**On the use of carbon black loaded N-doped carbon aerogel for the
electrosorption of sodium chloride from saline water**

G. Rasines^a, P. Lavela^{b,*}, C. Macías^a, M. C. Zafra^b, J. L. Tirado^b, C.O. Ania^c

^a Nanoquímica S.L., PCT Rabanales 21, Ed. Aldebarán M.4.7., 14014 Córdoba, Spain.

^b Laboratorio de Química Inorgánica, Universidad de Córdoba, Marie Curie, Campus de Rabanales, 14071 Córdoba, Spain.

^c Instituto Nacional del Carbón (INCAR, CSIC), Apartado 73, 33080 Oviedo, Spain.

Abstract

Highly micro-mesoporous carbon electrodes have been synthesized by the polycondensation of resorcinol-formaldehyde-melamine mixtures in the presence of a carbon conductive additive. The materials showed high surface functionalization (N- and O- groups) provided by the precursors. Despite the low amount used, the conductive additive had a marked effect on the porosity of the aerogels; for a given series, the carbon black loaded materials showed similar micropore volumes and a more developed mesoporosity than the pristine aerogels. Furthermore, the activation treatment under CO₂ atmosphere led to an increase in the surface area along with a widening of the mesoporosity. The synthesized aerogels were explored as electrodes for the electro-assisted removal of sodium chloride from saline water. A desalting capacity of 7.3 mg/g was obtained for monolith electrodes of sample MRF-Act/CB, along with an excellent chemical stability upon charge and discharge at high polarization voltages. Such good electrochemical performance is due to the combination of an adequate pore network and surface functionalization with an enhanced electrical conductivity achieved upon the incorporation of the carbon black additive during the polycondensation of the aerogel precursors.

Keywords: Carbon Aerogel; Electrosorption; N-doped; Carbon black.

*Corresponding author. Tel/Fax: 34957218637 E-mail: iq11acap@uco.es (P. Lavela)

1. Introduction

Fresh water supply is one of the most concerning issues in modern civilization, as water shortages become increasingly serious due to extreme climate events. Among water reuse and recycling, desalination of brackish and seawater remain as a useful strategy to overcome the water scarcity. Capacitive deionization (CDI) is a promising technology for the removal of ions from water, which may overcome shortcomings of conventional processes such as multi-stage flash evaporation, reverse osmosis, and electrodialysis [1, 2]. The physical principle of CDI is based on the formation of the electrical double layer at an electrode–electrolyte interface, and the storage of the ionic species on the surface of the charged electrode due to electrostatic interactions with the ions of opposed charge. When the electrodes are discharged, the adsorbed ions are released and a concentrated ionic solution is eluted. Since the process is based on pure electrostatic interactions it is highly reversible, and the energy consumed to charge the electrodes' surface can be recovered during the subsequent cell discharge. The process is conducted at low voltages, room temperature, ambient pressure and does not require membranes. Although some drawbacks due to the limited charge efficiency during the charge/discharge cycling must still be improved, the low energy consumption makes it an environmentally benign process [3-5].

Due to their versatility of forms, architectures and composition, carbons are among most performing electrode materials in numerous electrochemical applications. However, the limited electrical conductivity of highly nanoporous carbons (where the formation of the double layer is maximized) is still a challenge. In this regard, doping of carbons with heteroatoms such as oxygen, nitrogen, and sulfur has recently deserved much attention for electrochemical applications due to the enhanced performance of the doped materials due to the contribution of pseudofaradic reactions involving the surface groups [6-8]. In addition, incorporating polar groups to the carbon surface provides an enhanced wettability of the electrode, which favors the electrode/electrolyte interactions and accelerates the diffusion of the ions from the bulk solution towards the electrode surface [9-11]. Particularly, N-doping of a wide range of carbon materials [12-15] has been studied for the electrochemical energy storage in supercapacitors because of the possibility of obtaining carbon electrodes with high surface area and narrow pore size distribution [16,17] coupled with superior electronic conductivity and wettability provided by the electronic configuration of the N atoms incorporated to the carbon matrix.

Several authors have also investigated the effects of blending different materials to achieve an improvement of the electrode performance. Thus, ion-exchange resins [18], alumina [19], silica transition [20], metal oxides [21, 22], conducting polymers [23] and other forms of carbons [24-27] have been envisaged as interesting electrode materials to enhance the desalting capacity of carbon materials. Similarly, the incorporation of carbon back as additive in the manufacturing of the electrodes is commonly used to overcome the conductivity limitation of

most carbon electrodes [28, 29]. Particularly, we have reported the superior electrochemical response of carbon black loaded resorcinol-formaldehyde (RF) aerogels when the additive is incorporated during the sol-gel polymerization instead of the final stages of the synthesis [30]. It was reported that the carbon conductive additive exerts a main role by directing the synthesis towards the formation of less branched polymer clusters favoring the formation of large mesopores in the carbon-black loaded aerogels. Otherwise, we have recently described a novel approach based on the prepolymerization of melamine-resorcinol-formaldehyde mixtures for the preparation of N-doped meso-macroporous carbon aerogels [31]. These N-doped materials displayed outstanding electrochemical characteristics despite of their lower porous features, compared to non-doped aerogels, and limited electrical conductivity. Bearing the beneficial effect of both carbon black loading and nitrogen doping, the objective of this work was to explore the likely synergic effect of incorporating carbon black into N-doped aerogels prepared from melamine-resorcinol-formaldehyde mixtures for the electroassisted removal of ionic species from solution.

2 Experimental

2.1 Materials preparation

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. The molar ratio of the reactants used were as follows: R:M:F of 2:1:7, (M+R)/C of 90 and (M+R)/W of 0.052. The precursors were mixed following a prepolymerization procedure as described elsewhere [31]. 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 the final pH was eventually adjusted at 7.3 and stirred for 20 minutes at room temperature to further allow the cross-linking of the precursors. Finely powdered carbon black was added at this stage (0.63% w/v solution) and the solid powder-sol mixture was magnetically stirred until the solidification of the polymerized gel. The carbon black content was fixed below 1 wt.% as a balance between high dispersion of the additive in the reactants mixture based and the beneficial effect on both the nanotexture and electrical conductivity of carbon aerogels observed in our previous studies [30, 39]. Then, these hydrogels were subjected to aging at 40 °C for 24 h and then at 70 °C for 120 h, and water-acetone exchange, before being dried CO₂ supercritical conditions. The dried hydrogels were thermally treated at 750°C for 2 hours (heating rate 2 °C min⁻¹ up to 400 °C and hold for 60 min followed by heating up to 750 °C and hold for 120 min) either in nitrogen (series carbonized) or in CO₂ atmosphere (series activated) to obtain denser carbon aerogels. Samples are denoted as MRF-Pyr or MRF-Act indicating the thermal treatment followed (*Pyr*

for carbonization and *Act* for activation). Also, /CB is included when carbon black was added during the synthesis.

2.2 Structural and textural characterization

X-Ray diffraction (XRD) patterns were recorded with a Bruker D8 Discover A25 diffractometer furnished with Cu K α radiation and a graphite monochromator. The patterns were scanned between 10 and 80° (2 theta degrees) at a 0.025°/s scan rate. Raman spectroscopy was performed by excitation with green laser light (532 nm) in the range between 1000 and 2000 cm⁻¹. The spectra were acquired in a Renishaw Raman instrument (InVia Raman Microscope), equipped with a Leica microscope. The profiles were deconvoluted by using the Peakfit v. 4.11 software package. X-ray Photoelectron Spectrometry (XPS) was performed in a SPECS Phobios 150MCD spectrometer provided with Al K source and a chamber pressure of 4 × 10⁻⁹ mbar. Powdered samples were deposited as thin films on a holder and subjected to high vacuum overnight. The C 1s line of the adventitious carbon located at 284.6 eV was used as reference for binding energy values. An Elemental CHNS Eurovector EA 3000 analyzer was used for the chemical analysis of C and N. The nanotexture of the gels was characterized by measuring nitrogen adsorption-desorption isotherms at -196 °C (ASAP 2010, Micromeritics). Before the experiments, the samples were outgassed under vacuum (ca. 10⁻³ torr) at 120 °C overnight. The isotherms were used to calculate the specific surface area, S_{BET}, and total pore volume, V_T. The pore size distributions were calculated by using the 2D-NLDFT-HS model for carbons with energetically heterogeneous and geometrically corrugated pore walls [32, 33]; the micropore volume was also evaluated by the DR method.

2.3 Electrochemical characterization

Electrochemical measurements were performed in three-electrode SwagelokTM type cells. For the aerogels modified with carbon black as additive during the synthesis, the working electrode consisted of 90 wt.% of the carbon aerogel active material and 10 wt.%, binder (polyvinylidene fluoride). For the aerogels prepared without the addition of the carbon black, the working electrode was manufactured blending the active material (70 wt.%) with carbon black (20 wt.%) and binder (10 wt.%). The powdered mixtures were slurred in N-methyl pyrrolidone and the pastes were spread on a 13 mm titanium disk current collector. The electrodes were dried at 70°C overnight. A platinum wire was used as a counter electrode, while the cell potential was measured versus a Hg/Hg₂SO₄ reference electrode. A 0.1 M solution of NaCl (ca. 6 g/L) in deionized water was used as electrolyte, mimicking the composition of brackish water. Cyclic voltammograms were recorded between -0.5 and +0.5 V vs. the reference electrode at sweep rates ranging from 0.5 to 10 mV s⁻¹ in a Biologic VMP multichannel potentiostat. Electrochemical impedance spectroscopy (EIS) allowed analyzing the kinetic

response of the electrodes to the adsorption reaction. The spectra were recorded in an Autolab PGSTAT12 system, using 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 performed in symmetric batch-type cells assembled with two monolithic carbon aerogel electrodes previously cut and polished to achieve a flat surface. The monoliths were washed in deionized hot water for 30 minutes and then assembled between titanium current collectors using two Whatman glass GF/A fiber sheets as a separator. The electrodes were immersed in 20 mL of the electrolyte and kept under continuous stirring to avoid mass transfer restrictions from the bulk solution. The deionization experiments were carried out by applying a sequence of constant voltage pulses of 0.9 V (3 cycles), 1.2 V (2 cycles) and 1.5 V (2 cycles). for 120 min, while discharge was performed at open-circuit conditions (ca. 0 V) for the same period of time. A conductivity meter was used to monitor the change in the ionic concentration.

3. Results and discussion

3.1. Structural characterization of the aerogels and chemical analysis.

A visual comparison between the as prepared hydrogel monoliths showed differences in color and opacity allowing to evidence the presence of the additive (Fig. 1a). Also, the homogenous opacity of the composite synthesized with the carbon black reflects the good dispersion of the additive. In order to discern, the presence of the carbon black additive on the composites, we recorded TEM pictures of the carbon black additive further used for the preparation of the aerogel composites (Fig. 1b) show. As can be seen, primary nanometric particles with ca. 30 nm in diameter have a highly distorted round shape with a thick outer shell. These morphological features clearly differ from those commonly observed in the aerogels prepared in related conditions [31] and consequently its presence should be clearly distinguished in the composite. In fact, TEM images of MRF-Pyr/CB and MRF-Act/CB revealed the presence of dark domains of large and rounded particles attached to the matrix of the aerogels, which have been indicated by an arrow in the picture, and assigned to carbon black nicely dispersed within the amorphous carbon matrix (Fig. 1c and d).

The XRD patterns of the prepared materials (Figure 2) show that the incorporation of the carbon black has a low effect on the profiles, which was rather expected given the low amount of additive used. The broad bands at ca. 24.5 and 43.2°(2 θ) characteristic of the (002) and (100) reflections in disordered carbons [34] are clearly seen in all the cases. For the samples loaded with carbon black, the reflection of 25.5° (2 θ) become somewhat more conspicuous due to the presence of the carbon black; this effect, visible on the carbonized aerogel was not as

clear in the activated sample, suggesting that the structural order incorporated by the carbon black additive is counteracted by the activation procedure. The first-order Raman spectra of the aerogels (see Fig. S1 in the supplementary information file) also showed a similar trend with no significant changes in the profiles after the incorporation of the carbon black other than a slight increase in the I_G/I_D ratio (Table 1). The activation in CO_2 atmosphere also led to a slight increase of this ratio. Moreover, the continuous decrease in the width of the signals can also be considered as a proof of a higher structural order of the carbon framework. The activation leads to an increase of the porosity which may involve some structural disordering. Notwithstanding, it is well known that the mild oxidation conditions also promote a partial burn-off of the amorphous carbon lodged into the micropores [35]. This effect may contrarily contribute to a structural ordering. Most probably, the latter effect has been more effective in the CO_2 activation of our sample and therefore involving the slight increase of the structural order observed by Raman spectroscopy.

The surface chemistry of the aerogels was analyzed by XPS. The relative contributions of the surface functional groups were evaluated by deconvolution of the C 1s, O 1s, and N 1s core elements level are provided in Figure 3. The assignments of the different surface groups were made according to the literature [36, 37] and based on the position of the chemicals shifts in the core elements level; further details are provided in Table S1 in the supplementary information file. Note that for the pristine samples prepared without carbon black, the majority of carbon element is in C-C configuration, and about 38-40 % in oxidized forms, with very little variation upon the incorporation of the carbon black additive or the activation post-treatment. The overall amount of nitrogen and oxygen is similar in all the samples (Table 2), with small differences in the distribution of surface groups. As seen in Figure 3, nitrogen is mainly in pyrrolic (N5)/pyridine (N6) configurations regardless the thermal treatment (carbonization or activation) or the incorporation of the carbon black additive, with lower contributions of quaternary and N-X. This effect was more pronounced for the activated aerogels as compared to their pyrolyzed counterparts. These results indicate that the amount of carbon black used in the synthesis is too low to produce any remarkable changes in the chemical environments of C, N or O atoms. In contrast, the activation reaction involved an increase in the abundance of O-groups for MRF-Act, though this effect was not observed for the carbon black loaded sample.

The chemical composition was also determined by elemental analysis, and compared to surface composition provided by XPS. As a general rule, higher nitrogen contents were measured by elemental analysis than XPS (Table 2). This has been commonly attributed to the effectiveness of melamine to incorporate nitrogen atoms into the graphenic framework (melamine accept up to two formaldehyde molecules to achieve the full methylation) [38], hence decreasing the surface concentration of this element. The aerogels containing carbon black featured slightly lower overall nitrogen contents than their corresponding pristine

counterparts, although differences are subtle. It could be expected that the absence of nitrogen in the carbon black may exert a mass dilution effect. Anyway, the decrease in the nitrogen content is so weak that is expected to be counterbalanced by the presence of the conductive carbon black phase.

3.2. Textural characterization of the aerogels.

The nitrogen isotherms at -196 °C of the prepared carbon aerogels are shown in Fig. 4. All the samples display a large textural development in the mesopore range, which is in good agreement with our previous study reporting the benefits of the prepolymerization step when melamine is used as N-precursor [31]. Regardless the incorporation of the carbon additive, the isotherms belong to type IV according to BDDT classification [39]; the marked hysteresis loops in the desorption branch at relative pressures above 0.7 indicate the presence of large mesopores (Fig. 4a). The shape of the hysteresis loops was similar for all four samples, with parallel adsorption and desorption branches (type H1), characteristic of pore systems with uniform pore size distributions. Despite the low amount of carbon black used in the synthesis, the effect on the porosity of the prepared materials was remarkable. Differences apply mainly to the pore volume -with an increase accounting for 45-55% for both carbonized and activated series-, rather than to the position and shape of the hysteresis loop in the isotherms (Fig. 4a). Indeed, the aerogels loaded with the carbon additive present a more developed mesoporosity, with ca. a 1.5 fold increase in the mesopore volume in both series (carbonized and activated). A similar effect on the development of mesoporosity upon the addition of carbon black during the condensation of the reactants was observed in resorcinol-formaldehyde mixtures, although it was only seen for much higher carbon black loadings [30]. While the effect on the textural features of N-free resorcinol-formaldehyde (RF) aerogels was almost negligible for carbon black loadings below 1 w/v % [30], it was quite outstanding for a loading of 0.63 w/v % in melamine-resorcinol-formaldehyde mixtures.

This is more clearly seen in the textural parameters obtained from the adsorption isotherms compiled in Table 3. Overall, the prepared samples present lower values of surface area and micropore volumes compared to N-free RF aerogels obtained from similar procedure, due to the incorporation of melamine in the reactants mixture [40].

It should be noted that all the samples displayed a well-developed porosity after the carbonization and activation treatments, indicating that the collapse of the pore network typically observed in hydrogels and xerogels -due to the surface tensions applied to the backbone during the decomposition of volatiles- does not apply to these materials [41]. Hence, the incorporation of melamine in the precursor's mixture followed by supercritical drying rendered mechanically resistant aerogels. As for the activation, changes affected both the micro- and mesoporosity. Besides the expected increase in the micropore volume and surface area of

the samples due to the activation reaction, note that the hysteresis loop of the isotherms became larger (i.e., extend over a wider pressure range) after activation and regardless the carbon black additive (Fig. 4 c and d). The shape of the loop did not change, but showed an increase in the volume at relative pressures close to unity, suggesting a slight enlargement of the average mesopore size. This was further confirmed by the analysis of the distribution of pore sizes presented in Fig. 4b; calculated by using the 2D-NLDFT-HS model for carbons that is free of common artifacts usually obtained in the PSD analysis and provides an excellent fitting for micro-mesoporous carbons with ultrahigh pore volumes [42]; along with the expected trend in the micropore range, the mesopore distribution after activation become wider. A similar effect on the mesoporosity has been reported for the chemical activation of carbon xerogels, where activation under CO₂ atmosphere originated the collapse of the porosity [42].

Based on the evolution of the porosity of the synthesized aerogels, it seems that the incorporation of the carbon black conductive additive affects the polymerization mechanism of the precursors. According to literature [43-45], in MRF mixtures the polycondensation reaction occurs among the hydroxymethyl groups between Melamine-Formaldehyde (MF) and RF to form methylene and methylene ether bridged polymers, which condense to form small clusters of branched polymeric species. Controlling the rate kinetics of the MRF polymerization reaction is a challenging issue, as melamine accelerates the formation of the clusters by increasing the nucleation rate and decreasing the time of the growth stage. As a result, MRF mixtures typically give rise to low porous materials unless a prepolymerization step is performed [31, 43, 44].

The addition of the carbon black to the MRF system appears as an option to slow down the fast assembling reactions of the prepolymerized clusters, decreasing the chain branching and crosslink density of the polymer network. The finely dispersed carbon black aggregates (Figure 1) would allow a more efficient spatial packing of the colloidal aggregates that would become more stable in the nucleation regime; hence they can assemble together in larger and weakly branched clusters creating a more open porous structure before spinodal decomposition. The fact that the effect is more visible for MRF mixtures than for N-free RF ones -despite the much lower amount of carbon black added- is attributed to the faster nucleation reaction boosted by melamine.

3.3. Electrochemical performance of the carbon aerogels .

The electrochemical behavior of the prepared carbon aerogels was initially explored by cyclic voltammetry in 0.1 M and 0.025 M NaCl at 0.5 mV s⁻¹ (Figure 5a). The rectangular shape of the voltammograms evidenced the predominant capacitive character of the electrodes in the neutral electrolyte used, resulting from the charge accumulation in the electric double layer at the electrode-electrolyte interface [46]. The pristine aerogels showed lower capacitance values (ca. 79 and 83 F g⁻¹ for MRF-Pyr and MRF-Act, respectively, at 0.5 mV s⁻¹) than their

corresponding counterparts prepared in the presence of the carbon black additive (ca. 85 and 98 F g⁻¹ for MRF-Pyr/CB and MRF-Act/CB, respectively), pointing out the outstanding effect of the carbon additive in the electrochemical response of the electrodes. Indeed, for a given series (either carbonized or activated), the textural features in terms of surface area and micropore volume are very much alike (Table 3 and Figure 4). Thus the enhanced performance of the electrodes is attributed to the carbon black present in the materials, boosting the electrical conductivity of the carbon aerogel matrix. The capacitance values also show a good correlation with the structural order of the electrodes (i.e., I_G/I_{D1} ratio); since the order of the materials is linked to the presence of the carbon black, this confirms the outstanding role of the additive in the electrochemical behavior of the electrodes. The effect of activation is also seen in the ca. 7-15 % increase in the capacitance values of the activated aerogels, in agreement with their higher surface area and micropore volumes compared to the carbonized samples (Table 3). The capacitive profiles of experiments performed in 0.025 M NaCl preserved the rectangular shape, though capacitance values decreased to 51 and 53 F g⁻¹ for MRF-Pyr and MRF-Pyr/CB and 64 and 69 F g⁻¹ for MRF-Act and MRF-Act/CB. This trend is expected due to the lower availability of ions in the electrolyte solution.

Voltammograms recorded at 10 mV s⁻¹ showed a distortion of the rectangular shape which eventually becomes a leaf-like shape (see Fig. S2 in the supplementary information file). Such deviation from the ideal box shape at high scan rates is commonly attributed to either Faradaic currents and/or limited diffusion time of ions from the bulk phase into the inner pores of the electrodes.

Cyclic voltammograms were also recorded at ca. 0.025 M NaCl) for MRF-act/CB for several of cycles at 0.5 mV s⁻¹ (Fig. 5b). A comparison of the profiles revealed the good stability of the sample, with 70 F g⁻¹ after 30 cycles. The region ascribable to the potential of zero charge (PZC) is indicated in Fig. 5b with an arrow. According to literature, a shift in the PZC to more positive values after extended cycling can be associated to slow oxidation of the carbon's surface under a positive potential [47, 48]. Although the rectangular profile of the voltammograms hinders an accurate identification of the PZC, the absence of a shift in the region ascribable to the potential of zero charge suggests the stability of the electrode after 30 cycles. This was also corroborated by the *post-mortem* XPS analysis of the electrodes after CDI experiments, as discussed below.

A measurement of the kinetic response of the carbon aerogel to the ion migration at the electrode/electrolyte interface can be inferred from the polarization resistance (R_{pol}) obtained from impedance spectra [49, 50]. Figure 6a displays the Nyquist plots recorded for the prepared carbon aerogel electrodes. The characteristic profiles can be described by a semicircle at intermediate frequencies followed by a straight line. Nevertheless, factors as the polycrystalline character and high porosity of these samples led to a distortion of the profile as compared to an

ideal capacitor. The polarization resistance (R_{pol}) comes from the charge transfer reaction between the polarizable carbon electrode and the electrolyte solution [49]. The high-frequency response is ascribable to the low ohmic drop at the bulk resistance solution (R_{el}), which contribution to the cell resistance is here neglected. The description of the circuit also contains the Warburg impedance (W), and the constant phase element (CPE) which is used to overcome the non-ideal behavior of the electrode. The R_{pol} values were calculated by fitting the plots to the equivalent circuit included as an inset in Fig. 6a. The effect of the carbon black on the conductivity of the electrodes can be quantified by the polarization resistance obtained from impedance measurements. As seen, the lowest R_{pol} values were calculated for carbon black containing samples MRF-Pyr/CB ($0.80 \Omega \times g$) and MRF-Act/CB ($0.64 \Omega \times g$). Contrarily, higher polarization resistance values were calculated for MRF-Pyr ($1.15 \Omega \times g$) and MRF-Act ($0.94 \Omega \times g$). The enhanced conductivity of the carbon black loaded samples reveals a close dependence with the mesoporosity, as the lowest values were obtained for the samples with the largest mesopore volumes (Table 3), corroborating the beneficial effect of mesopores as intermediate paths favoring the migration of ions from inside the pore network of the electrodes. The beneficial effect of the carbon black on the electrochemical response of the prepared electrodes can also be evidenced by comparing the polarization resistance values with those corresponding to carbon aerogels previously reported (Fig. 6b) [31, 40, 51].

The desalting capacity of the two series of electrodes prepared with and without the carbon conductive additive was determined at several constant voltage pulses using symmetric batch-type cells assembled with monolithic electrodes immersed in 0.025 M NaCl solution (ca. 1.5 g/L), and the corresponding charge and discharge electrosorption curves are shown in Figure 7. The best performance was observed for sample MRF-Act/CB (7.3 mg/g), likely due the combined effects of an adequate porosity obtained upon activation and the presence of carbon black additive finely dispersed in the electrode. Table 4 shows the desalting capacities of herein synthesized aerogels compared to those reported in the literature [31, 40, 52-54]. Data reveals that the N-doped carbon aerogel/carbon black composites are competitive electrode materials for the removal of ionic species from saline water. The increase in the electrolyte concentration to 0.1 M revealed that the better electrosorption capacity of carbon black containing samples is preserved (Fig. 7c). The beneficial effect of the intimate contact of the mesoporous aerogel with the highly crystalline and conductive carbon black phase for an enhanced salt uptake is also evidenced on the performance of the electrodes operating at harsh polarization conditions, as for example 1.5 V. Moreover, MRF-Act/CB is capable of maintaining the electrosorption capacity for a number of cycles. This fact was confirmed by performing a number of cycles of adsorption-desorption in a symmetric cell assembled with MRF-Act/CB in a 0.025 M NaCl solution at a 1.2-0 V regime (Figure 8). Aurbach et al. have demonstrated the reliability of XPS spectroscopy to detect changes in the surface chemistry of

cycled electrodes which may affect to the desalting efficiency [55]. Thus, a *post-mortem* analysis of the best performing sample (MRF-Act/CB monolith) after being subjected to several charge/discharge cycles was carried out by XPS spectroscopy. Fig. 9 shows a comparison of the relative contributions of the main C, N and O components deconvoluted from the spectra at the C1s, O1s and N1s core levels. As seen, the distribution of N and C species remained rather constant while small changes are detected in the oxygen containing groups. A slight increase in the relative contributions of C=O of the cycled electrode was noticed, although the overall oxygen content remained barely unchanged after the electrosorption process.

4. Conclusions

Highly porous carbon composites consisting of N-doped aerogels and carbon black have been synthesized by the polycondensation of resorcinol-formaldehyde-melamine mixtures in the presence of a carbon black as conductive additive. The obtained materials displayed a combined micro/mesopore structure with good electrochemical features as electrodes for the electroassisted removal of sodium chloride from saline water.

The electron micrographs confirmed the excellent distribution of the carbon black additive within the mesoporous matrix of the N-doped aerogels; as a result, the carbon black loaded aerogels displayed a superior structural order than the pristine materials. The chemical analysis of the carbon aerogels showed a large N- and O-doping in the samples, with pyridinic and pyrrolic nitrogen as main components.

The textural properties inferred from the nitrogen isotherms evidenced that the incorporation of carbon black in the reactants mixture boosted the formation of an interconnected mesopore network in the aerogels. For a given series, the aerogels presented similar micropore volumes while the composites showed larger mesopore volumes. Furthermore, the activation affected both the micro- and mesoporosity, leading to an important increase in the surface area along with a widening of the average mesopore size.

The synergistic effect of combining an adequate pore network and high surface functionalization with the incorporation of the carbon black additive was observed in the electrochemical response of the N-doped aerogel composites. The largest capacitance was measured for sample MRF-Act/CB, which displayed high surface area and mesoporosity and structural ordering. Low polarization resistance values were also recorded for the carbon black loaded aerogels, showing the enhanced electrical conductivity provided by the conductive additive. The deionization experiments performed using monolith electrodes confirmed the good electrochemical response of these materials, with moderate desalting capacities (ca. 7.3 mg/g) for MRF-Act/CB and high stability at high polarization voltages.

Acknowledgements

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 Energia and Proingesa. University of Córdoba thanks to SCAI for technical and FEDER and Junta de Andalucía (FQM-288) for financial supports.

References

- [1] M.A. Anderson, A.L. Cudero, J. Palma, Capacitive deionization as an electro-chemical means of saving energy and delivering clean water. Comparison to present desalination practices: Will it compete?, *Electrochim. Acta* 55 (2010) 3845.
- [2] D. Qi, L. Zou, E. Hu, Electrosorption; An alternative option for desalination, *Res. J. Chem. Environ.* 11 (2007) 92.
- [3] Y.A.C. Jande, W.S. Kim, Predicting the lowest effluent concentration in capacitive deionization, *Sep. Purif. Technol.* 115 (2013) 224.
- [4] Y. Oren, Capacitive deionization (CDI) for desalination and water treatment – past, present and future (a review), *Desalination* 228 (2008) 10.
- [5] T.J. Welgemoed, C.F. Schutte, Capacitive deionization technology (TM): an alternative desalination solution, *Desalination* 183 (2005) 327–340
- [6] E. Frackowiak, G. Lota, J. Machnikowski, C. Vix-Guterl, F. Béguin, Optimisation of supercapacitors using carbons with controlled nanotexture and nitrogen content, *Electrochim. Acta* 51 (2006) 2209.
- [7] D.W. Wang, F. Li, Z.G. Chen, G.Q. Lu, H.M. Cheng, Synthesis and electrochemical property of boron-doped mesoporous carbon in supercapacitor, *Chem. Mater.* 20 (2008) 7195.
- [8] D. Hulicova-Jurcakova, M. Seredych, G.Q. Lu, T.J. Bandoze, Combined Effect of Nitrogen- and Oxygen-Containing Functional Groups of Microporous Activated Carbon on its Electrochemical Performance in Supercapacitors, *Adv. Funct. Mater.* 19 (2009) 438.
- [9] C.O. Ania, V. Khomenko, E. Raymundo-Piñero, J.B. Parra, F. Béguin, The large electrochemical performance of microporous doped carbon obtained by using a zeolite template, *Adv. Funct. Mater.* 17 (2007) 1828.
- [10] D. Hulicova-Jurcakova, A.M. Puziy, O.I. Poddubnaya, F. Suárez-García, J.M.D. Tascón, G.O. Lu, Performance of supercapacitors from phosphorus-enriched carbons, *J. Am. Chem. Soc.* 131 (2009) 5026.
- [11] D. Shin, S. Bae, C. Yan, J. Kang, J. Ryu, J.H. Ahn, B.H. Hong, Synthesis and applications of graphene electrodes, *Carbon Lett.* 13 (2012) 1.
- [12] Y. Chang, G. Han, J. Yuan, D. Fu, F. Liu, S. Li, Using hydroxylamine as a reducer to prepare N-doped graphene hydrogels used in high-performance energy storage, *J. Power Sources* 238 (2013) 492.

- [13] K.-S. Kim, S.-J. Park, Easy synthesis of polyaniline-based mesoporous carbons and their high electrochemical performance, *Microporous Mesoporous Mater.* 163 (2012) 140.
- [14] D. S. Dhawale, G. P. Mane, S. Joseph, C. Anand, K. Ariga, A. Vinu, Enhanced Supercapacitor Performance of N-Doped Mesoporous Carbons Prepared from a Gelatin Biomolecule, *ChemPhysChem* 14 (2013) 1563.
- [15] Y. S. Yunemil, H. H. Parkemil, H.-J. Jin, Pseudocapacitive Effects of N-Doped Carbon Nanotube Electrodes in Supercapacitors, *Materials* 5 (2012) 1258.
- [16] W.Y. Kim, J. Joo, N.D. Kim, S.G. Oh, J. Kim, J.H. Yi, Preparation of nitrogen-doped mesoporous carbon nanotubes for the electrochemical double layer capacitor, *Carbon* 47 (2009) 1407.
- [17] D. Hulicova, J. Yamashita, Y. Soneda, H. Hatori, M. Kodama, Supercapacitors prepared from melamine-based carbon. *Chem. Mater.* 17 (2005) 1241.
- [18] J.-B. Lee, et al., Desalination performance of a carbon-based composite electrode, *Desalination* 237 (2009) 155.
- [19] L. Han, K.G. Karthikeyan, M.A. Anderson, J.J. Wouters, Kelvin B. Gregory, Mechanistic insights into the use of oxide nanoparticles coated asymmetric electrodes for capacitive deionization, *Electrochim. Acta* 90 (2013) 573.
- [20] J.J. Wouters, J.J. Lado, M.I. Tejedor-Tejedor, M.A. Anderson, Low Surface Area Carbon Fiber Electrodes Coated with Nanoporous Thin-Films of γ - Al_2O_3 and SiO_2 : Relationship between Coating Conditions, Microstructure and Double Layer Capacitance. *J. Electrochem. Soc.* 159 (2012) A1374.
- [21] J. Yang, L. Zou, H. Song, Z. Hao, Development of novel MnO_2 /nanoporous carbon composite electrodes in capacitive deionization technology, *Desalination* 276 (2011) 199.
- [22] M.C. Zafra, P. Lavela, G. Rasines, C. Macías, J.L. Tirado, C.O. Ania, A novel method for metal oxide deposition on carbon aerogels with potential application in capacitive deionization of saline water, *Electrochim. Acta* 135 (2014) 208.
- [23] C. Yan, L. Zou, R. Short, Polyaniline-modified activated carbon electrodes for capacitive deionisation, *Desalination* 333 (2014) 101.
- [24] H. Wang, L.Y. Shi, T.T. Yan, J.P. Zhang, Q.D. Zhong, D.S. Zhang, Design of graphene-coated hollow mesoporous carbon spheres as high performance electrodes for capacitive deionization, *J. Mater. Chem. A* 2 (2014) 4739.
- [25] K. Dai, L. Shi, D. Zhang, J. Fang, NaCl adsorption in multi-walled carbon nanotube/active carbon combination electrode. *Chem. Eng. Sci.* 61 (2006) 428.
- [26] Y. Wimalasiri, L. Zou, Carbon nanotube/graphene composite for enhanced capacitive deionization performance, *Carbon* 59 (2013) 464.
- [27] K. Park, J. Lee, P. Park, S. Yoon, J. Moon, H. Eum, C. Lee, Development of a carbon sheet electrode for electrosorption desalination, *Desalination* 206 (2007) 86–91

- [28].- S. Nadakatti, M. Tendulkar, M. Kadam, Use of mesoporous conductive carbon black to enhance performance of activated carbon electrodes in capacitive deionization technology Desalination 268 (2011) 182.
- [29] A.G. Pandolfo, A.F. Hollenkamp, Carbon properties and their role in supercapacitors, J. Power Sources 157 (2006) 11.
- [30] C. Macías, M. Haro, J.B. Parra, G. Rasines, C.O. Ania, Carbon black directed synthesis of ultrahigh mesoporous carbon aerogels, Carbon 63 (2013) 487.
- [31] P. Lavela, G. Rasines, C. Macías, M. C. Zafra, J. L. Tirado, J. B. Parra, C. O. Ania, N-doped monolithic carbon aerogel electrodes with optimized features for the electrosorption of ions, Carbon 83 (2015) 262.
- [32] J. Jagiello, J.P. Olivier, 2D-NLDFT adsorption models for carbon slit-shaped pores with surface energetical heterogeneity and geometrical corrugation, Carbon 55 (2013) 70.
- [33] J. Jagiello, J.P. Olivier, Carbon slit pore model incorporating surface energetical heterogeneity and geometrical corrugation, Adsorption 19 (2013) 777.
- [34] D.Y. Qu, Investigation of oxygen reduction on activated carbon electrodes in alkaline solution, Carbon 45 (2007) 1296.
- [35] M. Noked, A. Soffer, D. Aurbach, The electrochemistry of activated carbonaceous materials: past, present, and future, J. Solid State Electrochem. 15 (2011) 1563.
- [36] A. Stein, Z. Wang, M.A. Fierke. Functionalization of porous carbon materials with designed pore architecture. Adv. Mater. 21(2009) 265.
- [37] T. Li, G. Yang, J. Wang, Y. Zhou, H. Han. Excellent electrochemical performance of nitrogen-enriched hierarchical porous carbon electrodes prepared using nano-CaCO₃ as template, J Solid State Electrochem. 17 (2013) 2651.
- [38] J. Zidar, M. Pavlin, I. Mihelice, P. Ogorelec, J. Plavec, J. Mavri, Stability and reactivity of progressively methylolated melamine derivatives, Comput. Theor. Polym. Sci. 1006 (2013) 85.
- [39] F. Rouquerol, J. Rouquerol, K. Sing, Adsorption by Powders and Porous Solids, Academic Press, London, 1999.
- [40] G. Rasines, P. Lavela, C. Macías, M. C. Zafra, J. L. Tirado, C.O. Ania, Mesoporous carbon black-aerogel composites with optimized properties for the electro-assisted removal of sodium chloride from brackish water, J. Electroanal. Chem. 741 (2015) 42.
- [41] S.A. Al-Muhtaseb, J.A. Ritter, Preparation and properties of resorcinol formaldehyde organic and carbon gels, Adv. Mater. 15 (2003) 101.
- [42] E. I. Páez, M. Haro, E.J. Juárez-Pérez, R.J. Carmona, J.B. Parra, R. Leyva-Ramos, C.O. Ania, Fast synthesis of micro/mesoporous xerogels: textural and energetic assessment, Microporous Mesoporous Mater. 209 (2015) 18.

- [43] H. Zhou, S. Xu, H. Su, M. Wang, W. Qiao, L. Ling, D. Long, Facile preparation and ultra-microporous structure of melamine–resorcinol–formaldehyde polymeric microspheres, *Chem. Commun.* 49 (2013) 3763.
- [44] J. Yu, M. Guo, F. Muhammad, A. Wang, G. Yu, H. Ma, G. Zhu, Simple fabrication of an ordered nitrogen-doped mesoporous carbon with resorcinol–melamine–formaldehyde resin, *Microporous Mesoporous Mater.* 190 (2014) 117.
- [45] H.F. Gorgulho, F. Gonçalves, M.F.R. Pereira, J.L. Figueiredo, Synthesis and characterization of nitrogen-doped carbon xerogels, *Carbon* 47 (2009) 2032.
- [46] K.L. Yang, S. Yiacoumi, C. Tsouris, Electrosorption capacitance of nanostructured carbon aerogel obtained by cyclic voltammetry, *J. Electroanal. Chem.* 540 (2003) 159.
- [47] X. Gao, A. Omosebi, J. Landon, K. Liu, Enhancement of charge efficiency for a capacitive deionization cell using carbon xerogel with modified potential of zero charge, *Electrochem. Commun.* 39 (2014) 22.
- [48] X. Gao, A. Omosebi, J. Landon, K. Liu, Dependence of the Capacitive Deionization Performance on Potential of Zero Charge Shifting of Carbon Xerogel Electrodes during Long-Term Operation, *J. Electrochem Soc.* 161 (2014) E159.
- [49] S.J. Seo, H. Jeon, J.K. Lee, G.Y. Kim, D. Park, H. Nojima, J. Lee, S.H. Moon, Investigation on removal of hardness ions by capacitive deionization (CDI) for water softening applications, *Water Res.* 44 (2010) 2267.
- [50] C. Macías, P. Lavela, G. Rasines, M. C. Zafra, J. L. Tirado, C.O. Ania, Improved electro-assisted removal of phosphates and nitrates using mesoporous carbon aerogels with controlled porosity, *J. Appl. Electrochem.* 44 (2014) 963.
- [51] M. C. Zafra, P. Lavela, G. Rasines, C. Macías, J. L. Tirado, Effect of the resorcinol/catalyst ratio in the capacitive performance of carbon xerogels with potential use in sodium chloride removal from saline water, *J Solid State Electrochem.* 18 (2014) 2847.
- [52] P. Xu, J.E. Drewes, D. Heil, G. Wang, Treatment of brackish produced water using carbon aerogel-based capacitive deionization technology, *Water Res.* 42 (2008) 2605.
- [53] C. Tsouris, R. Mayes, J. Kiggans, K. Sharma, S. Yiacoumi, D. DePaoli, S. Dai, Mesoporous Carbon for Capacitive Deionization of Saline Water, *Environ. Sci. Technol.* 45 (2011) 10243.
- [54] H.H. Jung, S.W. Hwang, S.H. Hyun, K.H. Lee, G.T. Kim, Capacitive deionization characteristics of nanostructured carbon aerogel electrodes synthesized via ambient drying, *Desalination* 216 (2007) 377.
- [55] Y. Bouhadana, M. Ben-Tzion, A. Soffer, D. Aurbach, A control system for operating and investigating reactors: The demonstration of parasitic reactions in the water desalination by capacitive de-ionization, *Desalination* 268 (2011) 253.

Table 1. Raman shift and width values for the D1 and G bands calculated from the deconvoluted spectra

	I_G / I_{D1}	D1 shift (cm^{-1})	G shift (cm^{-1})	D1 FWHM (cm^{-1})	G FWHM (cm^{-1})
MRF-Pyr	0.54	1348.53	1594.85	180.05	81.39
MRF-Act	0.57	1345.51	1597.13	174.98	80.41
MRF-Pyr/CB	0.57	1346.72	1596.15	177.83	78.78
MRF- Act /CB	0.62	1347.85	1598.67	170.60	76.51
CB	1.64	1340.25	1569.81	45.20	37.61

Table 2. Chemical composition (wt.%) determined by elemental analysis and XPS spectroscopy of the synthesized carbon aerogels.

Sample	Elemental analysis			XPS			
	N / %	C / %	N/C	N/C	N / %	C / %	O / %
MRF-Pyr	4.9	78.9	0.06	0.05	4.0	87.4	8.5
MRF-Act	5.5	76,5	0.07	0.05	4.4	82.4	13.2
MRF-Pyr/CB	4.1	78.7	0.05	0.05	4.1	87.9	8.1
MRF-Act/CB	5.1	73.1	0.07	0.05	4.5	87.5	7.9
Cycled MRF-Act/CB				0.05	4.5	87.7	7.8

Table 3. Main textural parameters of the synthesized carbon aerogels derived from the nitrogen isotherms at -196 °C.

Samples	S_{BET} $\text{m}^2 \text{ g}^{-1}$	$^a V_{\text{T}}$ $\text{cm}^3 \text{ g}^{-1}$	$^b V_{\text{MIC}}$ $\text{cm}^3 \text{ g}^{-1}$	$^b V_{\text{MES}}$ $\text{cm}^3 \text{ g}^{-1}$
MRF-Pyr	324	0.47	0.09	0.39
MRF-Act	544	0.60	0.17	0.42
MRF-Pyr/CB	316	0.68	0.06	0.61
MRF-Act/CB	574	0.93	0.15	0.79

^a total pore volume evaluated at $p/p_0 \sim 0.99$

^b micro / mesopore volumes evaluated by the 2D-NLDFT-HS method

Table 4. Comparison of the desalting capacities(mg NaCl/g electrode) of various carbon aerogels.

Reference	Applied voltage (V)	Initial concentration (M)	Adsorption capacity (mg g^{-1})
52	1.3	0.034	7.1
53	1.2	0.085	5.8
54	1.5	0.0171	7.0
39	1.5	0.025	7.1
31	1.5	0.025	5.4
This work	1.5	0.025	7.3

Figure captions

- Fig. 1** (a) Picture of the supercritically dried N-doped hydrogels without (left) and with carbon black (right). TEM images of (b) carbon black additive; (c) MRF-Act. and (d) MRF-Act/CB. The domains ascribable to the aerogel and the carbon black additive have been identified by arrows.
- Fig. 2** X-ray diffraction patterns of the N-doped aerogels and their corresponding composites with carbon black. Patterns have been shifted for clarity.
- Fig. 3** Plot of the relative contributions of functional groups assigned from the XPS spectra at the a) C1s, b) N1s and c) O1s core levels of the pristine N-doped aerogels and their composites with carbon black.
- Fig. 4** a) N_2 adsorption isotherms recorded at 77 K of the N-doped carbon aerogels and their composites with carbon black; b) Pore size distribution plots. Inset: Cumulative pore volume plot; c and d) Zoom of the N_2 adsorption isotherms shown in a) to reveal details of the hysteresis loops.
- Fig. 5** a) Cyclic voltammograms of the N-doped aerogels and their composites with carbon black recorded at 0.5 mV s^{-1} in 0.1 M and 0.025 M of NaCl solution. b) Cyclic voltammograms for MRF-Act/CB recorded at 0.5 mV s^{-1} in 0.025 M NaCl solution for a number of cycles. PZC domains at the anodic and cathodic curves have been indicated with arrows.
- Fig. 6** a) Nyquist plots derived from impedance spectra recorded for the N-doped aerogels and their corresponding composites with carbon black. Inset: Equivalent circuit applied to the fitting of the impedance spectra; b) Comparison of the polarization resistance values of MRF-Act/CB (black) with those of other activated aerogels recently reported by our group [31, 40, 51].
- Fig. 7** Electrosorption capacity of sodium chloride for the activated N-doped aerogels and their corresponding composites with carbon black, a) MRF-Act and MRF-Act/CB; b) MRF-Pyr and MRF-Pyr/CB in a 0.025 M electrolyte solution. c) MRF-Act and MRF-Act/CB in a 0.1 M electrolyte solution. Open symbols (with carbon black), closed symbols (without carbon black). The experiments were recorded at different applied voltages.
- Fig. 8.** Cycling behavior of a symmetric cell assembled with MRF-Act/CB in a 0.025 M NaCl solution and applying a 1.2-0 V regimen.
- Fig. 9.** Plot of relative contributions of functional groups assigned from the XPS spectra at the C1s, O1s and N1s core levels for fresh and cycled MRF-Act/CB electrodes.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure

Figure

Figure 8

Figure 9

ELECTRONIC SUPPORTING INFORMATION

Fig. S1 Raman spectra of the N-doped aerogels (MRF-Pyr and MRF-Act) and composites with carbon black (MRF-Pyr/CB and MRF-Act/CB). The Raman modes are indicated in the figure.

Table S1. Relative contributions calculated from the deconvolution of XPS N1s, O1s, C1s spectra of N-doped carbon aerogels and composites with carbon black.

Envelope N1s					
B.E. (eV)	398.6±0.2	400.5±0.2	401.7±0.2	403.6±0.1	
Assignment	N-6	N-5	N-Q	N-X	
MRF-Pyr	36.1	32.7	21.1	10.1	
MRF-Act	41.0	35.5	16.5	6.9	
MRF-Pyr/CB	36.2	40.7	15.4	7.6	
MRF-Act/CB	39.3	39.9	13.7	7.0	
Envelope O1s					
B.E. (eV)	531.3±0.1	533.1 ±0.1	534.6±0.2	536.6±0.1	
Assignment	C=O	C-O-	COO-	Occluded CO or CO₂	
MRF-Pyr	25.1	41.7	28.1	5.2	
MRF-Act	16.5	51.0	30.4	2.0	
MRF-Pyr/CB	35.5	40.9	20.2	3.3	
MRF-Act/CB	30.8	42.6	23.5	3.1	
Envelope C1s					
B.E. (eV)	284.6±0.1	285.9±0.1	287.2±0.2	289.2±0.1	291.2±0.1
Assignment	C-C	Csp²-N/ C-OH	Csp³-N/C=O	O-C=O	π-π*
MRF-Pyr	60.3	17.5	10.2	7.4	4.7
MRF-Act	60.2	21.6	9.5	7.3	1.4
MRF-Pyr/CB	61.6	15.2	12.0	6.6	4.4
MRF-Act/CB	61.9	11.2	15.7	7.5	3.7