**Effect of nanostructure on the supercapacitor performance of
activated carbon xerogels obtained from hydrothermally carbonized
glucose-graphene oxide hybrids**

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Abstract

Activated carbon xerogels with a cellular morphology were obtained from hydrothermally carbonized glucose-graphene oxide (GO) hybrids and tested as supercapacitor electrodes. The effect of the chemical activation (using KOH) on the nanometer-scale morphology, local structure, porous texture and surface chemistry of the resulting carbon materials was investigated and correlated with their electrochemical behaviour. The electrochemical performance of the activated xerogels was studied in a three-electrode cell using 1 M H₂SO₄ as the electrolyte. The results underlined the relevant role played by the xerogel nanomorphology; more specifically, xerogels with cellular structures exhibiting well-connected, continuous and very thin (~5-15 nm) carbon walls (prepared with lower amounts of activating agent) favored ionic diffusion and electronic conduction compared to materials with broken, thicker walls (obtained from higher amounts of activating agent). The effect of nanomorphology and local structure was also made apparent when the xerogels were used as actual supercapacitor electrodes. Particularly, a symmetric capacitor assembled from a carbon xerogel with very thin walls and relatively high graphitic character delivered a much higher specific capacitance than that of a commercial activated carbon (223 vs 153 F g⁻¹ at 100 mA g⁻¹) as well as a significantly improved retention of capacitance at high current densities.

1. Introduction

Beyond conventional activated carbons, the discovery of graphene has provided new horizons in the energy field [1]. Arising from its particular two-dimensional structure, graphene has superior electrical conductivity, highly accessible surface area and excellent chemical and mechanical properties. Supercapacitors (SCs) are devices that store energy by means of electrostatic charge separation as opposed to the electrochemical reactions in conventional batteries [2]. While the latter present serious power limitations and rarely provide immediate response to energy peak demands, SCs can store energy when it is produced in excess for fast releasing when necessary (high power density). Unfortunately, they cannot supply high capacitances or high energy densities as compared with batteries [3]. Commercial activated carbons are by far the most widely used material for SC electrodes; nevertheless, their capacitances are typically limited to 40–160 F g⁻¹ [4] in aqueous electrolyte. The intrinsic principle of charge storage in SCs consists of electrostatic adsorption of electrolyte ions on the electrode surface [2] and, consequently, the surface area is the main factor influencing the capacitance. However, there are other factors that strongly contribute to the capacitance of carbon-based electrodes. For example, the presence of functional groups on the carbon surface can enhance the electrode capacitance by fast reversible faradaic reactions between the electrode surface and the electrolyte (pseudocapacitance) [5] or by increasing the electrode wettability [6]. On the other hand, a suitable nanostructure enhancing both the electrolyte diffusion [7-9] and the electronic conduction [6, 10] is also expected to boost the electrochemical performance. In this context, the development of porous carbons comprising thin (nanometric) carbon walls produced by using graphene sheets or other structures as templates to afford, e.g., monolithic carbon

gels would be highly desirable, as the thin walls would bring such advantages as enhanced kinetics for ion diffusion [11, 12]. This type of gel material can be attained by coating the flat, non-porous conductive surface of graphene with a porous carbon layer. At present, carbon gels are most commonly prepared using highly toxic resorcinol/formaldehyde mixtures as carbon precursors [13, 14] and, consequently, a large amount of work has been dedicated to find alternative carbon precursors. For instance, biomass-derived products (pure carbohydrates and lignocellulosic substances) are considered as a potential carbon sources to produce valuable porous carbon materials [15], since they are a renewable resource available in high quantities. However, the utilization of pure carbohydrates (i.e., glucose, sucrose, fructose, starch, etc) for sol-gel synthesis has met with limited success, due to their poor reactivity in highly diluted media. The as-obtained carbon gels suffer from poor mechanical/chemical resistance and low carbon yields after carbonization. Recently, it has been found that more robust polymeric structures can be obtained by using certain condensation/polymerization promoters, including graphene oxide (GO) nanosheets. GO is an oxygen-rich material produced by the oxidative exfoliation of graphite. The acidic sites on GO have been shown to promote dehydration/condensation reactions of carbohydrates and other organic precursors whilst providing a scaffold that supports the growth of carbon xerogels, for example by hydrothermal means [16, 17]. Hydrothermal carbonization (HTC) is a mild process (180-250 °C) that has been largely demonstrated to promote the condensation, polymerization, and aromatization of saccharides in solution [18]. In fact, activated carbon xerogels produced by HTC of glucose-GO mixtures have been very recently reported [16]. These carbon materials are a priori good candidates for the development of a new family of carbon-based SCs since porous carbon-GO hybrids have already demonstrate to be good candidates for energy storage

applications, such as supercapacitors [19] or lithium-sulfur batteries [20, 21]. Therefore, in the present work we investigate the potential of these novel GO-based carbon xerogels towards their use as SCs and demonstrate the dominant role played by the xerogel nanostructure on their performance at real implementation conditions (high current densities).

2. Experimental

2.1. Synthesis of the activated carbon xerogels

The activated carbon xerogels were prepared by a slight modification of a recently reported procedure that makes use of GO sheets as morphology-directing agents in the HTC of glucose, affording hydrothermal carbon xerogels that are then chemically activated with KOH [16]. GO sheets (lateral size: $\sim 0.2\text{-}1\ \mu\text{m}$) in aqueous colloidal dispersion were obtained through oxidation (Hummers method) and subsequent sonication-induced exfoliation of natural graphite powder (Sigma Aldrich) following a protocol described elsewhere [22]. To obtain the hydrothermal carbon xerogels, glucose (2 g) was dissolved in 20 mL of aqueous GO suspension (GO concentration: $2\ \text{mg mL}^{-1}$), and the resulting mixture was transferred to a Teflon-lined autoclave (50 mL in capacity) and heated at $200\ ^\circ\text{C}$ for 16 h. The resulting wet hydrogels were thoroughly rinsed with deionized water, immersed consecutively in three volumes of neat acetone (30 mL, 15 min each time) and then allowed to dry under ambient conditions. We note that this washing procedure is significantly different (i.e., much more extensive) compared to that followed in a previous paper describing the synthesis of this type of material. This extensive washing afforded the extraction of a considerable amount of non-polar, low molecular weight compounds from the hydrogel (the originally transparent acetone turned brown due to this extraction). As noted below, the porous

texture of the activated carbon xerogels derived from this enhanced washing process was much less dependent on the activation parameters, which allowed us to investigate the effects of nanostructure on the supercapacitor performance of these materials. After the washing and drying steps, the resulting hydrothermal carbon xerogels were chemically activated with KOH. To this end, a given volume of an aqueous KOH solution of known concentration was drop-casted onto, and absorbed by, the xerogel, which was then allowed to dry under ambient conditions. Two KOH/hydrothermal carbon weight ratios were used, namely, 1 and 4. These KOH-impregnated samples were subsequently heat-treated at either 700 or 800 °C for 30 min under Ar flow (300 mL min⁻¹) to finally afford activated carbon xerogels, which were thoroughly washed with deionized water and dried at 90 °C for 12 h. The differently activated samples are denoted as K_x_T_y, where *x* stands for the KOH/hydrothermal carbon weight ratio (i.e., 1 or 4) and *y* is either 7 or 8, which refers to the activation temperature (i.e., 700 and 800 °C, respectively). For comparison purposes, a hydrothermal carbon was prepared using the same synthesis conditions but in absence of the GO suspension. The resulting hydrothermal carbon obtained by hydrothermal carbonization of glucose only (without GO) was activated with a KOH/hydrothermal carbon weight ratio of 1/1 at 800 °C and was denoted as Glu_K1_T8.

2.2. Characterization techniques

An Autosorb-1 volumetric adsorption analyzer (Quantachrome) was used to measure N₂ adsorption-desorption isotherms, at -196 °C in the relative pressure range of 10⁻⁷ – 0.99. Samples were degassed at 250 °C overnight under vacuum. The BET surface area (*S*_{BET}) was calculated according to the BET model [23] from the nitrogen isotherms in the relative pressure range of 0.01- 0.15. The micropore volume [*V*_{DR} (N₂)] were

calculated by applying the Dubinin-Radushkevich (DR) method [23] in the relative pressure ranges of 10^{-6} – 0.15. The total pore volume (V_T) was calculated as the amount of N_2 adsorbed at the relative pressure of 0.95. The QSDFT [23] method (slit-cylindrical pores, equilibrium) was used to obtain the pore size distributions (PSDs). Field emission scanning electron microscopy (FE-SEM) imaging of the samples was conducted with a Quanta FEG 650 microscope (FEI Company) operated at 30 kV. Raman spectra were recorded with a LabRam apparatus (Horiba Jobin-Yvon) using a 532 nm wavelength laser at an incident power of 0.5 mW to avoid damage/modification of the xerogel samples due to excessive heating. X-ray photoelectron spectroscopy (XPS) was carried out on a SPECS system under a pressure of 10^{-7} Pa using a non-monochromatic Mg K_{α} X-ray source operated at 11.81 kV and 100 W.

2.3. Electrochemical measurements

2.3.1. Electrode preparation

The obtained carbon xerogels were hand-milled to obtain a particle size below 100 μm . A carbon paste was prepared by mixing 10 wt% of polytetrafluoroethylene (PTFE) in absolute ethanol and 90 wt% of the activated xerogels. Then, 5-10 mg of the resulting paste was pressed into a mould (3 ton, 15 s). The as-prepared carbon pellets (0.78 cm^2) were sandwiched between two stainless steel meshes (w/w %: Fe 67.77%, 0.08% C; 0.04% P; 1.95% Mn; 0.50% Si; 0.03% S; 10.30% Ni; 17.65% Cr; 1.68% Mo) and pressed (3 ton, 15 s). The obtained electrodes were vacuum-degassed for 4 h at 120 $^{\circ}\text{C}$, soaked into the electrolyte and kept immersed into the solution during 1 day. The cell assembly process was reported in our previous work [24]. Nitrogen gas was bubbled into the electrolyte for 15 min prior to the measurements to remove the O_2 present into

the electrolyte solution. The electrochemical characterization was performed on a PGZ 402 Voltalab potentiostat (Radiometer Analytical) by using both three-electrode and two-electrode cell configurations

2.3.2. Three-electrode configuration

The electrochemical behavior of the prepared carbons was studied in a beaker-type cell in 1 M H₂SO₄ with an Ag/AgCl (KCl 1M) reference electrode. The counter electrode was prepared by sandwiching 20 mg of Norit DCL Supra 50® carbon paste in the stainless steel meshes. The working and counter electrodes were arranged in a stack, separated by filter paper and connected to two Pt wires as current collectors. Nitrogen gas was bubbled through the electrolyte for 15 min prior to the measurements to remove the O₂ present in the electrolyte solution. Cyclic voltammetry (CV) was performed in a voltage window of -0.2 to 0.6 V at 2 mV s⁻¹. The specific gravimetric capacitance (C, F g⁻¹) of a single electrode was calculated by the formula:

$$C = \frac{1}{2 r m V_w} \int_{V_0}^{V_1} I(V) dV \quad (1)$$

where r is the scan rate (V s⁻¹), m the mass of the active material within the working electrode (g), V_w the voltage window (i.e, V₁-V₀, measured in Volt) and I the current (A). Electrochemical impedance spectroscopy (EIS) was applied to the fully discharged cell at 0 V in the frequency region of 10 kHz to 10 mHz with AC amplitude of 10 mV.

2.3.3. Two-electrode configuration

Two electrodes made from a given activated carbon xerogel were used as symmetric working electrodes in a two-electrode cell. Charge-discharge (CD) experiments were conducted up to 0.8 V and different current intensities (100-3000 mA

g⁻¹). The specific gravimetric capacitance (F g⁻¹) of a single electrode was calculated by the formula:

$$C = \frac{2 I \Delta t_d}{m \Delta V_d} \quad (2)$$

where I is the constant current (A), Δt_d the time of discharge to the fixed potential window (s), m the mass of the active material within the working electrode (g) and ΔV_d the potential difference (V) between the start and end of the discharge process after omitting the internal resistance (IR) drop. The long-term stability of the electrodes was studied by means of consecutive charge/discharge cycles of the cell (up to 100 mA during 10000 cycles).

3. Results and discussion

3.1. Morphology, structure, texture and surface chemistry of the activated carbon xerogels.

The micrometer- and nanometer-scale morphology of the activated carbon xerogels prepared as described in the Experimental section was investigated by FE-SEM. In general terms, the morphological features seem to be mostly determined by the amount of KOH used in the chemical activation step. Figure 1a-c shows representative FE-SEM images recorded for sample K1_T8. The material activated with the same amount of KOH at a lower temperature (i.e., sample K1_T7) is not significantly different from what can be seen in Figure 1a-c, so the corresponding images are not shown to avoid repetition. Both xerogels exhibit a cellular or capsule-like morphology, comprising a high density of rounded voids enclosed by very thin walls. The voids are typically between ~200 and 800 nm in diameter (see Figure 1b and c), whereas the walls are ~5-15 nm thick. The xerogels are made up of ensembles of GO sheets covered by thin

layers of hydrothermally carbonized and KOH-activated glucose [16]. This peculiar cellular morphology has been previously demonstrated to develop during the chemical activation step, and has been interpreted to result from the generation of spherical droplets of molten KOH at temperatures above 360 °C that displace and squeeze the GO-hydrothermally carbonized glucose structures on the droplet surface [16]. The morphology of xerogels activated with a large amount of KOH (i.e., samples K4) is noticeably different, as exemplified in Figure 1d-f for sample K4_T8. Specifically, these samples incorporate much larger voids, typically between a few and several micrometers in diameter. Such a result could be reasonably attributed to the formation of larger droplets of molten KOH. However, more significantly, the walls enclosing the voids are not smooth and continuous structures as in the case of the K1 samples, but are frequently broken up into loosely connected, platelet-like pieces instead (Figure 1d). Furthermore, these platelet-like fragments are considerably thicker (~40-80 nm, see Figure 1e and f) than the smooth walls of their K1 counterparts. By contrast, if GO was excluded from the production process, the resulting activated carbons (e.g., Glu_K1_T8) were not obtained in xerogel form but rather as a loose powder. As evidenced from SEM images (not shown) and, typical for common hydrothermal carbons, this powder was made up of individual, micrometer-sized (1-2 μm in diameter) spheres. Therefore, the presence of GO sheets during the hydrothermal carbonization step was critical in achieving the peculiar nanostructures described above for the activated xerogels.

Figure 1. FE-SEM images of samples K1_T8 (a-c) and K4_T8 (d-f).

Raman spectroscopy was used to probe the structural order of the activated carbon xerogels. Figure 2 shows representative spectra recorded for the different xerogels, which are all dominated by two intense peaks located at about 1340 (D band) and 1585 (G band) cm^{-1} , together with weak bands observed in the 2500-3300 cm^{-1} region (including the 2D band at $\sim 2680 \text{ cm}^{-1}$). These features are known to be indicative of sp^2 -based carbons with a graphitic character but possessing a high density of structural imperfections [25, 26]. The latter point was quantitatively evaluated by determining the integrated intensity ratio of the D and G bands (I_D/I_G ratio), which yielded reasonably similar values for all the samples (between 1 and 1.3). However, some small differences in the 2D band are consistently observed between samples. In particular, its intensity tends to be higher for the xerogels activated at 800 $^{\circ}\text{C}$ compared with their counterparts activated at 700 $^{\circ}\text{C}$. The emergence of an intense 2D band is known to be related to increased graphitic order in carbon materials [27, 28], suggesting that the structural order is somewhat better for the materials activated at the higher temperature, as could

be expected a priori. Nevertheless, these are relatively minor differences and, overall the Raman spectroscopy data suggest that all the xerogels are structurally similar.

Figure 2. Raman spectra of the different activated carbon xerogels.

We note that the activated carbon xerogels investigated here comprise a GO-derived carbon framework, which possesses an sp^2 -based but highly defective nature, and a porous carbon derived from hydrothermally carbonized and KOH-activated glucose, the structure of which is also expected to be based on sp^2 bonding and to be highly defective. Therefore, it would be interesting to ascertain the mass fraction of these two components in the xerogels. However, determining their relative weight is far from straightforward, as analytical techniques that could be used to discriminate both

components based on structural differences will most probably not succeed in doing so. Indeed, we used thermogravimetric analysis under air flow to see if we could detect differences in gasification temperatures that could be attributed to either the GO- or the glucose-derived components, but only a single, continuous mass loss without individual features could be observed. However, we note that an estimate of the mass fraction of the GO-derived component in our activated xerogels could be made resorting to literature data on the KOH activation of reduced graphene oxide alone. Specifically, Srinivas et al [29] have provided the yield of porous carbons obtained from GO thermally reduced at 250 °C (not very different to our hydrothermal carbonization temperature) and activated with KOH under the same KOH/precursor mass ratios and temperatures used in our case. Using these data and taking into account the mass of our final activated carbon xerogels, we estimate the mass fraction of GO-derived material in our xerogels to be of the order of 50%. Figure 3a displays the N₂ adsorption/desorption isotherms recorded at -196°C for the activated xerogels. The studied carbons display only slightly different isotherm shapes depending on the activation conditions: (i) K1_T7 presents a combination of types I and IV isotherm with an H4 hysteresis loop characteristic of micro-mesoporous materials with slit-shaped porosity, (ii) K1_T8 shows similar adsorption branch shape than K1_T7 but differs in the desorption branch showing a smaller hysteresis loop and (iii) Glu_K1_T8 and samples activated with higher amount on KOH (series K4) present type I isotherms characteristics of microporous materials. Even though all the studied materials yield similar textural features, the use of lower amounts of KOH (K1 samples) leads to somewhat higher specific surface areas (S_{BET} , Table 1). The PSDs of the activated xerogels analyzed by applying QSDFT to the adsorption isotherms are represented in Figure 3b and the cumulative pore volumes are displayed in Table 1. Regardless of the activation

temperature, K1 samples yield slightly higher micropore volumes ($V_{p<1\text{ nm}}$ and $V_{p<2\text{ nm}}$) and noticeable larger mesopore volumes [$(V_p\text{ (2-50 nm)})$]. Therefore, the use of a lower amount of KOH during the activation step can be associated in the present case to a slightly more developed microporous texture and a significantly more developed mesoporous structure (although mesopore volumes are modest at best; see Table 1).

Figure 3. (a) N_2 adsorption/desorption isotherms at -196°C for the activated carbon xerogels. (b) PSDs of the xerogels calculated from the adsorption isotherms by the QSDFT method.

Table 1. Textural parameters obtained from N₂ adsorption-desorption isotherms.

Sample	V _T (cm ³ g ⁻¹)	S _{BET} (m ² g ⁻¹)	V _{DR} (cm ³ g ⁻¹)	QSDFT method		
				V _{p<1nm} (cm ³ g ⁻¹)	V _{p<2nm} (cm ³ g ⁻¹)	V _{p (2-50 nm)} (cm ³ g ⁻¹)
K1_T7	0.85	1513	0.58	0.40	0.56	0.30
K4_T7	0.63	1333	0.54	0.32	0.52	0.05
K1_T8	0.79	1412	0.56	0.36	0.54	0.16
K4_T8	0.63	1257	0.49	0.30	0.49	0.08
Glu_K1_T8	0.64	1450	0.57	0.48	0.56	0.03

The surface elemental composition and nature of the chemical groups in the carbon xerogels was investigated by XPS. As could be anticipated, only carbon and oxygen were detected. The O/C atomic ratio of the different samples, derived from their corresponding survey spectra (not shown), are given in Table 2. Moderate values are obtained in all cases (O/C ratios between ~0.03-0.07), but they tend to be somewhat lower for the K4 samples. To explain this result, the following points have to be taken into account. First, the HTC process of glucose and other saccharides is known to yield carbonaceous products that are rich in oxygen and possess a complex structure consisting of small, unoxidized sp²-based aromatic domains (or oxidized only at their periphery) interspersed with furanic rings and aliphatic moieties terminated in hydroxyl and carbonyl groups [16, 18]. Second, during the chemical activation step, KOH reacts with carbon atoms from the hydrothermally obtained xerogel, so that this element is removed in the form of K₂CO₃, creating porosity in the activated carbon material that is left behind [30]. Because the extent of KOH-carbon reaction is controlled by the amount

of KOH employed, this reaction is expected to be selective towards carbon atoms from disordered environments compared with unoxidized aromatic domains, and therefore to lead also to the removal of the oxygen species that are associated to such disordered carbonaceous regions. Consequently, we should expect a higher degree of removal of the oxygen rich disordered environments and so a lower O/C ratio in the final activated carbon for samples activated with a larger amount of KOH, as it is actually observed for the K4 xerogels compared with their K1 counterparts (see Table 2). As will be further discussed below in the light of the electrochemical characterization results, a potential consequence of the extensive removal of oxygen atoms is that the remaining aromatic domains could incorporate significant amounts of unsaturated, highly reactive edges [31, 32], particularly when activation is carried out at a lower temperature that is less likely to favor edge annealing (e.g., this could be the case of the xerogel activated with the larger amount of KOH at the lower temperature, i.e. sample K4_T7). The different types of oxygen functional groups left behind in the carbon xerogels following activation were evaluated from their high resolution C 1s core level XPS spectra, which are shown in Figure 4 (left column). The spectra could be fitted into four components (C1-C4), which are located at about 284.6 eV (C1 component, ascribed to carbon atoms in an unoxidized C=C graphitic environment), 285.8 eV (C2, attributed to carbon single-bonded to oxygen in, e.g., hydroxyl or ether groups), 287.0 eV (C3, carbon atoms double-bonded to oxygen in, e.g., carbonyls) and 288.8 eV (C4, carbon atoms from carboxylic and ester functionalities). Generally, the C 1s XPS spectrum of a pure graphitic material without heteroatoms presents an asymmetric shape. This will affect the curve fitting procedure, an asymmetric peak shape being needed for the graphite-like structure, while a gaussian peak is required for an aliphatic structure [33]. Therefore, the C1 component was fitted to a Doniach-Sunjic line-shape with an

asymmetry parameter of $\alpha = 0.12$ [32]. On the other hand, C2-C4 peaks were adjusted to a symmetric 80 % Gaussian-Lorentzian line-shape. The relative weight of each component in the different samples is given in Table 2. The distribution of the different oxidized carbon species is relatively similar for all the activated xerogels. However, the proportion of highly oxidized carbon atoms (i.e., those in carbonyl and carboxyl/ester groups) tends to be larger for the K1 xerogels (compare the high binding energy tails of the spectra for the K1 and K4 samples in Figure 4). Concerning the high resolution O 1s core level spectra (Figure 4, right column), these were satisfactorily peak-fitted to yield three components. The component centered at 530.7 eV (O1) was ascribed to C=O bonds in aromatic moieties, whereas that located at about 532 eV was attributed to C=O bonds in ester and anhydride groups, -OH bonds in alcohols and C-O bonds in ethers. Finally, the component at about 533.7 eV (O3) was associated to C-O bonds in ethers in esters and anhydrides. It can be observed that the peaks associated to carbonyl functionalities (O1 and O2) tend to be higher for K1 samples, which is consistent with their higher extent of oxidation as deduced from the O/C ratios and with the C 1s region analysis.

Figure 4. High resolution C1s (left column) and O1s (right column) core level spectra for the different activated carbon xerogels. The C 1s spectra have been peak-fitted into four components: C1 (284.6 eV), C2 (285.8 eV), C3 (287.0 eV) and C4 (288.8 eV). The O 1s spectra have been peak-fitted into three components: O1 (530.7 eV), O2 (532 eV), O3 (533.7 eV).

Table 2. O/C atomic ratios and relative area of the different C 1s and O1s components for the activated carbon xerogels as determined from the survey and high resolution XPS spectrum.

Sample	O/C atomic ratio	Relative area of C 1s component (%)				Relative area of O 1s component (%)		
		C1 (284.6 eV)	C2 (285.8 eV)	C3 (287.0 eV)	C4 (288.8 eV)	O1 (530.7 eV)	O2 (532 eV)	O3 (533.7 eV)
K1_T7	0.066	86	7	4	2	45	21	34
K4_T7	0.033	95	4	1	1	26	40	34
K1_T8	0.068	87	8	2	3	20	52	28
K4_T8	0.042	95	1	2	2	20	49	31

3.2. Electrochemical characterization

The electrochemical behaviour of the activated xerogels was investigated in a three-electrode cell configuration in aqueous electrolyte (1 M H₂SO₄). Figure 5a displays the cyclic voltammograms recorded for the different xerogels at a scan rate of 2 mV s⁻¹. Samples K4_T8 and Glu_K1_T8 display a square-shaped curve with almost no redox peaks, indicating mainly capacitive storage for such electrodes. By contrast, two humps for both the positive (~0.2 V) and the negative (~0.16 V) scan are observed for the K1_T7, K1_T8 and K4_T7 electrodes. For carbon electrodes, this type of feature is generally associated to faradaic currents arising from redox reactions involving oxygen functional groups [34-36]. Quite unexpectedly, the most intense humps are noticed for sample K4_T7, which exhibits the lowest extent of oxidation of all the investigated xerogels (Table 2). As commented above, larger amounts of KOH and lower activation temperatures probably lead to carbon materials possessing aromatic domains with a significant fraction of unsaturated, highly reactive edges. Therefore, in line with

previous reports on carbon materials made up of small aromatic domains and high fractions of reactive edges, such as zeolite-templated carbons [37, 38], it was observed that the K4_T7 xerogel undergoes electrochemical oxidation when submitted to strongly acidic media. In other words, the humps observed for this sample can be ascribed to oxygen groups generated during the voltammetric measurement. This phenomenon is made evident in Figure 5c, where the evolution of the voltammetric curves with the number of cycles is compared for K4_T7 and K4_T8 samples. The area inside the curve increases for both samples throughout the measurement due to an increase in the electrode wettability. Hence, the evolution to more squared curves reveals a better capacitive performance derived from a proper infusion of the electrolyte into the electrode porosity. On the other hand, sample K4_T7 showed a notorious and progressive increment of the redox humps located around 0.2 V, whereas sample K4_T8 displayed no changes in this potential range. The voltammetric curves seemed to stabilize after 50 cycles for both electrodes. On this basis, the faradaic activity of the investigated samples is suggested to arise both from oxygen groups originally present on the xerogels and from oxygen groups that could have originated by incipient electrooxidation during the first stages of the voltammetric measurement or even during the conditioning of the samples for the electrochemical measurement. We note that the electrodes were soaked in the electrolyte solution (1 M H₂SO₄) for one day to allow proper wetting before the electrochemical measurements were carried out. This conditioning could have induced some extent of oxidation in the sample. To test this, we soaked a certain amount of sample K4_T7 in 1 M H₂SO₄ for one day and examined it by XPS. We noticed that the amount of oxygen increased very significantly in this sample after H₂SO₄ soaking (the O/C ratio increased from 0.033 to 0.22). Indeed, its high resolution C 1s spectrum revealed an increased fraction of carbon atoms in the

285.5-287.5 eV binding energy range (C-O and C=O configurations) compared with the non-soaked sample (results not shown). Furthermore, in the presence of both H₂SO₄ and a current during the cyclic voltammetry measurements, further oxidation of the sample can be expected, as suggested by Fig. 5c. These results provide additional support to the claim that (electro) chemical oxidation takes place for the K4_T7 electrodes. We also note that the extent of the contribution of intrinsic and induced oxidation to the observed faradaic currents could well depend on the sample characteristics. In fact, the faradaic activity observed for the K1_T7 and K1_T8 electrodes is more likely to arise from the quinone/hydroquinone redox pair [2, 39], as C=O groups were shown to be relatively abundant in these two xerogels (see Table 2). The global specific capacitances (sum of capacitive and pseudocapacitive contributions) were calculated from the cyclic voltammograms (Fig. 5a) and are listed in Table 3. The K4_T8 xerogel exhibits a significantly lower capacitance (143 F g⁻¹) compared with that of the other activated xerogels (211-239 F g⁻¹). This result could be expected a priori if we take into account the relatively low surface area (Table 1) and low oxygen content (Table 2) of the K4_T8 sample. Conspicuously, Glu_K1_T8 presents very similar capacitance to the analogous hybrid material (218 F vs 225 g⁻¹). The electrolyte diffusion and electronic conductivity of the activated carbon electrodes were analyzed by EIS. The overall cell resistance (R_s), internal electrode resistance (R_p), as well as equivalent series resistance (ESR), were calculated from the recorded Nyquist plots (Figure 5b) and are listed in Table 3. The presence of the GO-derived graphenic sheets embedded throughout the xerogels together with a more continuous, interconnected nanostructure appears to contribute to electron transport if one considers the difference in the ESR values for K1_T8 (1.50 Ω) and Glu_K1_T8 (2, 17 Ω) samples. We can also notice that the K4 electrodes, K4_T8 in particular, display the highest ESR values (2.04 and 2.87 Ω). Hence, activation with a

lower amount of KOH can be associated to a better electronic conduction within the electrode. Similarly, the analysis of medium-high frequencies (Warburg region) in the Nyquist plots reveals that K1 xerogels also exhibit a lower resistance to electrolyte diffusion compared with their K4 counterparts. Rather than being mostly due to the texture and/or surface chemistry characteristics of the xerogels, which are relatively similar for all the investigated materials, we believe such a behaviour to be mainly governed by their nanostructural features. In fact Glu_K1_T8, which exhibited a loose morphology of micrometer-sized carbon spheres, displayed a much larger resistance to ionic diffusion in the Warburg region as compared to the activated carbon materials that incorporated GO sheets. As discussed above, the K1 xerogels comprise smooth, continuous (i.e., well interconnected) and very thin ($\sim 5\text{-}15$ nm) carbon walls, whereas the nanostructure of their K4 counterparts is dominated by considerably thicker (40-80 nm) as well as frequently broken and partly detached walls (see Figure 1). Therefore, in agreement with the EIS results, we would expect (i) a lower electronic conduction for the carbon materials with broken, partly detached walls (i.e., the K4 xerogels), as this would hamper the movement of charge carriers throughout the electrode, and (ii) a higher resistance to electrolyte diffusion for the carbon materials with thicker walls (again, the K4 xerogels), because it would take longer for the ions to fully occupy the inner porosity of their walls [11].

Figure 5. Electrochemistry of the activated carbon xerogels examined in a three-electrode cell configuration (1 M H₂SO₄). (a) Cyclic voltammograms recorded at a scan rate of 2 mV/s. (b) Nyquist plots extracted from EIS data.

3.3. Supercapacitor performance.

The performance of the activated xerogels as SC electrodes was tested in a two-electrode cell in aqueous medium (1 M H₂SO₄). The results of the measurements are collected in Figure 6. The generally conductive character of all the prepared xerogels is evidenced by the square shape of their corresponding cyclic voltammograms (Figure 6a). The presence of a broad hump during the cathodic sweep at voltages lower than 0.4 V suggests the occurrence of some redox processes on the electrode surface [35]. The capacitive behavior of the electrodes was evaluated by galvanostatic CD experiments up to 0.8 V at a current density of 100 mA g⁻¹, as shown in Figure 6b. All the samples display symmetrical CD curves with a small deviation from linearity, which could be attributed to the faradaic activity. As noticed from Table 3, xerogels activated at 800 °C present almost identical capacitance values for both the cell configurations (compare three- and two-electrode data for samples Glu_K1_T8, K1_T8 and K4_T8). This is not the case for xerogels activated at 700 °C, which shows a ~10% decrease in capacitance when tested on the SC device. The dependence of specific capacitance on the current density applied was examined by charging-discharging the electrodes from 100 to 3000 mA g⁻¹ (Figure 6c). For comparative purposes, an electrode made from a commercial activated carbon (Norit DLC Supra 50) was also tested in the same set-up. Compared with the other electrodes, the performance of both K4_T7 and Supra 50 deteriorates significantly with increasing current density. Moreover, the commercial activated carbon possess a much lower capacitance (153 F g⁻¹ at 100 mA g⁻¹) than that of the investigated xerogels (except K4_T8), despite its much higher surface area (2090 m² g⁻¹). It is also noteworthy that, despite having been activated under the same conditions as those used for the K1_T8 xerogel and exhibiting very similar porous texture, the

capacitance of Glu_K1_T8 drops dramatically with increasing current density. We attribute this outcome to hindered diffusion of the electrolyte ions into and out of the innermost porosity present in the micrometer-sized spheres that comprise the Glu_K1_T8 sample. By contrast, being made of very thin ($\sim 5\text{-}15$ nm) and highly accessible porous carbon walls, hindered diffusion is much less of a problem in the case of the K1_T8 xerogel. The relevance of enhanced electrolyte diffusion through very thin pore walls is therefore highlighted by the superior electrochemical behaviour of the K1 xerogels, i.e. the pathway that the electrolyte ions complete within the K1 xerogels is expected to be particularly short (carbon walls $\sim 5\text{-}15$ nm thick), and furthermore, to be assisted by the presence of some mesoporosity (see Table 1). It should be noted that K4_T8 also yields good capacitance retention (Figure 6c and Table 3), but in such case this could be probably caused by a significant capacitive/negligible pseudocapacitive storage on the electrode (see Figure 5a). The key role played by the nanostructural features of the activated carbon xerogels prepared here towards their electrochemical performance is also made evident by comparison with other materials reported in the literature. Activated xerogels prepared by HTC generally present poor capacitance retention at high current densities, which is an important hurdle when considering their actual implementation as electrodes for supercapacitor devices. For instance, HTC carbons derived from hemicellulose [40], rye straw and cellulose [41] or sucrose [42] suffer from a 50 % reduction of their initial capacitance by increasing the current density from 25 to 1000 mA/g in aqueous electrolyte. On the other hand, the capacitance is well known to increase with increasing conductivity of the electrode [6], which should have also contributed to the fact that K1_T8 exhibited the best electrochemical performance: this xerogel not only possesses enhanced ionic diffusion derived from a thin-walled cellular morphology (Figure 1a-c) but also a low electron

resistance (Table 2). The electrochemical stability of K1_T8 was hence studied by consecutive CD cycles (voltages up to 0.8 V at 1000 mA g⁻¹, 10000 cycles). As noticed from Figure 6d, the good cycling behavior of this xerogel is revealed by high capacitance retention (~87%) and an acceptable preservation of the columbic efficiency.

Figure 6. Electrochemical performance of the activated carbon xerogels in aqueous 1 M H₂SO₄ under a two-electrode configuration. (a) Cyclic voltammograms at a scan rate of 2mV/s. (b) Galvanostatic charge-discharge profiles at a current density of 100 mA/g. (c) Evolution of the specific capacitance with current load ranging from 100 to 3000 mA/g. (d) Cyclability test for the K1_T8 electrode at 1 A/g for 10000 cycles.

Table 3. Electrochemical parameters for the activated carbon xerogels extracted from measurements with three- and two-electrode configurations.

	Three-electrode configuration				Two-electrode configuration	
	Cyclic	Electrochemical impedance				
	voltammetry	spectroscopy			Charge-discharge	
Sample	C (F g ⁻¹) ^a	Rs (Ω) ^b	Rp (Ω) ^c	ESR (Ωc) ^d	C _{100mA g-1} (F g ⁻¹) ^e	C _{ret} (%)
K1_T7	211	0.23	2.07	1.84	192	79
K4_T7	239	0.28	2.32	2.04	212	65
K1_T8	225	0.22	1.72	1.50	223	81
K4_T8	143	0.25	3.12	2.87	140	81
Glu_K1_T8	218	0.24	2.38	2.14	220	46

^a calculated from Equation 1.

^b calculated from the point of intersection with the x -axis in the high frequency region.

^c calculated from the point of intersection with the x -axis from medium frequency region.

^d diameter of the semicircle at high frequency region (Rp-Rs).

^e calculated from Equation 2.

4. Conclusions

Activated carbon xerogels have been prepared by hydrothermal carbonization of glucose in the presence of graphene oxide nanosheets as morphology-directing agents, followed by chemical activation with KOH. The resulting xerogels exhibit an outstanding electrochemical performance when tested towards supercapacitor electrodes, with values of specific capacitance and capacitance retention outperforming those of a commercial activated carbon commonly studied as supercapacitor electrode and having a significantly more developed porosity than that of the present xerogels. Morphological, structural, textural and chemical characterization of the activated xerogels suggests that their electrochemical behavior is mainly dictated by their peculiar nanostructure. Specifically, the use of a lower amount of KOH during the activation step affords xerogels with a well-developed cellular morphology comprising smooth, continuous (well interconnected) and very thin porous carbon walls, which favors both the electronic conduction and ionic diffusion in the corresponding electrodes. By contrast, the electrochemical performance is impaired when using a higher amount of KOH, as this leads to activated xerogels with much thicker, broken and partly detached carbon walls. These specific nanostructural features originate from the combined effect of GO as a morphology directing agent and KOH as an activating agent. Overall, the present results suggest these activated carbon xerogels to be good candidates for capacitive energy storage, especially at high current densities.

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