent, by the loss of electrical conductivity after oxidation (Figure 7). As mentioned above, these factors have a significant influence on the power density of the device. Thus, at 6 A g⁻¹, the power density of AXO-9% is only 2900 W kg⁻¹ compared to 25000 W kg⁻¹ for AX-9% recorded under the same working conditions. The Nyquist plot (Figure 8d) exhibits a widening of the loop at high frequencies and, similarly to AX-9%, a vertical appearance of the Warburg zone. This essentially means that, the cell presents a higher inner resistance while its wettability (the contact between the electrolyte and electrode) does not show any appreciable improvement.

Interestingly, the performance of AXO-9% is inferior to that of not only AX-9% but also AXO, despite having a more appropriate porous structure (a larger volume of micro and mesopores and wider mesopores) and a higher conductivity. As mentioned above, one possible reason for this might be that during oxidation the oxygen-containing functional groups prefer to become linked to the more amorphous part of the structure. In addition, as can be seen in Figure 2d, oxidation also destroys a part of the ordered platelets present in the original sample. As a consequence, the sample experiences a drastic change in its structure [10, 45]. The main consequence of this is a loss in conductivity, which plays a key role in the power of the supercapacitor and also in the capacitance and energy values, especially when working at high intensities.

4. Conclusions

Two hybrid carbon xerogel-graphene samples with different graphene percentages have been used to demonstrate that there is a maximum amount of graphene addition beyond
which no further capacitance improvements are obtained when these materials are used as electrodes in supercapacitors.

The incorporation of graphene is important because it prevents the collapse of the xerogel structure during drying, and as a consequence, it causes a slight increase in the size of mesopores that widen as more graphene is added. Moreover, electrical conductivity increases linearly with the addition of graphene. Thus, the electrical conductivity of AX-9% is 135 and 321% greater than those of AX-3% and AX, respectively. The appropriate PSD and the high electrical conductivity of AX-9% ensure that when this material is used as electrode in supercapacitors, the resistance of the cell is reduced, thus better power densities are obtained. However, AX-9% does not show any capacitance improvement compared to AX-3%, which has less graphene. This is attributed to the increase in the hydrophobicity of AX-9% resulting from the incorporation of more graphene into the polymeric structure.

When AX and AX-9% were oxidized with air (obtaining AXO and AXO-9%, respectively), it was observed that oxidation affected the samples in different ways. Although the hybrid carbon xerogel had less oxygen grafted into its structure, its porosity was more reduced and its electrical conductivity also experienced a greater decrease compared to the pure xerogel sample, because the ordered platelets of the sample were destroyed. As a consequence, when the hybrid sample (AXO-9%) was used as electrode in supercapacitors, we observed no improvement in capacitance for any current density range. Moreover, due to the reduction in electrical conductivity and increase in cell resistance, the power density of the device also worsened.

Therefore, we can conclude that although air oxidation improves the interaction between the electrode and electrolyte, it needs to be carried out under highly controlled conditions in order to preserve the carbon structure of the active material. Moreover,
when high capacitances are required, adding 3 wt% of graphene is sufficient to obtain an efficiently performing supercapacitor, whereas for higher power requirements 9 wt% of graphene is needed to ensure a good performance.

Acknowledgements

The authors gratefully acknowledge the financial support from the Ministerio de Economía y Competitividad of Spain, MINECO (Project CTQ2014-54772-P) and the Garantía Juvenil employment plan.

References


Figure 1. Electrical conductivities of the electrodes formed by carbon xerogels as a function of the percentage of graphene added.
Figure 2. HRTEM images: (a) AX carbon xerogel (b) AX-3% and (c) AX-9% hybrid samples, and (d) AXO-9% oxidized sample.
Figure 3. Capacitance behaviour of the studied samples as a function of current density when $U = 1$ V.
Figure 4. Nyquist plots of the studied carbon xerogels.
Figure 5. Percentage of oxygen as a function of oxidation time.

Figure 6. O1s XPS spectra of the oxidized samples: (a) AXO and (b) AXO-9%.
Figure 7. Electrical conductivity of the electrodes formed by the studied samples as a function of the oxygen percentage in their structures.
Figure 8. Capacitance values per electrode calculated from the charge-discharge tests and Nyquist plots of the oxidized samples.
Table 1. Porous properties of the studied carbons obtained from N\textsubscript{2} adsorption-desorption isotherms.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(V_p) (cm(^3) g(^{-1}))</th>
<th>(V_{meso}) (cm(^3) g(^{-1}))</th>
<th>(D_{meso}) (nm)</th>
<th>(S_{BET}) (m(^2) g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>AX</td>
<td>1.3</td>
<td>0.6</td>
<td>6</td>
<td>2091</td>
</tr>
<tr>
<td>AX-3%</td>
<td>2.3</td>
<td>1.4</td>
<td>11</td>
<td>2487</td>
</tr>
<tr>
<td>AX-9%</td>
<td>2.7</td>
<td>1.9</td>
<td>16</td>
<td>2498</td>
</tr>
<tr>
<td>AXO</td>
<td>1.1</td>
<td>0.5</td>
<td>6</td>
<td>1710</td>
</tr>
<tr>
<td>AXO-9%</td>
<td>1.6</td>
<td>0.9</td>
<td>14</td>
<td>1916</td>
</tr>
<tr>
<td>YP-80F</td>
<td>1.2</td>
<td>0.4</td>
<td>3</td>
<td>2312</td>
</tr>
</tbody>
</table>

Table 2. Electrochemical properties of the studied samples tested at 0.2, 6, and 16 A g\(^{-1}\) current densities.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(K)</th>
<th>(C_{0.2})</th>
<th>(C_6)</th>
<th>(C_{16})</th>
<th>(E_{0.2})</th>
<th>(E_6)</th>
<th>(E_{16})</th>
<th>(P_{0.2})</th>
<th>(P_6)</th>
<th>(P_{16})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S m(^{-1})</td>
<td>F g(^{-1})</td>
<td>F g(^{-1})</td>
<td>F g(^{-1})</td>
<td>Wh kg(^{-1})</td>
<td>Wh kg(^{-1})</td>
<td>Wh kg(^{-1})</td>
<td>W kg(^{-1})</td>
<td>W kg(^{-1})</td>
<td>W kg(^{-1})</td>
</tr>
<tr>
<td>AX</td>
<td>240</td>
<td>141</td>
<td>106</td>
<td>78</td>
<td>20</td>
<td>15</td>
<td>11</td>
<td>19000</td>
<td>21000</td>
<td>17000</td>
</tr>
<tr>
<td>AX-9%</td>
<td>1010</td>
<td>151</td>
<td>118</td>
<td>103</td>
<td>21</td>
<td>16</td>
<td>14</td>
<td>27000</td>
<td>25000</td>
<td>21000</td>
</tr>
<tr>
<td>AXO</td>
<td>170</td>
<td>159</td>
<td>116</td>
<td>53</td>
<td>22</td>
<td>16</td>
<td>7</td>
<td>7000</td>
<td>4700</td>
<td>2300</td>
</tr>
<tr>
<td>AXO-9%</td>
<td>870</td>
<td>147</td>
<td>70</td>
<td>-</td>
<td>20</td>
<td>10</td>
<td>-</td>
<td>6400</td>
<td>2900</td>
<td>-</td>
</tr>
<tr>
<td>YP-80F</td>
<td>120</td>
<td>168</td>
<td>107</td>
<td>62</td>
<td>23</td>
<td>15</td>
<td>9</td>
<td>8300</td>
<td>5000</td>
<td>2200</td>
</tr>
</tbody>
</table>
SUPPLEMENTARY MATERIAL

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

María Canal-Rodríguez, J. Angel Menéndez, Ana Arenillas*

Instituto Nacional del Carbón, CSIC, Francisco Pintado Fe, 26, 33011 Oviedo, Spain

*Corresponding author: Tel. +34985119090, Fax: +34985297662, Email: aapuente@incar.csic.es

Figure S1. N$_2$ adsorption-desorption isotherms and pore size distributions of the samples studied.
Figure S2. Charge-discharge plots of the samples studied (a) AX, (b) AX-3%, (c) AX-9% and (d) YP-80F at different current intensities.
Figure S3. CO and CO$_2$ profiles obtained by TPD analysis of the carbon xerogels studied and the reference material.
Figure S4. Cyclic voltammetry (CV) curves of the carbon xerogels studied: (a) AX, (b) AX-9% (c) AXO and (d) AXO-9% with a scan rate of 2 mV s⁻¹ and a voltage window from 0.6 V to 1.2 V.