On the correlation between the porous structure and the electrochemical response of powdered and monolithic carbon aerogels as electrodes for capacitive deionization

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Abstract

The combined effect of resorcinol/catalyst ($100 \leq R/C \leq 800$) and resorcinol/water ($0.04 \leq R/W \leq 0.13$) molar ratio on the textural and capacitive properties of carbon aerogels with potential application for capacitive deionization has been evaluated. Activated and pyrolyzed aerogels were synthesized by the sol-gel polymerization of resorcinol-formaldehyde mixtures and dried in supercritical conditions. Data show that high R/C and R/W molar ratios lead to materials with large pores in the mesopore range, whereas the surface area and micropore volumes remain somewhat the same. The activation of the aerogels increased the differences in the specific surface and micropore volumes due to the development of microporosity. This effect was more remarkable for the samples with low R/C whatever the R/W ratio, indicating that the carbon aerogel obtained using high amounts of catalyst are more prone to be activated. Regarding the electrochemical features of the aerogels, low capacitance values were measured in aerogels combining low R/W and high R/C and reciprocally low R/C and high R/W molar ratios, due to their higher resistance. Polarization resistances were found to be slightly higher for the pyrolyzed than for activated aerogels, and followed a decreasing trend with the mesoporosity, indicating the outstanding contribution of the mesoporous network to provide a good kinetic response. The desalting capacity of monolithic aerogels showed a simultaneous dependence with the surface area and the resistivity of the electrodes, pointing out the importance of performing electrochemical measurements in adequate cell configurations (i.e., desalting units) upon the intended application.

Keywords

Carbon Aerogel; Electrosorption; Voltammetry; Impedance spectroscopy.

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1. Introduction

Capacitive deionization (CDI) is currently considered one of the most promising technology to purify low and medium saline water streams in terms of cost and desalting efficiency. CDI is based on the electrostatic interactions of ionic species dissolved in an electrolyte with oppositely charged electrodes. Hence, high desalting capacities can only be achieved in high conductive large surface area electrodes, which pore structure would favor the adsorption of the solvated ions. Electrodes based on carbon materials are being regarded as the most suitable for CDI applications. Carbon materials such as carbon nanotubes [1,2], mesoporous carbon [3,4], hierarchically porous carbon [5], hollow carbon spheres [6], graphene [7-9] and their composites have been developed as highly efficient electrodes. Among carbon materials, carbon aerogels (CAG) could also be considered as candidates for CDI applications [10-12].

The sol-gel processing of resorcinol-formaldehyde (RF) mixtures alongside with the supercritical drying with CO₂ are the pillars of the method proposed by Pekala and coworkers to yield nanoporous organic aerogels [3]. Since then, much research has been carried out on the carbonized products because of their interesting features as highly porous materials with good electrical and thermal conductivity, corrosion resistance, and suitable mechanical properties. All these advantageous properties, and cost effectiveness, are responsible of their numerous applications in catalysis [16], energy storage [17-19] and environmental [20-22].

An optimal porosity in carbon aerogels requires an appropriate selection of the synthesis parameters. Ritter et al. reviewed the preparative factors, as reactants concentration, pH, solvent-exchange, drying method, influencing on the textural properties of the carbon aerogels [23] and Baumann et al. described the synthesis of hierarchical aerogel monoliths with bimodal (macroporous and microporous) pore size distributions using acid pH [24]. More recently, Suss et al applied these materials in a flow-through CDI systems, and compared the performance with other deionization technologies [25]. Also, the thermal treatment of the organic aerogel is crucial to set the porous properties of the carbonized product. Particularly, the temperature of the pyrolysis and the activation conditions (time, temperature, activation agent) are important factors to be taken into account, often yielding porosity values and surface areas exceeding, respectively, 80% and 2000 m² g⁻¹ [23,26, 27].

There are several examples in the literature on the potential application of carbon aerogels in capacitive deionization, including our own studies [25,28-34], discussing the effects of the different synthesis parameters as the precursor's molar ratio [26-28], thermal treatment [29] and porous features [32-34]. However, most of the studies focus on the electrochemical performance of powder electrodes of small dimensions at lab scale [32-36], and data are extrapolated to larger and self-supported monolithic electrodes used in the large scale applications of CDI. At converse, studies on self-supported monolith electrodes are rather scarce. In this regard, our

previous work [29-30] has revealed that the monolithic morphology can provide different features, leading to superior CDI performance, lower oxidation resiliency and thus improved stability of the electrodes.

Bearing all this in mind, the objective of this work was to screen the electrochemical performance of a series of aerogel electrodes (both in monolithic and powder morphology) for their potential application in CDI processes. We have correlated the capacitive deionization performance with their physicochemical properties, linking them with the main synthesis parameters as R/C and R/W. For this purpose, we have selected a series of aerogels with different R/C (ranging from $100 \leq R/C \leq 800$), and R/W molar ratio ($0.04 \leq R/W \leq 0.13$), while trying to optimize the textural and capacitive properties towards the removal of ions from solution.

2. Experimental section

2.1 Materials preparation

The carbon aerogels were synthesized by the sol-gel polymerization of resorcinol (R) and formaldehyde (F) mixtures in water (W), using sodium carbonate as catalyst (C). Details on the experimental procedure have been reported elsewhere [26-29]. Briefly, the R/F molar ratio was set at 0.5, the R/C molar ratio was varied from 100 to 600, while R/W ranged from 0.04 to 0.13. The reactants were vigorously stirred in sealed glass moulds to ensure a homogeneous polymerization, and the obtained hydrogel was aged in an oven at 40 °C for 24 h and then at 70 °C for 120 h. Drying was performed using CO₂ at supercritical conditions (40°C and 100 bar). In order to avoid the shrinkage of the gel and ensure CO₂ solubility during the drying process, a previous controlled water-acetone exchange is required. Pyrolysed aerogels were prepared at 800 °C under nitrogen atmosphere (i.e., heating rate 2 °C min⁻¹ up to 400 °C and hold for 60 min followed by heating up to 800 °C and hold for 60 min). A second batch of aerogels was prepared by activation of the carbonized ones under a CO₂ stream at 800 °C for 2 hours. The nomenclature of the samples is (R/C)-(R/W)-(tt) where *tt* refers to the thermal treatment of the hydrogels (*py* for pyrolysed and *act* for activated samples).

2.2 Textural characterization

N₂ adsorption-desorption isotherms were recorded at -196 °C (ASAP 2010, Micromeritics). For this purpose, the carbon aerogels were previously outgassed under primary vacuum at 120 °C overnight (heating ramp of 2 °C min⁻¹). The specific surface area, S_{BET}, total pore volume, V_T, and micro-/ mesopore volumes were calculated from the gas adsorption isotherms. The pore size distributions were calculated by using the new 2D-NLDFT-HS method [37]. Transmission electron microscopy was performed in a JEOL-JEM 2010.

2.3 Electrochemical characterization

Experiments were performed by assembling the electrode components in three-electrode Swagelok™ type cells. The working electrode consisted of a mixture of active material (70%), Superior graphite (20%) and PVDF binder (10%). The mixture was slurried in N-methyl pyrrolidone and spread on a 13 mm titanium disk, and then the electrode was dried at 70°C overnight. A Hg/Hg₂SO₄ and a platinum wire were respectively used as reference and counter electrode. A 0.1 M NaCl solution in deionized water was used as electrolyte. Cyclic voltammetry experiments were conducted between -0.5 and +0.5 V versus the reference electrode at 0.5 mV s⁻¹ and monitored with a Biologic VMP multichannel potentiostat. The polarization resistances were determined from the electrochemical impedance spectra (EIS) recorded on freshly assembled cells by using an Autolab PGSTAT12 system. The equilibrium voltage was perturbed with an AC voltage signal of 5 mV over the frequency range 25 kHz to 10 mHz. The polarization resistance (R_{pol}) was calculated by fitting the recorded spectra according to an equivalent circuit formed by the bulk solution resistance (R_{el}) and the stance where the polarization resistance (R_{pol}) connected in series to a Warburg impedance element and in parallel to a CPE is a constant phase element. The high-frequency response was ascribed to the bulk resistance of the solution (R_{el}). The resistance to ion migration through the pore structure (R_{pol}) was determined from the real impedance of the semicircle at intermediate frequencies [38].

2.4 Desalting capacity

A symmetrical batch-type cell was assembled to perform the capacitive deionization experiments, using two monolithic aerogel electrodes (weight ca. 150 mg and ca. 0.3 cm³), separated by Whatman glass GF/A fiber sheets. Their surfaces were polished to ensure a good contact with the titanium current collector. The pieces were washed in deionized water for 30 minutes and then immersed into 15 mL of a 0.025 M NaCl solution (ca. 1.5 g/L) magnetically stirred to favor mass transfer from the bulk solution to the electrode. The cell was charged by applying a potentiostatic pulse (0.9, 1.2 or 1.5 V for 120 min). Afterwards, the electrodes were discharged at 0 V for the same period of time. A conductivity-meter was used to monitor the changes of the ionic conductivity and hence ion concentration. The gravimetric capacitances of the aerogel series in the CDI two-electrode cell have been computed from the charge/discharge current curves using equation 1:

$$C_w = \frac{1}{w_{et} E_{cell}} \int_{t_0}^{t_n} i dt \quad (1)$$

where C_w is the volumetric capacitance in Fg^{-1} , W_{cat} is the volume of the monolithic electrode (the one working as cathode) in g, E_{cell} is the voltage applied to the cell in volts, t_b and t_e are the times in seconds at the beginning and the end of the third cycle of charge and i is the current in amperes. The volumetric capacitances C_v have been computed in a similar way, using equation 1 but replacing the electrode weight by the electrode volume in cm^3 .

3. Results and discussion

Characterization of the aerogels

The main textural properties of the synthesized aerogels are compiled in Table S1. The effect of various synthesis conditions on the textural, chemical and morphological properties of carbon aerogels has been extensively discussed in the literature [23, 24,26,27]; we herein report the characterization of the textural characteristics of the prepared aerogels for interpretation of their electrochemical response when used as electrodes. The influence of R/C and R/W molar ratios on the porosity (in terms of surface area and pore volumes) is quite significant and follows different patterns depending on the thermal treatment (pyrolysis or activation) of the samples.

For the pyrolyzed aerogels, all the samples displayed quite closed microporosity and specific surface area, regardless the R/C and R/W molar ratios, as inferred from the values compiled in Table S1. This is more clearly seen in Figure 1 showing the dependence of the surface area of the pyrolyzed and activated aerogels with the R/C and R/W parameters.

As a general rule, the mesopore (and total pore) volumes followed an increasing pattern with the R/C molar ratio (regardless the R/W ratio) and up to ca. 200-300; for higher R/C values, the mesoporosity is gradually dropping. The position of the hysteresis loop in the nitrogen adsorption isotherm shifted towards higher relative pressures as R/C increases, indicating the enlargement of the mesopores. As seen in Figure S1, for the lowest value of R/W (0.04) in the pyrolyzed samples, the mesopores volume suffers a sharp increase from 1 to over $2 \text{ cm}^3/\text{g}$ when the R/C rises from 100 to 300; conversely, it dropped sharply to ca. $0.08 \text{ cm}^3/\text{g}$ when R/C was further risen to 600.

When R/W is increased to 0.06, the general trend is an almost linear decrease of the mesopores volume (from near 1 to around $0.1 \text{ cm}^3/\text{g}$), whilst for the highest values of R/W tested (i.e., 0.08 and 0.13), the trend seems to be the opposite. The same behavior was observed for the activated aerogels, indicating that the activation has almost no effect on the mesoporosity, which is governed by the R/C and R/W molar ratios. Furthermore the hysteresis loops also displayed different shapes (Figure S2); for the samples obtained with R/C of 150 and 200, except for high

R/W values, the loop is type H1 with quite parallel, smooth and long adsorption and desorption branches, characteristic of pore systems with narrow pore size distributions. As the R/C increases, the loop becomes less evident (type H3) with the adsorption branch resembling a Type II isotherms and the loop at relative pressures close to unity. This is typical of pore networks consisting of macropores which are not completely filled with pore condensate [39], and confirms the enlargement of the mesopores with the R/C.

Fig. 1 Correlation between the specific area and a) R/C and b) R/W molar ratios for the activated (empty symbols) and pyrolyzed (closed symbols) aerogels. The number between brackets at each point indicate the reciprocal R/W (plot a) or R/C (plot b) molar ratio. Lines are plotted for guiding the eyes.

The effect of R/W in the mesoporosity is also very remarkable; the position of the hysteresis loop in the nitrogen adsorption isotherms shifted towards lower relative pressures, indicating the enlargement of the mesopores as the R/W decreased. Similar effects on the R/W ratio have been reported in the literature [23,24,26,27,29]. For instance (Table S1 and Figure S2), for R/C ratio of 600, the formation of mesoporosity is higher for R/W of 0.13 as seen in the wide hysteresis loop compared to the sample with R/W of 0.06 (similar total pore volume but narrower hysteresis loop shifted towards higher relative pressures).

On the contrary, the differences in specific surface and micropore volumes become large for the activated aerogels series (Table S1, Figure S2), though the trend for the mesopore volumes is similar to that described for the pyrolyzed aerogels. For instance, surface area values are higher for the samples with lower R/C as low as 100 and 150, regardless the R/W ratio, indicating that they are more prone to be activated. Similarly, the influence of the R/W ratio depends on the R/C values. For instance, in the samples synthesized with R/C of 150, the activation treatment is more effective for low R/W values (i.e., 1328, 1145 and 746 m²/g for 150-0.04-act, 150-0.06-act, and 150-0.13- act, respectively), whereas for R/C of 600 the effect is smaller (i.e., 662, 781 and 801 m²/g for 600-0.04- act, 600-0.06- act, and 600-0.13- act, respectively). This is explained by the different nanostructure of the pyrolyzed aerogels and their differences in the evolution of the porosity upon CO₂ activation; the aerogels prepared using low R/C and R/W molar ratio display a low density of dense carbon clusters (Figure 2), allowing a good access of CO₂ to these clusters during the activation step, thereby widening the micropores.

In contrast, aerogels with high R/W ratios present a higher density of dense carbon clusters, somehow hindering the access of CO₂ and thus making gasification less effective. On the other hand, the aerogels synthesized using high R/C and low R/W molar ratios are characterized by the presence of low density clusters, easily accessible by CO₂ during the activation. In this case, the decrease in the surface area is due to the enlargement of the micropore structure. Hence, the lower the R/W, the higher the surface area, being the effect more pronounced for aerogels synthesized using low R/C molar ratio (Table S1).

Additionally, low R/C ratios render the so -called “polymeric gels” characterized by small particle sizes and high surface areas (Figure 2) that are typically very prone to shrink upon supercritical drying. Contrarily, “colloidal aerogels” are obtained at high R/C ratios, showing the opposite behavior concerning shrinkage on drying. The R/W molar ratio also influences the texture of the aerogels, with high R/W values giving rise to aerogels with low surface areas. These differences in porosity of the aerogels with varying the R/C and R/W molar ratios can also be explained by their different structure (Figure 2).

Fig. 2 Scheme showing the separated effect of R/C and R/W parameters on the textural properties of carbon aerogels.

At low R/C ratios, the polymeric aerogel consists of a tangle of cross-linked polymer chains which density depends on the R/W ratio. These textural trends can be verified in the TEM micrographs shown in Figure 3. Hence, at high R/W ratios the density is very high and the resulting gel has very low porosity (Table S1). This is also evidenced in the density of the aerogels (Figure 4). As R/W ratio decreased, the polymer chains entanglement becomes less dense and a more open porosity is developed, so surface area must increase. For a given low R/W molar ratio, if R/C is increased, the polymer chains rather form clusters (instead of a dense tangle), which average size depends on R/C. Also the polymer becomes less cross-linked, all of this causing the surface area to decrease drastically with the R/C increase. On the other hand, for a given high R/W, low R/C ratios give rise to barely porous networks, whereas as R/C increases, the polymer clusters arrange in a more open pore structure leading to a slight increase in surface area (Table S1, Figures 2, 3 and 4).

Fig. 3 Transmission electron micrographs of pyrolyzed aerogels at selected R/C and R/W ratios.

Electrochemical characterization of powdered aerogels

Initially, the capacitive behavior of the aerogels was investigated by recording the cyclic voltamograms in 0.1 M sodium chloride at 0.5 mV s^{-1} in three-electrode cells. In all the cases the profiles displayed the nearly rectangular shape (Figure S3) expected for a predominantly capacitive behavior when ions are effectively electrosorbed in the electric double layer formed at the electrode/electrolyte interface. In some samples, slight deviations of the rectangular shape (i.e., an anodic current increase at high potentials and/or broad humps) were observed and likely attributed to the occurrence of pseudo-faradaic reactions due to functional groups and/or electrolyte decomposition [40].

Fig. 4 Correlation between the density and the R/W molar ratio for the activated and pyrolyzed aerogels.

Figure 5 shows the relationship between capacitance and surface area for the pyrolyzed and activated aerogels, evidencing the progressive increase in the capacitance with the surface area of the materials. This behavior is typically observed in electrodes which electrochemical response is based on a pure capacitive phenomenon due to the electrostatic interactions between the ions of the electrolyte and the electric double layer created at electrode surface [41]. Thus, it was rather expected in the synthesized aerogels considering their chemical composition. The broad dispersion observed in the case of low surface area values, more evident in the case of pyrolyzed aerogels, can be ascribed to the non-negligible influence of the surface chemistry. Thus, pyrolyzed aerogels present low amounts of oxygen, responsible for pseudo-capacitive effects.

The capacitance values were also correlated to the polarization resistance. Fig. 6b shows that the R_{pol} values tend to decrease as the capacitance values increase. In addition, higher R_{pol} values were calculated for the pyrolyzed aerogels than for the activated ones. This trend can be correlated to the increased surface area of the former, which facilitates the ions migrating from the bulk electrolyte to reach the aerogel surface (Fig. 7a). Additionally, there seems to be a clear influence of the pore sizes, since low R_{pol} values were recorded for the aerogels with a large contribution of mesopores, whereas the volume of micropores does not seem to affect the R_{pol} (Fig. 7b). Similar results on the beneficial influence of a mesoporous network to provide a good

kinetic response have been reported in the literature [38, 42]. Fig. 8a shows the progressive rise of R_{pol} for the pyrolyzed aerogels with increasing R/C molar ratio, being the trend slightly more pronounced for those aerogels with low R/W. In turn, two opposed tendencies are visible for activated aerogels.

Fig. 5 Dependence of the gravimetric capacitance of powdered aerogel electrodes with the specific surface area.

Thus, those samples prepared with low R/W values significantly increased R_{pol} by increasing R/C. Contrarily, activated aerogels prepared with $R/W \geq 0.1$ evidenced a decrease in resistance. Similarly, the carbonization process led to notorious differences when the effect of the parameter R/W was evaluated (Fig. 8b). Thus, the influence of R/W was less significant for the pyrolyzed aerogels, though large resistance values were determined for the aerogels with the R/C=600. Otherwise, activated aerogel were more sensible to the increase of R/W. Thus, a significant decrease of R_{pol} is observed when R/W increases for aerogels with R/C = 600.

Fig. 6 a) Nyquist plot from impedance spectra recorded for an activated carbon aerogels in 0.1 M NaCl electrolyte solution. Inset: Equivalent circuit applied for fitting the impedance spectra; b) Capacitance versus polarization resistance of the activated (open symbols) and pyrolyzed (closed symbols) aerogels.

Fig. 7 Dependence of the polarization resistance with the specific surface area and the pore volume for activated (open symbols) and pyrolyzed (closed symbols) aerogels.

Fig. 8 Dependence of the polarization resistance with a) R/C and b) R/W molar ratio for the activated (open symbols) and pyrolyzed (closed symbols) aerogels.

Desalting capacity of monolithic aerogels

Besides the electrochemical characterization of the powdered aerogels electrodes in a 3-electrode cell configuration, it is crucial to investigate the electrochemical response of the (self-supported) monolithic electrodes in symmetric cells (ca. 2-electrode cell configuration) used in

desalting units. For this reason, we performed desalting studies of selected aerogels in symmetric cells using monolithic (self-supported) electrodes where the aerogel electrodes are were exposed to a bias voltage, one of them acting as anode (positive polarization) and the second one as cathode (negative polarization). Figure 9 shows the capacitance values obtained for the different aerogels in 2-electrode cell configuration and its dependence with the surface area of the electrode materials. As seen, there is not a straightforward correlation between the specific surface area and the desalting gravimetric capacity for either pyrolyzed or activated aerogels. The same trend was observed for the dependence with the polarization resistance (Figure S4). However, much of the capacitance variation of both series can be explained by analyzing the dependence of the volumetric capacitance with the combined effect exerted by both the specific surface area and the resistivity of the material. This is clearly seen in the multivariate polynomial regression analysis of both parameters using the following equations:

$$C_{pyr} = c_0 + c_1S + c_2R + c_3SR + c_4S^2 + c_5R^2 + c_6R^3 \quad (2a)$$

$$C_{act} = c_0 + c_1S + c_2R \quad (2b)$$

where C_{pyr} and C_{act} are respectively the volumetric capacitance of pyrolyzed and activated aerogels in $F\text{ cm}^{-3}$, S is the surface area in $\text{m}^2\text{ g}^{-1}$, R is the electrical resistivity in $\Omega\text{ cm}^{-1}$ and c_i are the polynomial coefficients of different orders.

The different polynomial fitting (c_i) and determination (r^2) coefficients for both series are compiled in Table S2. The fitting coefficient for the dependence of the capacitance with the surface area is positive for both series (pyrolyzed and activated samples), meaning that the capacity increases with the surface area; the regression coefficient for the dependence with the electric resistivity R follows the opposite trend (negative coefficient). In the case of pyrolyzed aerogels, a third order approximation was needed to get a good fit of the experimental values; consequently, errors propagate and amplify to a higher degree showing a higher intercept value.

The driving terms are the first order ones, while the second and third order coefficients have much smaller impact on the capacitance. In the case of surface area, the third order term is not meaningful and has been neglected. Furthermore, more than 96% of the capacitive response can be correlated to the combined effect of R and S following a linear dependence (since 2nd and 3rd order fitting coefficients are quite small). For the activated aerogels, almost 70% of capacitive response shows a linear dependence with R and S . Such low dependence suggests that the remaining 30% of the variation of the capacitance depends on the contribution of uncontrolled resistances in the cell setup likely arising from a poor contact of the monolithic electrode with the current collector (since activated monoliths show a much lower contact surface).

Fig. 9 a) Dependence of the gravimetric capacitance of monolithic aerogels recorded in symmetric cells with the specific surface; b) Correlation of the experimental (open symbols) and predicted (closed symbols) volumetric capacitance vs the specific surface area for pyrolyzed and c) for activated aerogels.

4. Conclusions

A series of activated and pyrolyzed aerogels have been prepared by the sol-gel polymerization of resorcinol-formaldehyde mixtures. The influence of the different R/C ($100 \leq R/C \leq 800$) and R/W ($0.04 \leq R/W \leq 0.13$) molar ratios on the textural and electrochemical properties has been determined. Data has confirmed the strong interdependence between R/C and R/W parameters, preventing a separated evaluation. For instance, a drastic decrease in the specific surface area was observed for the activated aerogels when either R/C or R/W increased, whereas the effect was not so remarkable for the series of pyrolyzed aerogels. Along with surface area, the mesoporosity was very much conditioned by the synthesis conditions, whereas the microporosity did not follow the same trend and most samples presented quite close micropore volumes. As for the electrochemical performance, an enhanced decrease of the capacitance was observed when R/C and R/W increase, while respectively preserving low R/W and R/C ratios low capacitance values were measured in those aerogels characterized by either low R/W or R/C molar ratios. This trend is correlated to the ohmic resistance of the electrodes that strongly depends on the R/W and R/C values and the textural features of the materials. Polarization resistances are slightly higher in the pyrolyzed aerogels, compared to the activated materials. Furthermore, lower R_{pol} values are obtained for the aerogels with higher contribution of mesoporosity, regardless the microporosity. The capacitive response of the aerogel monolithic electrodes, measured in a symmetric cell configuration, similar to those used in desalting units has been successfully correlated to the combined effect of surface area and electrical resistivity.

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Figure captions

- Fig. 1** Correlation between the specific area and a) R/C and b) R/W molar ratios for the activated (empty symbols) and pyrolyzed (closed symbols) aerogels. The number between brackets at each point indicate the reciprocal R/W (plot a) or R/C (plot b) molar ratio. Lines are plotted for guiding the eyes.
- Fig. 2** Scheme showing the separated effect of R/C and R/W parameters on the textural properties of carbon aerogels.
- Fig. 3** Transmission electron micrographs of pyrolyzed aerogels at selected R/C and R/W ratios.
- Fig. 4** Correlation between the density and the R/W molar ratio for the activated and pyrolyzed aerogels.
- Fig. 5** Dependence of the gravimetric capacitance of powdered aerogel electrodes with the specific surface area.
- Fig. 6** a) Nyquist plot from impedance spectra recorded for an activated carbon aerogels in 0.1 M NaCl electrolyte solution. Inset: Equivalent circuit applied for fitting the impedance spectra; b) Capacitance versus polarization resistance of the activated (open symbols) and pyrolyzed (closed symbols) aerogels.
- Fig. 7** Dependence of the polarization resistance with the specific surface area and the pore volume for activated (open symbols) and pyrolyzed (closed symbols) aerogels.
- Fig. 8** Dependence of the polarization resistance with a) R/C and b) R/W molar ratio for the activated (open symbols) and pyrolyzed (closed symbols) aerogels.
- Fig. 9** a) Dependence of the gravimetric capacitance of monolithic aerogels recorded in symmetric cells with the specific surface; b) Correlation of the experimental (open symbols) and predicted (closed symbols) volumetric capacitance vs the specific surface area for pyrolyzed and c) for activated aerogels.

Supplementary Information

On the correlation between the porous structure and the electrochemical response of powdered and monolithic carbon aerogels as electrodes for capacitive deionization

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Figure S1. Mesopore volume as a function of R/C ratio. Lines and R/W ratios are shown for clarity.

Figure S2. Nitrogen adsorption isotherms of pyrolyzed and activated carbon aerogels with different R/C and R/W ratios.

Figure S3. Cyclic voltammograms of a) pyrolyzed and b) activated carbon aerogels with different R/C and R/W ratios.

Figure S4. Dependence of the gravimetric capacitance of monolithic aerogels recorded in symmetric cells with the polarization resistance of pyrolyzed and activated carbon aerogels.a.

Figure S5. Dependence of the gravimetric capacitance with a) R/C and b) R/W molar ratios for the activated (empty symbols) and pyrolyzed (closed symbols) aerogels

Table S1. Summary of the main textural parameters obtained from N₂ adsorption isotherms at -196 °C on the studied aerogels.

Sample	R/C	R/W	S _{BET}	V _{TOTAL} ^A	V _{MICRO} ^B	V _{MESO} ^B
			m ² g ⁻¹	cm ³ g ⁻¹	cm ³ g ⁻¹	cm ³ g ⁻¹
100-0.04-py	100	0.04	757	1.2	0.17	1.02
100-0.08-py	100	0.08	707	0.75	0.20	0.55
150-0.04-py	150	0.04	659	1.27	0.14	1.09
150-0.06-py	150	0.06	749	1.03	0.20	0.82
150-0.13-py	150	0.13	564	0.46	0.17	0.27
200-0.06-py	200	0.06	712	1.29	0.17	1.10
300-0.04-py	300	0.04	671	2.44	0.19	2.23
300-0.10-py	300	0.1	566	0.78	0.16	0.62
400-0.06-py	400	0.06	718	1.17	0.25	0.63
400-0.10-py	400	0.1	657	0.93	0.20	0.71
600-0.04-py	600	0.04	587	0.26	0.24	0.08
600-0.06-py	600	0.06	701	0.72	0.25	0.45
600-0.13-py	600	0.13	618	0.67	0.19	0.48
800-0.06-py	800	0.06	626	0.35	0.24	0.13
100-0.04-act	100	0.04	1434	1.25	0.40	1.17
100-0.08-act	100	0.08	1126	0.92	0.34	0.54
150-0.04-act	150	0.04	1328	2.1	0.35	1.73
150-0.06-act	150	0.06	1145	1.30	0.33	0.93
150-0.13-act	150	0.13	746	0.52	0.25	0.26
200-0.06-act	200	0.06	1122	1.58	0.33	1.23
300-0.04-act	300	0.04	779	2.56	0.24	2.24
300-0.10-act	300	0.1	905	0.95	0.29	0.64
400-0.06-act	400	0.06	907	0.74	0.34	0.41
400-0.10-act	400	0.1	858	0.96	0.28	0.67
600-0.04-act	600	0.04	662	0.34	0.25	0.07
600-0.06-act	600	0.06	781	0.39	0.29	0.09
600-0.13-act	600	0.13	801	0.78	0.26	0.51
800-0.06-act	800	0.06	784	0.38	0.29	0.08

^A total pore volume evaluated at p/p₀ ~ 0.99

^B micro-, mesopore volumes evaluated by the 2DNLDFT-HS method

Table S2. Fitting (c_i) and determination (r^2) coefficients of the multivariate polynomial regression analysis (equations 1a and 1b) of the dependence of the surface area and capacitance values for the series of pyrolyzed and activated aerogels.

Term	Pyrolyzed	Activated
c_0	178.921	7.590
c_1	1.089	0.026
c_2	-18.797	-0.142
c_3	0.032	-
c_4	-0.004	-
c_5	0.254	-
c_6	-0.001593	-
r^2	0.966	0.688