N-doped monolithic carbon aerogel electrodes with optimized features for the electrosorption of ions

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Abstract

N-doped carbon aerogels were synthesized by the polycondensation of resorcinol-formaldehyde-melamine mixtures. The prepolymerization of the precursors was determinant for the preparation of meso/macroporous aerogels with varied nitrogen content, regardless the solution pH and M/R molar ratio. The effect was more pronounced at pH 6, as the hydrogels prepared by the one-step route displayed essentially a microporous character, as opposed to the mesoporous network after prepolymerization. The prepolymerized carbon aerogels presented large capacitance values due to the optimum balance between pore structure, improved wettability and low polarization resistance for the highly doped materials. Salt deionization capacity revealed the importance of the macropore structure in the monolithic configuration of the aerogels for a fast electrosorption of ions.

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1. Introduction

Carbon aerogels are interesting materials consisting of interconnected and uniform particles with well-defined pore architectures that arise from the growth and aggregation of cross-linked polymer clusters following a sol-gel reaction of adequate monomeric precursors [1,2]. Usually prepared from resorcinol and formaldehyde reagents, their suitable electrical and thermal conductivity, adequate corrosion resistance, low thermal expansion coefficient, density and elasticity makes them outstanding materials for a wide range of applications including energy storage [3,5], catalysis [6] and environmental applications [7-9]. Highly porous carbon aerogels are especially interesting for their use as electrodes in electrochemical applications for ions removal and water desalination, where it has been proven that the reversible electro-trapping of ions can be advantageous compared to well-established separation processes [7-10]. Particularly, this technology has proven that can be competitive for water with a salinity below 5 g/L, usually called as brackish water [11].

On the other hand, the incorporation of heteroatoms within the carbon matrix is a well-known approach to improve the basicity and wettability of carbon surface and to provide pseudo-capacitive effects while preserving long cyclability [12, 13]. These effects depend on the chemical state of the nitrogen groups (i.e. nitrogen can be incorporated either to edge or basal planes of the graphitic structure), and can contribute significantly to promote electron transfer reactions [14-16]. For this, the synthesis of nitrogen-doped carbon aerogels has been reported in the literature using a wide variety of precursors such as melamine [17-19], urea [20], 3-hydroxypyridine [21], or ammonia [22]. Also, innovative proposals make use of porphyrins [23] and biomass [24] for the preparation of nitrogenated carbons. Dai et al. have achieved ordered mesoporous N-doped carbon by soft-templating polymeric composites in ammonia [25]. Despite the synthesis and applications of N-doped carbon aerogels as electrodes for energy storage in supercapacitors have been widely studied [7, 11, 13] to our knowledge, the

benefits of the nitrogen doping of carbon electrodes on their electrosorption capacity have not been addressed. Thus the objective of this work is to examine the effect of N-doping of monolithic carbon aerogels on their electrochemical performance applied to the electro-assisted removal of ionic species in aqueous solution.

For this purpose, a series of carbon aerogels were prepared by simple modifications of the conventional polycondensation reaction of resorcinol/formaldehyde mixtures, to allow the sol-gel aggregation of the hydrogel precursors in the presence of melamine as N-precursor. To achieve this goal, a prepolymerization step of the precursors was introduced in the synthetic route; the effect of the solution pH of the hydrogel precursors and the melamine/resorcinol ratio were also investigated. The structural, morphological and physico-chemical properties of the N-doped aerogels were characterized, as well as their electrochemical performance as electrodes in the removal of ionic species in saline water.

2. Experimental

2.1 Materials synthesis

Hydrogels were synthesized by the polycondensation of Melamine (M), Resorcinol (R) and Formaldehyde (F) using sodium carbonate as catalyst (C) and deionized water (W) as solvent. Two different R/M ratios were selected (0.5 and 2) to ensure a meaningful variability of nitrogen content and its influence on the properties of the aerogels. Otherwise, the number of moles of F was fixed at 9 in all cases. The final pH of the precursors was eventually adjusted to 4, 6 or 8 by adding either acetic acid or sodium carbonate, respectively. In a first series, all the reagents were mixed together in a sealed glass mould, named as non-prepolymerized hydrogels. A second series of samples was synthesized following a prepolymerization procedure. Briefly, a solution containing R, F, C and W (solution A) was stirred for 1 h at 40 °C. Separately, a solution containing M, F, W and C (solution B) was stirred for 30 min at

70 °C. Subsequently, solutions A and B were mixed together and stirred for 20 minutes at room temperature to further allow the cross-linking of the precursors. With the latter procedure, we expect a more efficient polymerization reaction yielding highly mesoporous aerogels. Hydrogels were then kept in an oven at 40 °C for 24 h and then at 70 °C for 120 h to allow gelation and aging. After a controlled water–acetone exchange, the hydrogels were dried under CO₂ supercritical conditions and carbonized at 750 °C under nitrogen atmosphere (ca. 2 °C/min) [10]. The carbon aerogels were further activated using CO₂ at 750 °C for 90 min. Samples are denoted as MRF(n)-X-Y, where n=0 or 1 indicating, respectively, non-prepolymerized and prepolymerized aerogels; X accounts for the M/R molar ratio and Y for the pH value.

2.2 Chemical, Structural and Textural Characterization

Nanotextural characterization was carried out by means of N₂ adsorption–desorption isotherms at -196 °C. Before the analysis, the samples were degassed under dynamic vacuum at 120 °C for 17 hours. Strict analysis conditions were programmed during the gas adsorption measurements to ensure equilibrium data, thus the average elapsed time for each isotherm was 90-120 h, with over 100 equilibrium points. Each isotherm measurement was performed in duplicate to guarantee the accuracy of the experiments (error was below 0.1%) and to obtain reproducible data. Ultrahigh purity nitrogen (i.e., 99.9992%) was supplied by Air Products. The isotherms were used to calculate the specific surface area using the Brunauer–Emmett–Teller theory, S_{BET} , and total pore volume, V_{T} . The full micro-meso pore size distribution was calculated using the 2D-NLDFT-HS model assuming surface heterogeneity of carbon pores [26]. Mercury porosimetry was also performed to analyze the large mesoporosity and the macroporosity of the samples. A Micromeritics Autopore IV apparatus working in the pressure range 1–2000 bars was used.

Raman spectra were recorded with a Renishaw Raman instrument (InVia Raman Microscope), equipped with a Leica microscope. The samples were acquired by excitation with a green laser light at 532 nm and the spectra were recorded between 1000 and 2000 cm^{-1} . The spectra were deconvoluted by using Peakfit software package. X-ray Photoelectron spectra were measured in a XPS, SPECS Phobios 150MCD Spectrometer provided with a monochromatic Al K source (1486.61 eV) at 300 W X-ray power and anode voltage of 12 kV. The base pressure in the ultra high vacuum chamber was 4×10^{-9} mbar. Spectra of powdered samples were recorded using pass energy of 60 eV for the survey spectra and 30 eV for the high resolution core level spectra. During data processing of the XPS spectra, binding energy values were referenced to the C 1s peak of the adventitious carbon at 284.6 eV [27]. The CasaXPS software package was used for acquisition and data analysis. A Shirley-type background was subtracted from the signals. Recorded spectra were always fitted using Gauss–Lorentz curves, in order to determine the binding energy of the different element core levels more accurately. The error in binding energy was estimated to be ca. 0.1 eV. Thermogravimetric analyses (TGA) were carried out by using a DTG-60/60H Shimadzu instrument. The samples were heated at 10 $^{\circ}\text{C min}^{-1}$ up to 850 $^{\circ}\text{C}$ under an argon flow (80 mL/min). Elemental analysis was performed in Eurovector EA 3000 equipment. The acidic/basic character of the aerogels was evaluated by a modification of the Boehm method [28]. Briefly, finely powdered aerogels were dispersed in previously degassed 0.05N HCl or NaOH solutions. The vials were sealed and the suspensions equilibrated under stirring for 24 h. Then, the aliquots were filtered and titrated with 0.05 N NaOH or HCl to measure the basic and acid groups.

2.3 Electrochemical characterization

The initial electrochemical characterization of the electrodes was performed in three-electrode SwagelokTM type cells. The working electrode was prepared from a homogeneous slurry

containing active material (70%), Superior graphite (20%) and PVDF binder (10%) in N-methyl pyrrolidone which was subsequently spread on a 13 mm titanium disk. The electrodes were dried at 70°C overnight. A Hg/Hg₂SO₄ (SME) and a platinum wire were respectively used as reference and counter electrodes. The electrolyte was a 0.1 M NaCl solution in deionized water. Cyclic voltammograms were performed between -0.5 and +0.5 V versus the reference electrode and controlled with a Biologic VMP multichannel potentiostat. The internal resistance at the electrode interphases was analyzed by electrochemical impedance spectroscopy (EIS). The cell is perturbed by an AC voltage signal of 5 mV vs equilibrium potential over the frequency range 25 kHz to 10 mHz.

2.4 Capacitive deionization

Capacitive deionization experiments were developed by using two monolithic aerogel electrodes. These pieces measured ca. 0.15 g and ca. 0.3 cm³ and were polished to achieve a flat surface ensuring a good contact, washed in deionized water for 30 minutes and then vacuum impregnated with the electrolyte. The electrodes were sandwiched between titanium current collectors using two Whatman glass GF/A fiber sheets as a separator. This symmetric cell was assembled in a bath cell containing 20 mL of the electrolyte under continuous stirring to avoid mass transfer restrictions from the bulk solution. The deionization experiments were carried out in 0.025 M and 0.1M NaCl solutions (ca.1.5 and 6 g/L, respectively) by applying a potentiostatic pulse of 0.9 V, 1.2V or 1.5V for 120 min. Then, the discharge of the electrodes was performed at 0 V for the same period of time. A conductivity-meter was used to monitor the changes in the ionic concentration of the solution upon polarization of the electrodes.

3. Results and discussion

3.1 Characterization of the materials

A series of N-doped carbon aerogels were prepared using melamine as nitrogen source and following a prepolymerization step of the precursors. Two M/R molar ratio of 0.5 and 2 were used, and solution pH of the mixtures was adjusted between 4-8. Attempts of preparing mechanically stable hydrogels at solution pH below 6 failed, regardless the M/R ratio used. Hydrogels prepared at $\text{pH} < 8$ and $\text{M/R}=2.0$ also presented an inconsistent appearance, thus all these samples were discarded for further characterization. We attribute this effect to a non homogeneous polymerization of resorcinol and melamine due to the low pH value. Indeed, a similar observation has been reported for phenol-formaldehyde-melamine gels, where pH is a key parameter that controls the condensation and cross-linking of the monomers, and thus the development of the pore structure [16]. The effect was not observed for low M/R ratio or upon carrying out the polycondensation at more basic conditions (ca. solution pH of 8).

Fig.1 shows the TG profiles of the N-doped hydrogels (before carbonization and activation), with slight differences on the total weight loss of the samples depending on the composition of the precursor mixtures and the polymerization route (see also Table S1 in ESI). A first step is observed between room temperature and 160 °C, accounting for about 11-13 wt.% for all the samples and that corresponds to the loss of water and other light organic molecules as formaldehyde [29]. A second step (ca. 6-8 wt %) between 160 to 360 °C is associated to the desorption of water adsorbed in the deepest pores of the hydrogels [21], and/or the evolution of methyl and hydroxyl groups from aromatic nuclei [30]. The sharp mass loss between 300-600 °C (ca. 34-45 wt.%) is associated to the release of by-products evolved from the decomposition of formaldehyde, ammonia and melamine [21]. This step was more pronounced for the hydrogels prepared with the highest melamine content (M/R of 2). Finally, the weight loss above 600°C was rather similar to all the samples (ca. 12-14 wt.%) and is

linked to the release of H_2 and CO_2 upon the decomposition of side chains attached to triazine rings [21, 30]. The overall yield of the carbonization at 850 °C varied from ca. 35 to 15 %, being higher for the gels with low melamine content. Due to the large mass loss of the hydrogels (and thus low carbon yield after carbonization), the amount of nitrogen incorporated in the carbon aerogels was determined by elemental analysis and XPS after carbonization and activation (Table 1).

Figure 1. Thermogravimetric profiles of the synthesized N-doped hydrogels. Open squares correspond to prepolymerized samples; closed circles correspond to non prepolymerized samples.

As seen, the N/C ratio determined by elemental analysis (bulk) is slightly higher than the values obtained by XPS (surface), although differences are not very large, indicating a rather homogenous distribution of nitrogen groups in the carbon matrix rather than on the surface. This fact has also been reported by other authors and attributed to the capability of melamine

to firmly incorporate the nitrogen atoms into the carbon network, hence decreasing the partial concentration of the doping element near the surface [20, 31, 32]. As expected, the amount of nitrogen incorporated in the carbon aerogels increased by rising the M/R ratio (samples MRF(0)-2-8 and MRF(1)-2-8) and the pH value. On the other hand, the effect of the prepolymerization step is not so clear. The amount of nitrogen decreased for the samples obtained using low M/R ratio, regardless the pH, although the aerogels prepared with M/R of 2 escaped to this trend.

Table 1. Chemical composition of the carbon aerogels determined by chemical analysis (wt.%) and XPS spectroscopy (wt.%).

	Chemical analysis (wt.%)			XPS data (wt.%)			
	N	C	N/C ratio	N	C	O	N/C ratio
MRF(0)-0.5-6	3.6	74.4	0.05	2.3	82.5	15.2	0.03
MRF(1)-0.5-6	4.8	73.8	0.07	3.0	83.9	13.1	0.04
MRF(0)-0.5-8	7.1	72.7	0.10	4.6	76.8	18.6	0.06
MRF(1)-0.5-8	7.8	66.9	0.12	5.1	75.4	19.5	0.07
MRF(0)-2-8	16.0	68.3	0.24	9.5	80.9	9.5	0.12
MRF(1)-2-8	11.1	79.4	0.14	5.6	80.2	14.2	0.07

The structural characterization of the N-doped carbon aerogels was performed by Raman spectroscopy (Fig. 2). The broad bands (D and G bands) in the region between 1000 and 2000 cm^{-1} characteristic of carbon materials are observed for all the samples. The D1 mode, appearing at ca. 1345 cm^{-1} is due to the lack of long range translation symmetry in disordered carbons. The G mode at ca. 1600 cm^{-1} is assigned to a Raman-allowed E_{2g} resulting from ‘in plane’ displacement of the carbons strongly coupled in the hexagonal sheets. The prevalence of these two modes belonging to sp^2 phases is explained as a result of the large polarizability

of the conjugated π bonds at the sp^2 sites [33]. A careful decomposition of the spectra reveals two additional gaussian components. A D3 band located at ca. 1535 cm^{-1} is ascribed to amorphous forms of carbon located at interstitial defects of disordered carbons, while a shoulder at ca. 1180 cm^{-1} , denotes as D4 mode is attributed to C–C and C=C stretching vibrations of polyene-like structures [34, 35].

Figure 2. Raman spectra of the activated N-doped carbon aerogels a) MRF(0)-0.5-6, b)MRF(1)-0.5-6, c)MRF(0)-0.5-8, d)MRF(1)-0.5-8, e)MRF(0)-2-8, f) MRF(1)-2-8.

The variation of the I_G/I_{D1} ratio is a measure of changes in the structural ordering of the carbon network, non-detectable by classical powder X-ray diffraction. Samples prepared at

pH=6 revealed I_G/I_{D1} values of 0.45; a meaningful increase of this ratio was detected when the solution pH was raised to 8, with values going from 0.50 for MRF(0)-0.5-8 and 0.56 for MRF(1)-0.5-8. The use of a high M/R ratio did not follow the same trend; despite the synthesis was carried out at pH of 8, the I_G/I_{D1} values decreased to 0.39 and 0.29 for, respectively, MRF(0)-2-8 and MRF(1)-2-8. This indicates that the incorporation of large amounts of nitrogen somehow induces the formation of less ordered structures. Similar results have been reported for related N-doped carbon aerogels [36].

3.2. Surface chemistry

As expected, the incorporation of N-containing groups to the carbon surface increased the basicity of the aerogels (Table 2) [20, 37-39]. This is known to have an important influence on the electrostatic and non-electrostatic interactions between the carbon electrode and the ionic species at the electrode-electrolyte interphase [37-39]. Although a clear relationship between basic and acid groups and the nitrogen concentration is not always clear [22], the prepolymerized aerogels displayed a higher contribution of basic groups, which is in agreement with the N-content determined by chemical analysis. This is expected to have beneficial effects on the gravimetric capacitance [37-39].

The details on the chemical bonding states of the surface N-groups are provided by XPS analysis. The concentration of elements on the surface is listed in Table 1. The C1s core level spectra were deconvoluted into five components which chemical shifts are assigned to graphitic carbon (sp^2 configuration, 284.6 eV), $Csp^2-N/C-OH$ (285.6 eV), $Csp^3-N/C=O$ (287.1 eV), and carboxyl (289.2 eV) groups (Fig. 3). Additionally, a broadened band appearing at ca. 291.2 eV is usually related to shake-up satellite peaks due to $\pi-\pi^*$ transitions in aromatic rings [40, 31]. The relative contributions of the various configurations are

summarized in Table 3. The most relevant features are the increased contributions of Csp²–N/C–OH and O–C=O in carboxylic groups in MRF(1)-0.5-6 and MRF(1)-2-8 aerogels.

Table 2. Textural parameters of the N-doped carbon aerogels determined from the nitrogen isotherms at -196°C, and concentration of acidic and basic surface groups measured by chemical titration.

	S _{BET}	V _T ^a	V _{MIC} ^b	V _{MESO} ^c	V _{MIC, CO2} ^d	Acid ^f	Basic ^f
	m ² g ⁻¹	cm ³ g ⁻¹	cm ³ g ⁻¹	cm ³ g ⁻¹	cm ³ g ⁻¹	mmol g ⁻¹	mmol g ⁻¹
MRF(0)-0.5-6	601	0.26	0.19	0.03	0.29	0.321	0.363
MRF(1)-0.5-6	725	0.80	0.20	0.56	0.26	0.205	0.463
MRF(0)-0.5-8	70	0.04	0.02	0.01	0.07	0.071	0.563
MRF(1)-0.5-8	92	0.05	0.05	0.01	0.14	0.238	0.430
MRF(0)-2-8	242	0.11	0.06	0.07	0.23	0.338	0.463
MRF(1)-2-8	701	0.27	0.20	0.01	0.21	0.271	0.396

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

^{b, c} micro-, mesopore volume evaluated by the 2DNLDFT-HS method applied to the N₂ adsorption isotherms at 77 K

^d narrow micropore volume evaluated from CO₂ adsorption isotherms at 273 K using DR method

^f acidic/surface groups evaluated by Boehm method

The O1s core level spectra showed marked differences in the profiles deserving some discussion (Fig. 3). Five components are mainly observed after the spectrum deconvolution of aerogels prepared at pH= 6. They are commonly ascribed to C=O in ketone/carbonyl (530.9 eV), O–C in lactone, phenol/ether/epoxy (532.5 eV), C=O in carboxylic acid (534.0 eV), occluded CO or CO₂ (536 eV) and adsorbed oxygen (537.9) [37-41]. The prepolymerization step involved an increase in the contribution of the signal at 534 eV assigned to carboxylic groups for MRF(1)-0.5-6 and MRF(1)-2-8. On increasing the pH value to 8, similar profiles are recorded for MRF(0)-0.5-8 and MRF(1)-0.5-8 in which the most remarkable features is

the non-negligible contribution of occluded CO or CO₂, which may arise from non-decomposed carbonate groups at the temperature employed in the carbonization process. Also, a new signal appears of at ca. 537.9 eV. This is a less common feature in our samples and only could be identified as adsorbed oxygen [40, 42]. Samples with the highest nitrogen content, MRF(0)-2-8 and MRF(1)-2-8, showed profiles in which the contributions of chemisorbed water is less significant and the signal at 537.9 eV is absent.

Figure 3. XPS spectra at the N 1s, C 1s and O 1s core levels of activated aerogels. a) MRF(0)-0.5-6, b) MRF(1)-0.5-6, c) MRF(0)-0.5-8, d) MRF(1)-0.5-8, e) MRF(0)-2-8, f) MRF(1)-2-8.

Table 3. Relative contributions calculated from the deconvolution of XPS N 1s, O 1s, C 1s spectra of N-doped carbon aerogels.

Envelope N 1s

B.E. (eV)	398.5 ± 0.2	400.4 ± 0.2	401.4 ± 0.1	403.4 ± 0.2	
Assignment	N-6	N-5	N-Q	N-X	
MRF(0)-0.5-6	36.6	36.7	19.6	7.7	
MRF(1)-0.5-6	36.9	33.1	21.9	8.0	
MRF(0)-0.5-8	36.5	42.4	13.1	8	
MRF(1)-0.5-8	28.3	46.4	15.1	10.2	
MRF(0)-2-8	43.9	40.6	10.3	5.1	
MRF(1)-2-8	44.9	39.9	10.5	4.7	
Envelope O1s					
B.E. (eV)	530.9 ± 0.1	532.5 ± 0.3	534.0 ± 0.3	536.0 ± 0.2	537.9 ± 0.1
				Ocluded CO or CO ₂	Adsorbed O ₂
Assignment	C=O	C-O-	COO-		.
MRF(0)-0.5-6	11.1	32.5	55.2	1.4	-
MRF(1)-0.5-6	9.7	22.8	57.9	9.6	-
MRF(0)-0.5-8	7.6	28.8	45.9	11.3	6.4
MRF(1)-0.5-8	2.1	31.5	40.4	17.3	8.9
MRF(0)-2-8	20.3	34.8	39.7	5.2	-
MRF(1)-2-8	13.1	35	48.8	3.1	-
Envelope C1s					
B.E. (eV)	284.6 ± 0.1	285.6 ± 0.2	287.1 ± 0.2	289.2 ± 0.3	291.1 ± 0.3
		Csp ² -N	Csp ³ -N		π-π*
Assignment	C-C	/C-OH	/C=O	O-C=O	transition
MRF(0)-0.5-6	45.09	32.5	14.8	7.1	0.5
MRF(1)-0.5-6	39.44	37.5	12.1	9.4	1.6
MRF(0)-0.5-8	37.1	34.5	15.3	8.6	4.5
MRF(1)-0.5-8	45.7	27.6	13.7	8	5
MRF(0)-2-8	49.4	28.9	13.1	6	2.7
MRF(1)-2-8	41.5	38.3	104	8.2	1.6

Most remarkable changes were observed in the N1s core level spectra of the synthesized aerogels. All the spectra could be decomposed into four different components attributed to N6 pyridinic (398.5 eV), N5 pyrrolic/pyridone (400.4 eV), N-Q quaternary (401.4 eV) and

pyridine N-oxide (403.4 eV) [16-19, 36, 43]. N-6 and N-5 were the dominant contributions in all the samples. The contribution of N-Q reached high values for the samples obtained at pH 6, and was slightly more favored in the prepolymerized samples. On increasing pH to 8, the decrease in the N-Q is accompanied by rise in pyrrolic/pyridone groups (N-5). A further increase of the nitrogen content in MRF(0)-2-8 followed the expected decrease in the N-Q component, along with the consequent loss of structural ordering in fairly agreement with data from Raman spectroscopy. For the series obtained using M/R ratio of 2, prepolymerization seemed to have a minor effect, as both samples showed quite similar relative abundance of N-groups.

The nature of the N-groups was further confirmed by FTIR (Fig. S1), where rather similar profiles were obtained for all the samples regardless the solution pH or polymerization procedure. Overall, the broad bands at ca. 3400 cm^{-1} attributed to either -OH and/or -NH moieties were detected, along with the bands at 1558 , 1470 and 1370 cm^{-1} , assigned to C-N stretching vibrations in triazine rings, and the C-N breathing mode, respectively [44-46]. Both demonstrate that nitrogen atoms are incorporated into the backbone of phenolic resin [17-19, 44, 45]. Additional peaks assigned to secondary amines (1200 cm^{-1}), and amides (670 cm^{-1}) were also observed.

3.3. Textural properties

Fig. 4 shows the nitrogen adsorption isotherms at $-196\text{ }^{\circ}\text{C}$ of the samples, along with the distribution of pore sizes. Interesting differences were noticed in the textural development of the aerogels depending on the composition of the precursors' mixture and the synthesis conditions, which are expected to be important in their electroassisted desalting capacities.

First of all, the prepolymerization step seems to be determinant for allowing an adequate development of the pore structure (both micro- and mesoporosity). In the case of the aerogels

prepared at pH 8 and M/R =0.5 (samples MRF(n)-0.5-8) this is more critical as according to the nitrogen adsorption data (Table 2) both samples displayed low surface areas and poor textural features; however, the analysis of the textural features by means of CO₂ adsorption isotherms revealed the presence of a non negligible narrow microporosity in the prepolymerized sample (Table 2). We attribute this to a low cross-linking degree of the monomers at high pH values, yielding mechanically and thermally unstable hydrogels that do not stand the supercritical drying and carbonization steps. As result, the structure collapses given rise to aerogels (ca. 70-90 m²/g) with a poor microporous network, only visible in the prepolymerized samples. For higher M/R ratio (samples MRF(n)-2-8) the formation of the microporosity is more pronounced, the prepolymerized aerogel showing a better defined porosity (type I isotherm and high surface area), suggesting a better cross-linking of the precursors. Similar results have been interpreted by others authors in terms of the shorter C-N bond length, which would induce a buckling of the basal plane and consequently a larger porosity [47].

Comparatively, the carbon aerogels prepared at pH 6 showed larger development of the porosity than their corresponding counterparts obtained at pH 8. Sousa et al. found a similar behavior in xerogels [20]. Furthermore, the effect of prepolymerization step is more visible at pH 6; as seen, low pH and M/R molar ratio favor the development of the mesoporous structure not evidenced in samples MRF(n)-x-8. For instance, sample MFR(0)-0.5-6 obtained by direct synthesis (non prepolymerized) showed a type I isotherm, as opposed to the type IV isotherm with a marked hysteresis loop at high relative pressure measured for prepolymerized MFR(1)-0.5-6. The position of the hysteresis loop at relative pressure above 0.8 indicates the presence of large mesopores, which agrees with the broad PSD centered between 10-45 nm obtained by fitting the experimental data (inset Figure 4b).

Figure 4. N_2 adsorption isotherms at 77 K of N-doped carbon aerogels after carbonization and activation activated aerogels. Inset: Pore size distribution plots obtained by using the 2D-NLDFT-HS method.

TEM micrographs displayed in Fig. 5 corroborated the different textural properties of the carbon aerogels above discussed. The pre-polymerization at pH 6 (sample, MRF(1)-0.5-6 corresponding to Fig 5B, H) clearly promotes the formation of nanometric particles, a few nm smaller than those of MRF(0)-0.5-6 (Fig. 5a, g). SEM images also show that MRF(0)-0.5-6 (Fig. 5g) is formed by large spherical particles, as opposed to more compact interconnected smaller particles for MRF(1)-0.5-6 (Fig. 5h). On increasing the pH value, large and densely packed particles are observed regardless the synthesis conditions (Fig. 5c-f), which corresponds to the samples presenting the lower surface area and porosity (Table 2). These differences in porosity and chemical composition will undoubtedly lead to distinct electrochemical performances.

Figure 5. TEM images of activated N-doped carbon aerogels, a) MRF(0)-0.5-6, b) MRF(1)-0.5-6, c) MRF(0)-0.5-8, d) MRF(1)-0.5-8, e) MRF(0)-2-8, f) MRF(1)-2-8. SEM micrographs of g) MRF(0)-0.5-6, h) MRF(1)-0.5-6.

3.4. Electrochemical characterization

Initially, the electrochemical characteristics of the aerogel electrodes were investigated on powder electrodes in a 3-electrode cell configuration. Fig. 6 shows the corresponding cyclic voltammograms at 0.5 mV/s in 0.1 M NaCl. Overall, the curves are characterized by the typical box-shape profile revealing the capacitive behavior when ions are retained by electrostatic interactions at the electrode surface upon polarization. According to literature, the

mechanisms involved in the retention of ionic species on the surface of carbon aerogels comprise specific adsorption and electrosorption [48]. Particularly, the specific adsorption is related to the affinity of the aerogel surface by ion species being adsorbed. Since we have used sodium chloride as electrolyte in all our experiments, electrosorption becomes the main factor to be taken into account.

Only in the case of the aerogels with high nitrogen contents (MRF(1)-2-8) a slight deviation of the rectangular shape is observed, with a broad hump in the anodic sweep at around 0.28 V, indicating the contribution of pseudofaradaic reactions of the O- and N-groups [49]. This contribution is more evident in the non prepolymerized aerogels. It is also worth pointing out that the voltammograms displayed somewhat positive slopes at high and low potential values, indicative of certain resistivity on the electrodes coming from a slow diffusion of ions into the micropores [50].

Figure 6. Cyclic voltammograms of activated carbon N-doped aerogels recorded at 0.5 mV/s in 0.1 M NaCl solution.

The effect of prepolymerization on the ions removal was quite positive, with capacitance values of 84 and 60 F/g for MRF(1)-0.5-6 (prepolymerized) and MRF(0)-0.5-6, respectively. Such large difference cannot be exclusively explained by the textural features of both samples as surface areas and micropore volumes are quite similar (Table 2). Additional factors as the large mesoporosity of the prepolymerized aerogel, or the larger concentration of acidic groups in MRF(0)-0.5-6 might also be responsible for this behavior. The electrochemical performance of the prepolymerized sample is larger than that obtained for a non-doped carbon aerogel prepared by the resorcinol-formaldehyde method (ca. 76 F/g) and featuring a similar porous structure ($733 \text{ m}^2\text{g}^{-1}$ and $0.881 \text{ cm}^3\text{g}^{-1}$ for the surface area and pore volume, respectively) [8]. This evidences the beneficial effect of the N-doping on carbon aerogels.

On increasing pH, a slight fall of the capacitance value is observed for MRF(1)-0.5-8 (70 F/g) as compared to its corresponding counterpart synthesized at pH 6. Otherwise, the capacitance of the non-prepolymerized MRF(0)-0.5-8 aerogel remained unchanged (59 F/g). It should be noted, however, that both samples MRF(0)-0.5-8 and MRF(1)-0.5-8 presented an ill-developed porous structure (Fig. 4, Table 2), for which the capacitance values are most outstanding as they indicate the contribution of the surface functionalities incorporated upon N-doping. On increasing the nitrogen content in MRF(0)-2-8 and MRF(1)-2-8, capacitance values of 73 and 83 F/g were recorded, respectively. As the non prepolymerized aerogel has poor textural features (Table 2), the large capacitance values indicate the effect of N-doping through pseudofaradaic reactions. Indeed, if the capacitance values are normalized vs the surface area, the correlation is not linear but the series follow a logical trend. The capacitance values do not seem to be only dependent on the porosity or nitrogen content and basicity, but rather on the adequate combination of all these features.

N-doping of carbon materials is also known to modify the wettability [51], as well as the electronic properties of the electrodes, due to the electronic configuration of nitrogen atoms

(N-dopant). In this sense, impedance spectroscopy was measured to evaluate the internal electrodes resistance to the electroadsorption process. Electrical conductivity and ion accessibility to inner pores undoubtedly influence the kinetic response at the electrode–electrolyte interphase assuming a mixed kinetic and charge transfer control [52]. The Nyquist plots recorded for the N-doped aerogels are shown in Fig. 7a. The profile of the Nyquist plots at intermediate and low frequencies would reveal a semicircle followed by a straight line for an ideal capacitor. Nevertheless, the complex porous structure of these aerogels samples induces distortion in the profile of the curves. For this reason, the polarization resistance values (R_{pol}) of each electrode material were calculated by fitting the experimental data (as symbols in Fig.7a) to the equivalent circuit in Fig. 7b. The calculated profiles are plotted as overlapped lines in Fig. 7a. From the intersection with the horizontal axis at high-frequency, the resistance of the electrolyte solution can be elucidated. This value is low and its contribution to the overall resistance is usually neglected. The different components of this circuit are the electrolyte solution resistance (R_{el}), the polarization resistance (R_{pol}), the Warburg impedance (W), a constant phase element (CPE) and a capacitor (C). The polarization resistance is mainly responsible for the resistance to the ionic migration into porous structure.

Figure 7. (a) Nyquist plots derived from the impedance spectra recorded in the 0.1 M NaCl solution. A modulated AC voltage signal of 5 mV versus equilibrium potential was applied. (b) Equivalent circuit used for the fitting of the spectra.

A low resistance value ($0.51 \Omega \times \text{g}$) was determined for MRF(1)-0.5-6, clearly evidencing the beneficial contribution of its large surface area and mesoporosity to ensure a suitable ion migration and accessibility. The high resistance obtained for MRF(0)-0.5-6 ($1.07 \Omega \times \text{g}$) despite the large surface area (Table 2) is in agreement with the lack of transport pores as the porosity of this aerogel is mainly comprised of narrow micropores (Fig. 4). The increase of the pH of the synthesis to 8 also resulted in high resistance values for MRF(0)-0.5-8 (1.55

$\Omega \times g$) and MRF(1)-0.5-8 ($1.0 \Omega \times g$), evidencing again that this modification of the synthetic route is deleterious for the electrode performance even if the prepolymerization step slightly reduced the effect. This could be due to the better wettability of the samples with higher nitrogen content, and is also supported by the low R_{pol} values determined for MRF(0)-2-8 ($0.54 \Omega \times g$) and MRF(1)-2-8 ($0.55 \Omega \times g$).

3.5. Capacitive deionization

Due to their adequate porous and electrochemical features regardless the polymerization procedure, samples MRF(0)-0.5-6 and MRF(1)-0.5-6 were selected to evaluate their desalting performance in capacitive deionization experiments on monolithic electrodes. Data obtained for NaCl 0.025 M (ca. 1.5 g/L) is shown in Fig. 8a. The profiles show an increase in the electrosorption capacity for the first two hours that corresponds to the period when the external voltage is applied to the cell and ions are electrosorbed on the carbon surface. Afterwards, the voltage was eventually cut off for the desorption stage, thus the capacity decreased as the ions are eluted to the electrolyte. The maximum desalting capacity usually corresponded to the value recorded after 120 minutes; these values have been selected for data interpretation comparing the performance of the aerogel electrodes at the different applied voltages.

Figure 8. Capacitive deionization experiments performed at different potentials in 0.025 M NaCl solution: a) Electrosorption capacity of MRF(0)-0.5-6 (closed symbols) and MRF(1)-0.5-6 (open symbols); b) rate of salt uptake at 0.025 and 0.1M NaCl at an applied voltage of 0.9, 1.2 and 1.5 V for MRF(0)-0.5-6 and MRF(1)-0.5-6.

Sample MRF(0)-0.5-6 unexpectedly outperformed its prepolymerized counterpart at all applied voltages and electrolyte concentrations, as opposed to data obtained using powdered electrodes (Fig. 6). For instance, electrosorption capacities of 8.2 and 5.4 mg NaCl/g were measured for MRF(0)-0.5-6 and MRF(1)-0.5, respectively, at 1.5 V and 0.025 M (Fig. 8a).

Both samples revealed to be more efficient at medium-low salt concentration ranges, as already reported for some other carbon aerogels [53]. Moreover, these adsorption values were higher than those reported for non-doped aerogels subjected to similar conditions evidencing the positive effect of doping on the electrochemical behavior [53]. This fact is clearly seen in Fig. 8b, where the rate of salt uptake per volume unit of electrode is plotted as a function of the applied voltage for both concentrations.

These results also reveal that the concentration of the electrolyte is a determinant factor affecting the salt adsorption speed, since a faster adsorption was obtained for the concentrated electrolyte (ca. 0.1 M NaCl). Similar findings pointing out the strong correlation between the initial concentration and the electrosorption capacity and ion selectivity have been reported elsewhere [54]. The fast adsorption of the MRF(0)-0.5-6 as compared to the prepolymerized aerogel at various cell voltages is clearly evidenced (ca. $2.73 \text{ mg h}^{-1} \text{ cm}^{-3}$ vs $2.12 \text{ mg h}^{-1} \text{ cm}^{-3}$ at 1.5 V and 0.025M NaCl) and (ca. $2.90 \text{ mg h}^{-1} \text{ cm}^{-3}$ vs $2.68 \text{ mg h}^{-1} \text{ cm}^{-3}$ at 1.5 V and 0.1M NaCl). Indeed, at the highest voltage, ion transport is mainly controlled by electromigration, where ion mobility is an important factor which is increased by a connected macroporous net. At the lowest voltage the process is controlled by diffusion, hence the small differences observed might be associated to the diffusivity of ions in materials showing different porosity. To understand this behavior we have analyzed the differences in porosity of the electrodes in powder and monolith morphology. Although the gas adsorption isotherms of the materials in the form of powders and monolith are alike, the characterization of the macroporosity of the samples in monolithic form by mercury porosimetry showed important differences between the studied samples that account for the different salt uptake measured in the 3-electrode and 2-electrode configurations.

Figure 9. a) Cumulative pore volume and b) Pore size distribution for MRF(0)-0.5-6 and MR(1)-0.5-6 calculated from mercury porosimetry.

Figure 9 shows the meso- and macroporosity of both aerogel electrodes determined by mercury porosimetry (note that the axis are different for both samples, to facilitate the comparison).. For the mesopore range, data is in good agreement with the PSD evaluated from gas adsorption (Figure 4b), with average mesopores at about 25 nm for sample MRF(1)-0.5-6. However, sample MRF(1)-0.5-6 has large macroporous network (above 200 nm) that cannot be detected by gas adsorption at atmospheric pressure and that is expected to facilitate the migration of ions through the bulk of the monolith. The effect of grinding for obtaining the powdered electrodes partially destroys the macroporosity of the monolith. Consequently, the poor performance of MRF(0)-0.5-6 powder electrodes recorded on cyclic voltammograms

(Fig. 6) is due to the loss of the macroporous network. Contrarily, the monolith preserves the whole macropore texture providing a low resistance path for the transport of ions and explaining the good performance in deionization experiments [55].

4. Conclusions

A series of nitrogen-doped carbon aerogel with a monolithic structure were synthesized by the sol-gel polycondensation of resorcinol-formaldehyde-melamine mixtures. A large variety of textural properties were achieved by modifying parameters of the synthesis such as pH, the content of the nitrogen precursor and the polymerization procedure. The analysis of the hydrogels by infrared spectroscopy revealed the presence of nitrogen groups. The thermal analysis of the precursors showed that the increase of the melamine content in the hydrogel enhanced the weight loss in the step III being attributed to the release of nitrogenated molecules. After the thermal activation, the deconvolution of the Raman spectra showed a significant increase of the structural ordering on increase the pH value to 8, while the opposite effect occurred by increasing the nitrogen content.

The chemical analysis of the carbon aerogels evidenced a rather large N-doping favored at high pH and M/R ratio, with quaternary nitrogen as main component. As for the textural features, the prepolymerization step favored the development of the pore structure, with higher surface areas in all cases, particularly for the carbon aerogels prepared at pH=6.

Large capacitance values were recorded as a result of a combination of several factors as a high nitrogen content, an improved wettability and high surface areas with an interconnected porous network. Also, the prepolymerization step favored the superior electrochemical performance of the carbon aerogels, with capacitance values about 83-84 F/g for the prepolymerized aerogels MRF(1)-0.5-6 and MRF(1)-2-8 displaying the highest nitrogen content. Low polarization resistance values were recorded for aerogels with the highest

content of nitrogen, showing the enhanced electrical conductivity provided by the nitrogen groups.

Deionization experiments revealed the importance of the macroporous structure in the monolithic configuration of the aerogels. The electrosorption capacity of MRF(0)-0.5-6 was significantly improved as compared to the performance of the powdered electrodes, due to the preservation of the connected macroporous network that facilitates the wettability and the ionic electromigration at high polarization voltages.

Acknowledgments

The authors are indebted to the MICINN (Contract IPT-2011-1450-310000 (ADECAR), and CTM2011/23378) for the financial support. We also thank the fruitful collaboration of Isolux Ingeniería, S.A., Fundación Imdea Energía and Proingesa. University of Córdoba thanks to SCAI for the technical support.

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Figure Captions

Figure 1. Thermogravimetric profiles of the synthesized N-doped hydrogels. Open symbols correspond to prepolymerized samples; closed symbols correspond to non prepolymerized samples.

Figure 2. Raman spectra of the activated N-doped carbon aerogels a) MRF(0)-0.5-6, b)MRF(1)-0.5-6, c)MRF(0)-0.5-8, d)MRF(1)-0.5-8, e)MRF(0)-2-8, f) MRF(1)-2-8.

Figure 3. XPS spectra at the N 1s, C1s and O1s core levels of activated aerogels. a) MRF(0)-0.5-6, b)MRF(1)-0.5-6, c)MRF(0)-0.5-8, d)MRF(1)-0.5-8, e)MRF(0)-2-8, f) MRF(1)-2-8.

Figure 4. a) N₂ adsorption isotherms at 77 K of N-doped carbon aerogels after carbonization and activation activated aerogels. B) Pore size distribution plots obtained by using the 2D-NLDFT-HS method.Inset: Pore size distribution augmented

Figure 5. TEM images of activated N-doped carbon aerogels, a) MRF(0)-0.5-6, b)MRF(1)-0.5-6, c)MRF(0)-0.5-8, d)MRF(1)-0.5-8, e)MRF(0)-2-8, f) MRF(1)-2-8. SEM micrographs of g) MRF(0)-0.5-6, h) MRF(1)-0.5-6.

Figure 6. Cyclic voltammograms of activated carbon N-doped aerogels recorded at 0.5 mV/s in 0.1 M NaCl solution.

Figure 7. (A) Nyquist plots derived from the impedance spectra recorded in the 0.1 M NaCl solution. A modulated AC voltage signal of 5 mV versus equilibrium potential was applied. (B) Equivalent circuit used for the fitting of the spectra.

Figure 8. Capacitive deionization experiments performed at different potentials in 0.025 M NaCl solution: a) Electrosorption capacity of MRF(0)-0.5-6 (closed symbols) and MRF(1)-0.5-6 (open symbols); b) rate of salt uptake at 0.025 and 0,1M NaCl at an applied voltage of 0.9, 1.2 and 1.5 V for MRF(0)-0.5-6 and MRF(1)-0.5-6.

Figure 9. a) Cumulative pore volume and b) Pore size distribution for MRF(0)-0.5-6 and MR(1)-0.5-6 calculated from mercury porosimetry.

Table Captions

Table 1. Chemical composition of the carbon aerogels determined by chemical analysis (wt.%) and XPS spectroscopy (wt.%).

Table 2. Textural parameters of the N-doped carbon aerogels determined from the nitrogen isotherms at -196°C , and concentration of acidic and basic surface groups measured by chemical titration.

Table 3. XPS parameters calculated from the deconvolution of N 1s, O 1s, C 1s spectra of N-doped carbon aerogels.

Supplementary Information

N-doped monolithic carbon aerogel electrodes with optimized features for the electrosorption of ions

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Table S1. Weight loss percentages (wt.%) recorded during the thermogravimetric analysis of the N-doped hydrogels.

	STEPS				Overall loss
	25-160°C	160-360 °C	300-600°C	> 600°C	
MRF(0)-0.5-6 hydrogel	11.3	6.5	34.5	13.1	65.3
MRF(1)-0.5-6 hydrogel	11.6	6.2	34.1	14.1	66.0
MRF(0)-0.5-8 hydrogel	12.5	7.9	36.2	9.3	65.9
MRF(1)-0.5-8 hydrogel	13.3	8.9	34.2	13.2	69.5
MRF(0)-2-8 hydrogel	13.0	8.0	49.2	15.4	85.6
MRF(1)-2-8 hydrogel	12.4	8.0	44.5	12.5	77.3

Figure S1. FTIR spectra of the synthesized N-doped hydrogels.