

Carbon 98 (2016) 280-284 (letter)
<http://dx.doi.org/10.1016/j.carbon.2015.11.017>

On the use of diatomite as antishrinkage additive in the preparation of monolithic carbon aerogels

C. Macías^{1*}, G. Rasines¹, T.E. García², C. Rodríguez², P. Lavela³, J.L. Tirado³, C.O. Ania^{4*}

¹ I+D Department, Nanoquimia S.L., 14014 Córdoba, Spain

² IUTA, Universidad de Oviedo, Campus Universitario, 33203 Gijón, Spain

³ Lab Química Inorgánica, Univ. Córdoba, Campus de Rabanales, 14071 Córdoba, Spain

⁴ Instituto Nacional del Carbón, INCAR-CSIC, Apdo. 73, 33080 Oviedo, Spain

*Corresponding author Email: carlosmacias@nanoquimia.com (C. Macias); conchi.ania@incar.csic.es (CO Ania)

Abstract

We have synthesized flexible monolithic carbon aerogels by incorporating diatomite as antishrinkage agent during the sol-gel polycondensation of the precursors. The materials displayed elastic properties and preserved their pristine dimensions upon densification by carbonization even after etching of the diatomite, due to the open pore structure of the siliceous additive in the material's matrix. The aerogels displayed a well-developed porous structure, confirming that the polymerization of the precursors is not impeded; the effect of the additive was independent of the formulation of the aerogels, as evidenced by the behavior of aerogels with varied composition (molar ratio, pH, N-doping).

After the early works of Pekala and coworkers on the synthesis of carbon aerogels by the sol-gel polycondensation of resorcinol (R) and formaldehyde (F) mixtures [1,2], the interest for these solids has raised due to their potential use in several fields. Despite their versatility, the technological applications of carbon aerogels have often been limited by their poor mechanical properties. The mechanical stiffness of carbon aerogels depends strongly on the

porosity and the degree of cross-linking of the precursors [2,3]. The usually fragile hydrogels are mechanically reinforced upon carbonization as they become more rigid with increased Young modules [2,3], but their deformation capacity decreases. In previous works we have reported the preparation of carbon aerogels using various precursors with enhanced conductivity and chemical resiliency to oxidation [4,5]. Despite the good electrochemical performance, the use of monolithic electrodes was limited due to the large shrinkage and deformation of the pieces after carbonization -leading to densification of the matrix- [5]; this is a challenge for electrochemical applications where the contact between the electrode material and the current collector is crucial to avoid efficiency losses due to resistance. Aiming at fabricating large monolithic electrodes with improved mechanical properties without adversely affecting their porosity and conductivity, we herein report the preparation of monolithic carbon aerogels with enhanced mechanical properties by using a low cost siliceous sacrificial additive (i.e. diatomite earth). The synthesis route is a simple modification of the conventional one reported elsewhere [4], and consists on allowing the sol-gel polymerization of the precursors in the presence of the additives; after the supercritical drying step, the hydrogels (series H-) were carbonized (series C-), and the siliceous additive was finally removed by HF etching (see further details in the ESI File). Selected formulations with different precursor's molar ratio (R, F and melamine, M) and additives (either diatomite (D), carbon black (B), or both) were prepared (Table 1), to show that the effect of the additive does not depend on the composition of the aerogels. From a macroscopic point of view (Fig. 1), the materials ranged from translucent (pristine) to opaque when either B or D additives were used; this was rather expected given the large amounts of additives added (ca. 10 and 50 wt.% for B and D, respectively). Fig. 1 also shows the typical shrinkage and deformation of monoliths of varied composition after carbonization to obtain carbon aerogels (series C-) due to the evolution of the volatiles. The shrinkage of the disks (Table 1) accounted for up to a 30 % reduction in volume, and it was observed regardless the composition of the aerogels; notwithstanding the deformation was more pronounced for the samples prepared using melamine and B additive. In contrast, the shrinkage and bending was not observed for the aerogels prepared in the presence of diatomite, as the carbonized disks preserved their

dimensions even after the removal of the siliceous skeleton. Since we did not observe cracks between the siliceous and carbonaceous phases (Fig. 2 and 3), and we attribute this to the open pore structure of the diatomite that facilitates the evolution of volatiles upon densification by carbonization.

Table 1. Summary of synthesis parameters, dimensions and textural characteristics of the monolithic aerogels showing the shrinkage and response to the Crushing Strength Tests. Samples before (H-) and after (C-) carbonization are compared.

Fig. 1. Images of the monolithic materials showing the shrinkage upon carbonization.

The aerogels ranged from brittle to sponge-like solids when D was incorporated -even after etching of the diatomite-. These differences in the consistency were also corroborated by the Crushing Strength Tests up to 30 N (Table 1) [6], a screening technique used to evaluate the mechanical properties of the aerogels. The pristine and B-loaded materials presented a conchoidal fracture after compression above 30 N (Fig. 2). On the other hand, the aerogels synthesized in the presence of the D (either etched or not) followed a different pattern; no fracture was observed in this case, and the materials were rather gradually deformed with increasing the compressive load, suggesting a plastic character. The extent of the deformation is clearly seen by the fingerprint left by the punch in the monoliths (Fig. 2).

Fig. 2. SEM micrographs of selected monolithic aerogels showing the deformation fingerprint and the mechanical fracture in the Crushing Strength Test at various loadings (between brackets).

Fig. 3. Load-displacement curves, parameters and images of the fingerprint in the specimens after the Small Punch Tests.

Fig. 4. N₂ adsorption isotherms at -196 °C and main textural parameters of selected aerogels.

The mechanical properties of selected monolithic aerogels were also investigated by means of Small Punch Tests performed under quasi-static conditions [7]. Fig. 3 shows the load-

displacement curves (LDC) from biaxially stretched tests performed on selected aerogels showing the effect of both additives. The characteristic shape of the curves demonstrates the change from a stiff and brittle behavior to a compliant and plastic character of the materials when the diatomite was used as additive in the synthesis. In the case of the aerogels without D, a steep initial slope was followed by a load drop associated with pop-in cracking. The onset of the first crack corresponds to the maximum load and determines the deformation capacity of the material (inset Fig. 3). The LDC curves exhibit a much more compliant behavior when D was used as additive and no sudden crack extensions took place; this is attributed to the presence of large voids inherited from the siliceous skeleton, as it can also be seen in the SEM images. The stiffness of the samples, evaluated from the initial slope of the LDC, decreased about one order of magnitude when the D additive was used. Furthermore, the mechanical properties induced by the D are retained after carbonization and/or etching off the additive. While the maximum load up to the first pop-in crack is quite similar for all the samples, the materials prepared in the presence of D exhibit much higher displacements before cracking and larger areas under the LDC, this last value being related to toughness.

In addition to being more mechanically compliant, the aerogels prepared in the presence of the diatomite exhibited large porosity, as inferred from the N₂ adsorption data (Fig. 4, Table 1). The textural features of the aerogels were slightly altered by the presence of the additives; all the samples displayed a well-developed nanoporosity (type IV isotherms), suggesting that the polymerization of the precursors in the presence of additives is not impeded [4]. However, the incorporation of D provoked a slight drop in total pore volumes and the enlargement of the mesopores turning into macropores, whereas the microporosity remained rather the same. The large pore volumes and hysteresis loops in the gas adsorption data suggest that the polycondensation of the monomers is slowed down in the presence of the additives (either B or D). This would lead to a lower degree of cross-linking of the structure, generating weakly branched clusters that tend to form larger colloidal aggregates in progressively larger pores (mesopore coarsening) [1,4]. As for the conductivity, it is mainly controlled by the presence of the carbon black (i.e., 2.1 and 7.7 mS/cm for C-MRF1 and C-MRF1-B; 1.0 and 3.9 mS/cm for C-RF1 and C-RF1-B; 2.2 and 4.3 mS/cm for C-MRF2-D and C-MRF1-BD, respectively);

after etching off the diatomite (insulator) the electrodes present conductivity values closed to those prepared without the siliceous additive, although differences also depend on the formulations (ca. N-doped aerogels display higher conductivity than RF ones) [4,5]. In summary, we have fabricated monolithic carbon aerogels with improved mechanical properties while maintaining outstanding porous features and improved electrical conductivity provided by the carbon black additive [4]. Both characteristics allow the implementation of the monolithic aerogels in electrochemical applications.

Acknowledgments

This work was partially funded by MINECO (CTM2014/56770-R, IPT-2011-1450-310000 ADECAR). The help of Mr. D.L. García in the preparation of the specimens is greatly appreciated.

References

- [1] Pekala RW. Organic aerogels from the polycondensation of resorcinol with formaldehyde. *J Mater Sci* 1989;24(9):3221–7.
- [2] Pekala RW, Alviso CT, LeMay JD. Organic aerogels: Microstructural dependence of mechanical properties in compression, *J. Non-Cryst. Solids* 1990;125:67–75.
- [3] Morales-Torres S, Maldonado-Hodar FJ, Perez-Cadenas AF, Carrasco-Marín F. Textural and mechanical characteristics of carbon aerogels synthesized by polymerization of resorcinol and formaldehyde using alkali carbonates as basification agents, *Phys. Chem. Chem. Phys.*, 2010;12:10365-72.
- [4] Macias C, Haro M, Rasines G, Parra JB, Ania CO. Carbon-black directed synthesis of mesoporous aerogels, *Carbon* 2013;63:487-97.
- [5] Rasines G, Lavela P, Macias C, Zafra MC, Tirado JL, Ania CO. On the use of carbon black loaded N-doped carbon aerogel for the electrosorption of sodium chloride from saline water, *Electrochim Acta* 2015;170:154-163.
- [6] Bemrose CR, Bridgewater J. A review of attrition and attrition test methods, *Powder Technology* 1987;49:97-126.

[7] Rodríguez C, Arencón D, Belzunce J, MasPOCH M. Small punch test on the analysis of fracture behaviour of PLA-nanocomposite Films, Polymer Testing 2014;33:21-9.

Table 1. Summary of synthesis parameters, dimensions and textural characteristics of the monolithic aerogels showing the shrinkage and response to the Crushing Strength Tests. Samples before (H-) and after (C-) carbonization are compared.

Sample (*)	S_{BET}^A [m ² g ⁻¹]	V_T^B [cm ³ /g]	Synthesis Parameters	Specimen dimensions ^C (mm)	Shrinkage on carbonization ^D (%)	Remarks on Crushing Strength Tests ^E
H-MRF1	458	0.99	(M+R)/C 90 (M+R)/W 0.052 (M+R)/F 0.428	4.97	--	Brittle, fracture upon load of 16 N
H-MRF1-B	450	1.55	(M+R)/C 90 (M+R)/W 0.052 (M+R)/F 0.428	4.97	--	fracture upon load of 27 N
C-MRF1	323	0.46	(M+R)/C 90 (M+R)/W 0.052 (M+R)/F 0.428	4.87/3.5	28.1	Brittle, no fracture upon load of 30N
C-MRF1-B	314	0.67	(M+R)/C 90 (M+R)/W 0.052 (M+R)/F 0.428	4.95 / 3.45	30.3	Brittle, no fracture upon load of 30N
H-RF1	592	1.32	R/C 200, R/F 0.5, R/W 0.06	5.2	--	Brittle, fracture after load of 15 N
C-RF1	862	1.48	R/C 200, R/F 0.5, R/W 0.06	5.2/3.93	24.4	Brittle, fracture after 18 N load
C-RF1-B	854	1.53	R/C 200, R/F 0.5, R/W 0.06	5.2/3.58	31.2	Brittle, fracture after 28 N load
C-RF2	894	1.17	R/C 200, R/F 0.5, R/W 0.08	5.2/3.87	25.6	Brittle, no fracture upon load of 30N
C-RF2-B	856	1.18	R/C 200, R/F 0.5, R/W 0.08	5.2/3.4	33.8	Brittle, fracture upon load of 21N
H-MRF2	212	1.44	(M+R)/C 135 (M+R)/W 0.052 (M+R)/F 0.428	5.1	--	Brittle, fracture upon load of 21N
H-MRF2-D	101	0.58	(M+R)/C 135 (M+R)/W 0.052 (M+R)/F 0.428	5.2	--	Flexible, characteristic fringerprint at loadings 5-30N
H-MRF2-BD	237	0.51	(M+R)/C 135 (M+R)/W 0.052 (M+R)/F 0.428	5.2	--	Flexible, characteristic fringerprint at loadings of 5-30N
C-MRF2	522	1.55	(M+R)/C 135 (M+R)/W 0.052 (M+R)/F 0.428	5.1/3.6	30.8	Brittle, fracture upon load of 14 N
C-MRF2-D	230	0.85	(M+R)/C 135 (M+R)/W 0.052 (M+R)/F 0.428	5.2/4.9	5.4	Flexible, characteristic fringerprint at loadings of 2-30N
C-MRF2-D (etched)	328	1.13	(M+R)/C 135 (M+R)/W 0.052 (M+R)/F 0.428	5.2/4.9	5.4	Flexible, characteristic fringerprint at loadings of 2-30N
C-MRF2-BD	118	0.41	(M+R)/C 135 (M+R)/W 0.052	5.2/5.0	4.6	Flexible, characteristic

			(M+R)/F 0.428			fringerprint at loadings of 5-30 N
C-MRF2-BD etched	237	0.51	(M+R)/C 135 (M+R)/W 0.052 (M+R)/F 0.428	5.2/4.9	5.2	Flexible, characteristic fringerprint at loadings of 2-30N

* Samples are labelled as series RF or MRF depending on the precursors; numbers indicate different formulations -for clarity- detailed in the synthesis parameters raw; "H" denotes hydrogels after supercritical drying and before carbonization; "C" denotes carbonized samples; "D" and/or "B" denote the presence of diatomite and/or carbon black additives.

^A Apparent surface area evaluated using BET at the N₂ adsorption isotherms at -196° C

^B Total pore volume evaluated at relative pressure of 0.99

^C Spherical specimens, dimensions before (samples H-) and after carbonization (samples C-) of the disks

^D evaluated from the dimensions before/after carbonization of the spherical specimens (samples H- vs samples C-)

^E evaluated from the Crushing Strength Tests (compression up to 30 N) of the spherical specimens

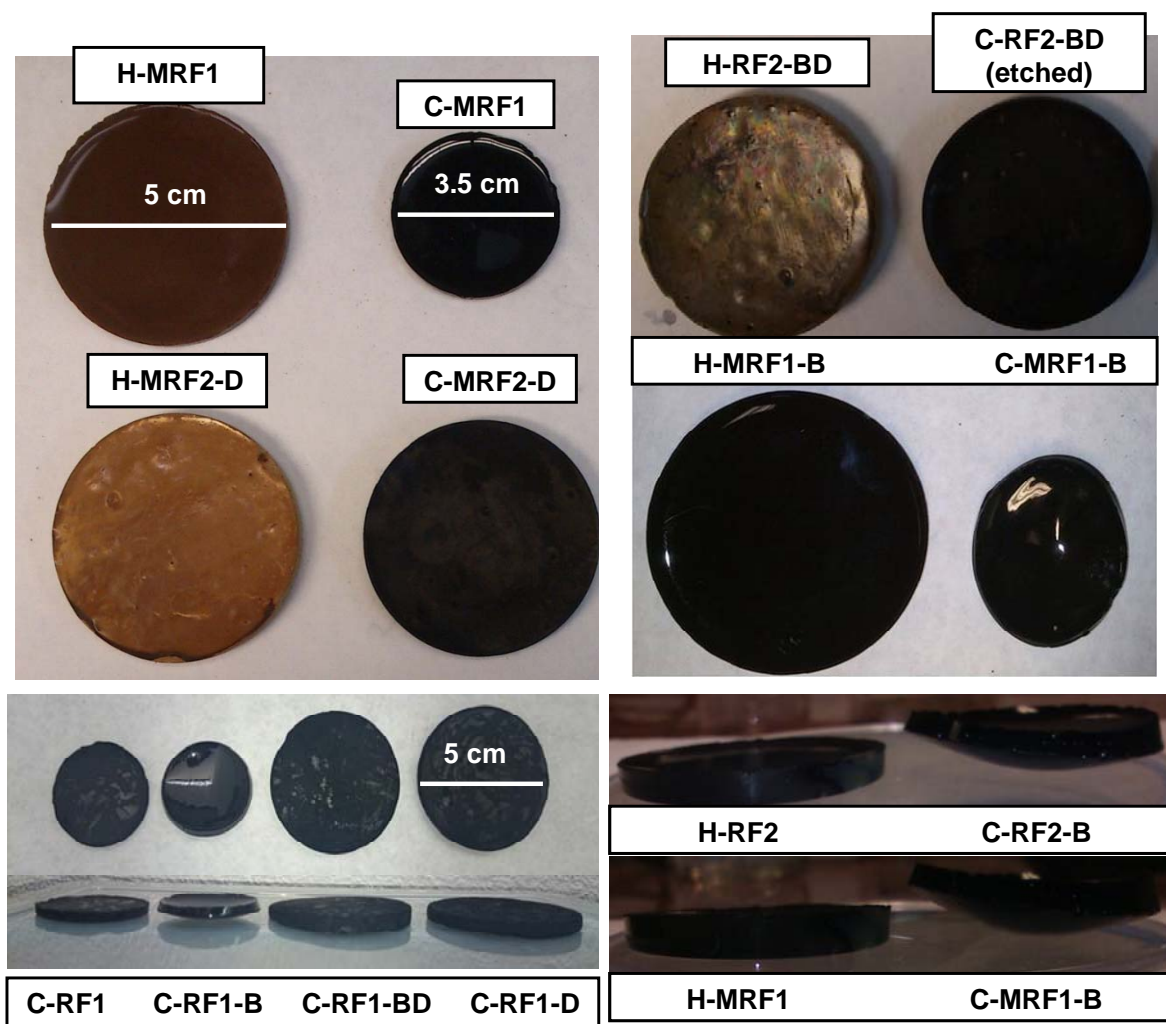


Fig. 1. Images of the monolithic materials showing the shrinkage upon carbonization.

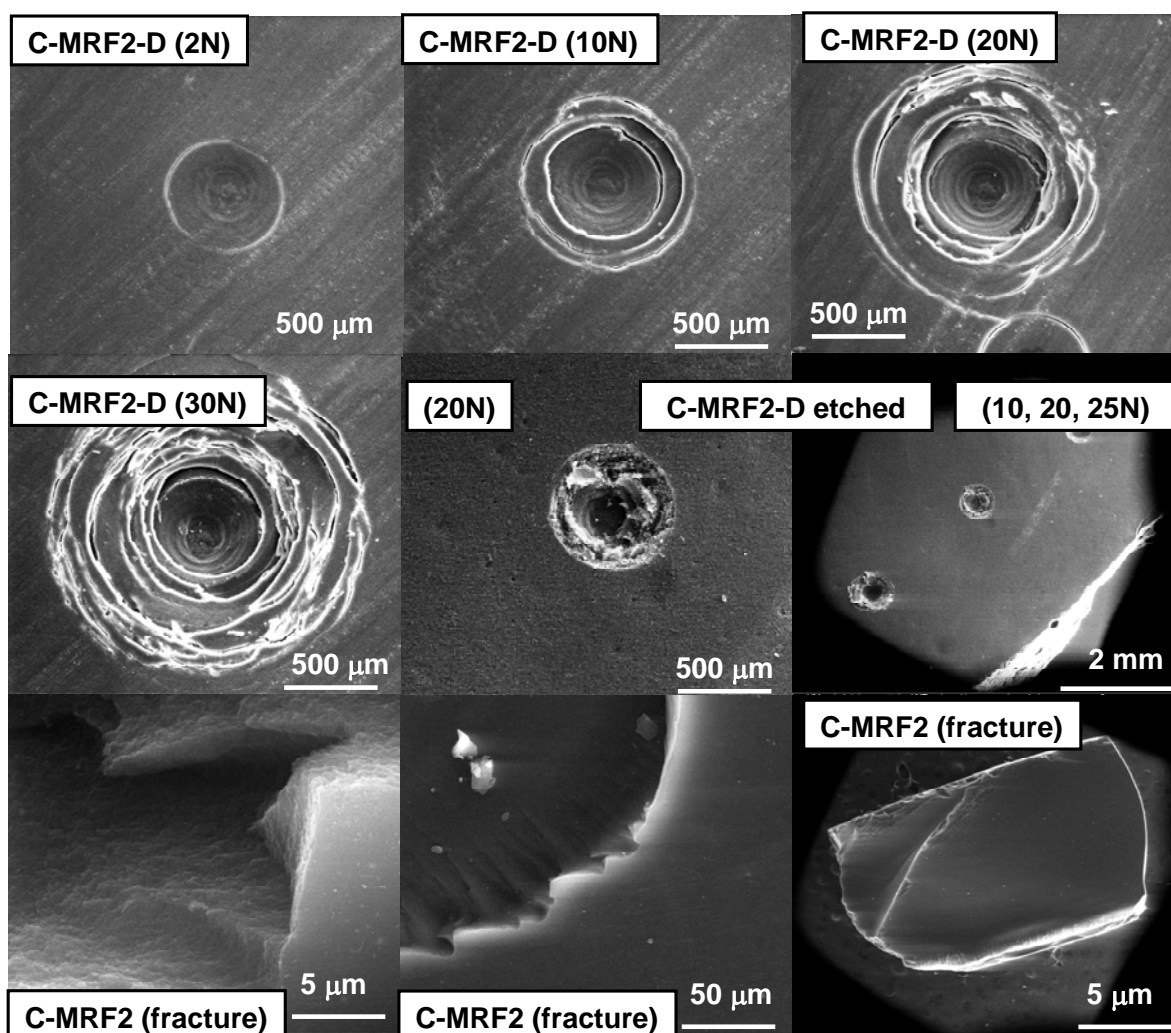


Fig. 2. SEM micrographs of selected monolithic aerogels showing the deformation fingerprint and the mechanical fracture in the Crushing Strength Test at various loadings (between brackets).

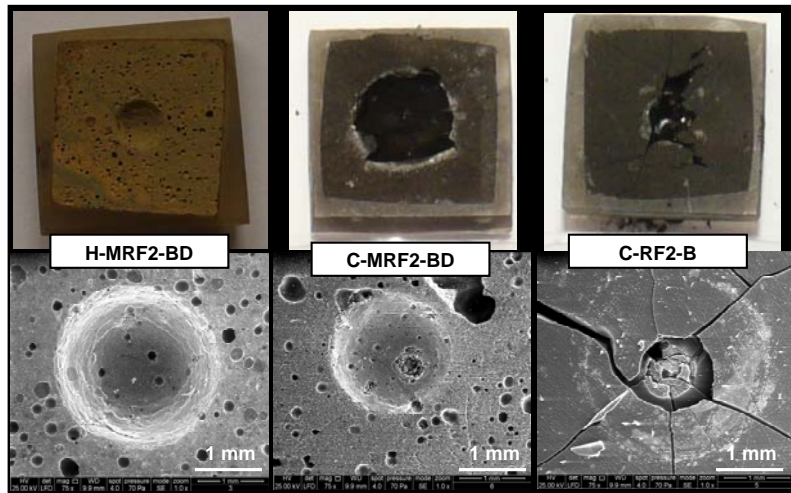
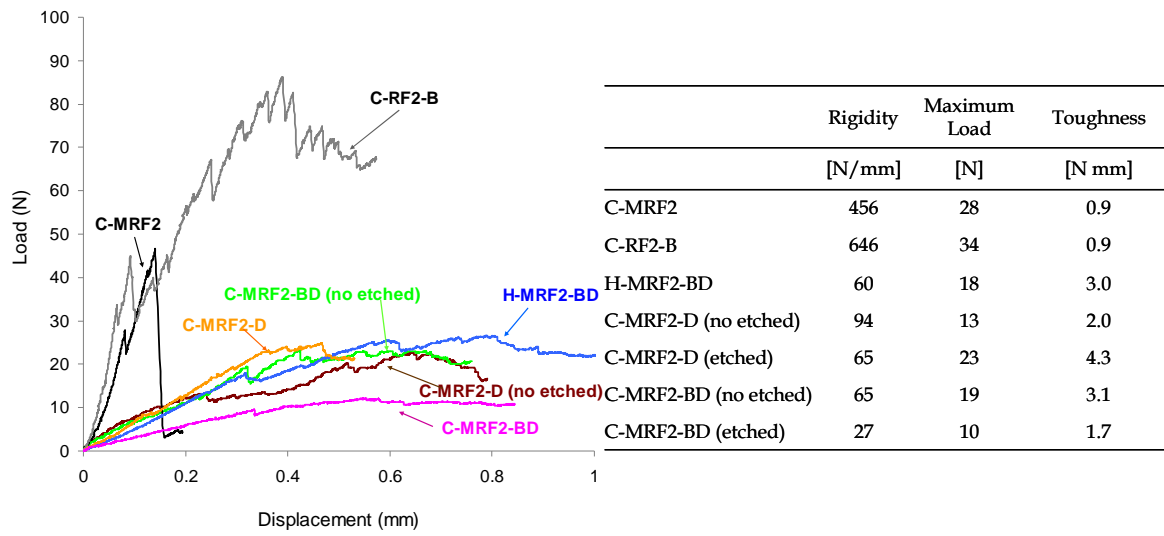


Fig. 3. Load-displacement curves, parameters and images of the fingerprint in the specimens after the Small Punch Tests.

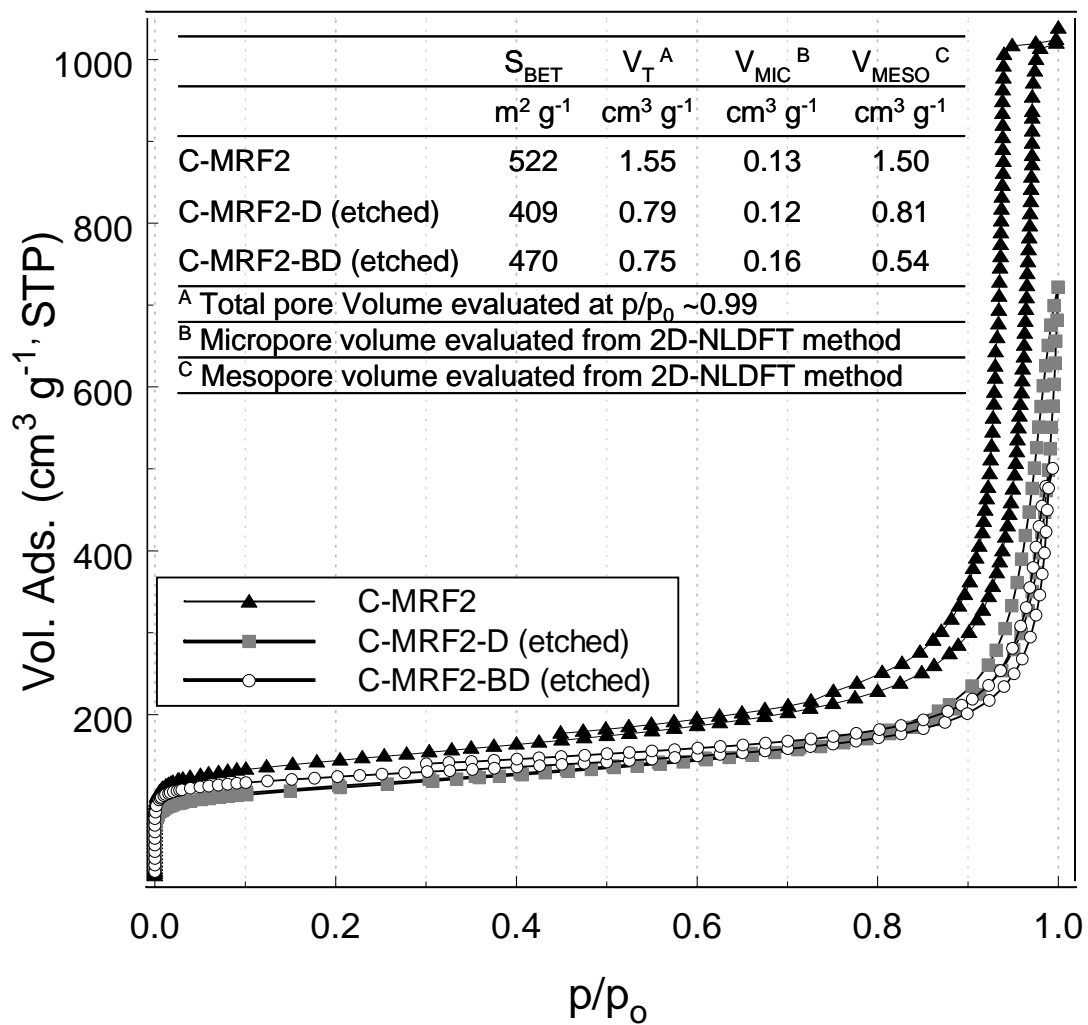


Fig. 4. N_2 adsorption isotherms at -196°C and main textural parameters of selected aerogels.

Supplementary Information File (ESI)

On the use of diatomite as antishrinkage additive in the preparation of monolithic carbon aerogels

C. Macías^{1*}, G. Rasines¹, T.E. García², C. Rodríguez², P. Lavela³, J.L. Tirado³, C.O. Ania^{4*}

¹ I+D Department, Nanoquímica S.L., 14014 Córdoba, Spain

² IUTA, Universidad de Oviedo, Campus Universitario, 33203 Gijón, Spain

³ Lab Química Inorgánica, Univ. Córdoba, Campus de Rabanales, 14071 Córdoba, Spain

⁴ Instituto Nacional del Carbón, INCAR-CSIC, Apdo. 73, 33080 Oviedo, Spain

*Corresponding author'Email: carlosmacias@nanoquimia.com (C. Macias); conchi.ania@incarcsic.es

(CO Ania)

Synthesis of the MRF aerogels

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. Carbon black (CB, Superior Graphite Co.) and diatomite (Nanolit K-6) were used as conductive and anti-shrinkage additives, respectively. Two different molar ratio of the reactants were used, as compiled in Table 1 (M+R/C of 90 and 135; M+R/W of 0.052 and 0.053, M+R/F of 0.43). The final pH of the precursors was eventually adjusted at 7.4 by adding acetic acid or sodium carbonate, respectively. For the MRF series, the samples were synthesized following a prepolymerization procedure described elsewhere [S1-S4]. 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. Before gelification, diatomite (50%w/v) and/or carbon black (ca. 10%wt.) were added and magnetically stirred to ensure a homogeneous dispersion. 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 supercritically dried with CO₂ and carbonized (ca. 2 °C/min) at 750 °C under nitrogen atmosphere. Diatomite was removed from the samples using HF, leaving a silica free carbon monolith.

Synthesis of the RF aerogels

The resorcinol-formaldehyde carbon gels were synthesized by the sol gel polymerization of resorcinol (R) and formaldehyde (F) in water (W), using sodium carbonate (C) as catalyst, carbon black (CB, Superior Graphite Co.) as conductive additive. Different aerogels were obtained by setting the R/W ratio at 0.06 and 0.08, while the R/F molar ratio was set at 0.5, the R/C at 200 and the amount of carbon black added to the solution was ca. 0.9% w/v. In a typical synthesis, the reagents were placed into sealed glass moulds under magnetic stirring and allowed to undergo gelation and aging in an oven at 40 °C for 24 h and 70 °C for 120 h. After the water-acetone exchange, the samples were dried under CO₂ supercritical conditions.

Finally, the aerogels were pyrolyzed at 800°C under a N₂ stream (heating ramp of 2 °C min⁻¹). For the sake of comparison, carbon gels prepared by the same synthetic route without the incorporation of the carbon black were also prepared.

Nomenclature of the samples

Series MRF: hydrogels synthesized by the polycondensation of melamine, resorcinol and formaldehyde.

Series RF: hydrogels synthesized by the polycondensation of resorcinol and formaldehyde.

Hydrogels are labeled as “H”, while carbonized samples are labeled as “C”.

The presence of Diatomite and Carbon Black in the samples is indicated by adding “D” or “B” to the nomenclature.

Mechanical Properties: crushing Strength Test and Small Punch Test

The Crushing Strength Tests were carried out by applying a normal force (up to 30N) to the as-prepared monoliths. This allows the evaluation of the resistance of the materials to fracture under a compressive strength limit, while measuring the characteristic fingerprint on the material upon deformation and/or fracture.

Small Punch Tests were performed under quasi-static conditions with a low speed tensile test machine on 1x1cm square specimens of 2-3 mm thickness. The specimens were polished to control the thickness and to obtain a flat surface, and framed in a resin framework (1 x 1 mm) surrounding the material while leaving the surface of the material uncovering to allow the contact with the punch head. The test consisted on fixing the specimen between two dies (initial load of 2 N), and then deforming the specimen quasi-statically up to failure by means of a small semi-spherical punch with a head of 2 mm of diameter (biaxial expansion). The test is speed controlled with a punching speed $v = 0.2$ mm/min. The displacement of the punch is measured by means of an extensometer, and after correction of the flexibility of the testing device, the displacement of the central point of the specimen is calculated.

Electrical conductivity measurements

The measurement of conductivity on the previously dried as-prepared monolithic samples was carried out using an Arbin BT2000 potentiostat-galvanostat. The specimens are packed between two metallic collectors and hold under constant pressure (several values were tested to assure proper contact) and a bias voltage between 0.2-1.2 V (0.2V/s step for 120 s) was applied. The resistance is calculated from the slope of the current-voltage profiles at each voltage. The area and thickness of the monoliths, needed to evaluate the resistivity, were measured by a spring micrometer.

References

- S1. Rasines G, Lavela P, Macias C, Zafra MC, Tirado JL, Ania CO, On the use of carbon black loaded N-doped carbon aerogel for the electrosorption of sodium chloride from saline water, *Electrochim Acta* 170 (2015) 154-163.
- S2. Rasines G, Lavela P, Macias C, Zafra MC, Tirado JL, Parra JB, Ania CO, N-doped monolithic carbon aerogel electrodes with optimized features for the electrosorption of ions, *Carbon* 83 (2015) 262-274.
- S3. Rasines G, Lavela P, Macias C, Zafra MC, Tirado JL, Ania CO, Mesoporous carbon black-aerogel composites with optimized properties for the electro-assisted removal of sodium chloride from brackish water, *J Electroanal. Chem*, 741 (2015) 42-50
- S4. Macias C, Haro M, Rasines G, Parra JB, Ania CO, Carbon-black directed synthesis of mesoporous aerogels, *Carbon* 63 (2013) 487-497.

Table S1. Main characteristics of the additives used (diatomite and Carbon Black).

Sample	S _{BET} ^A [m ² g ⁻¹]	V _{PORES} ^B [cm ³ /g]	Selected characteristics	Remarks
Carbon Black	22	0.17	Volatiles < 0.15 wt.% Ash < 0.05 wt.% Density 160 kg/m ³ Average particle size 6 μm	Superior Graphite Co FN-6 / Celatom
Diatomite	28	0.08	Average particle size 12 μm Permeability (Darcy) 0.020 Apparent density (dry) 190 g/L Apparent density (wet) 420 g/L	Fine-grained siliceous sediment of biogenic origin (skeletal remains of microscopic single-celled diatoms) SiO ₂ (89.2 wt.%), Al ₂ O ₃ (4 wt.%), Fe ₂ O ₃ (1.7 wt.%), CaO (0.5 wt.%), MgO (0.3 wt.%)

^A Apparent surface area evaluated from N₂ adsorption isotherms at -196° C

^B Total pore volume evaluated at relative pressure of 0.99

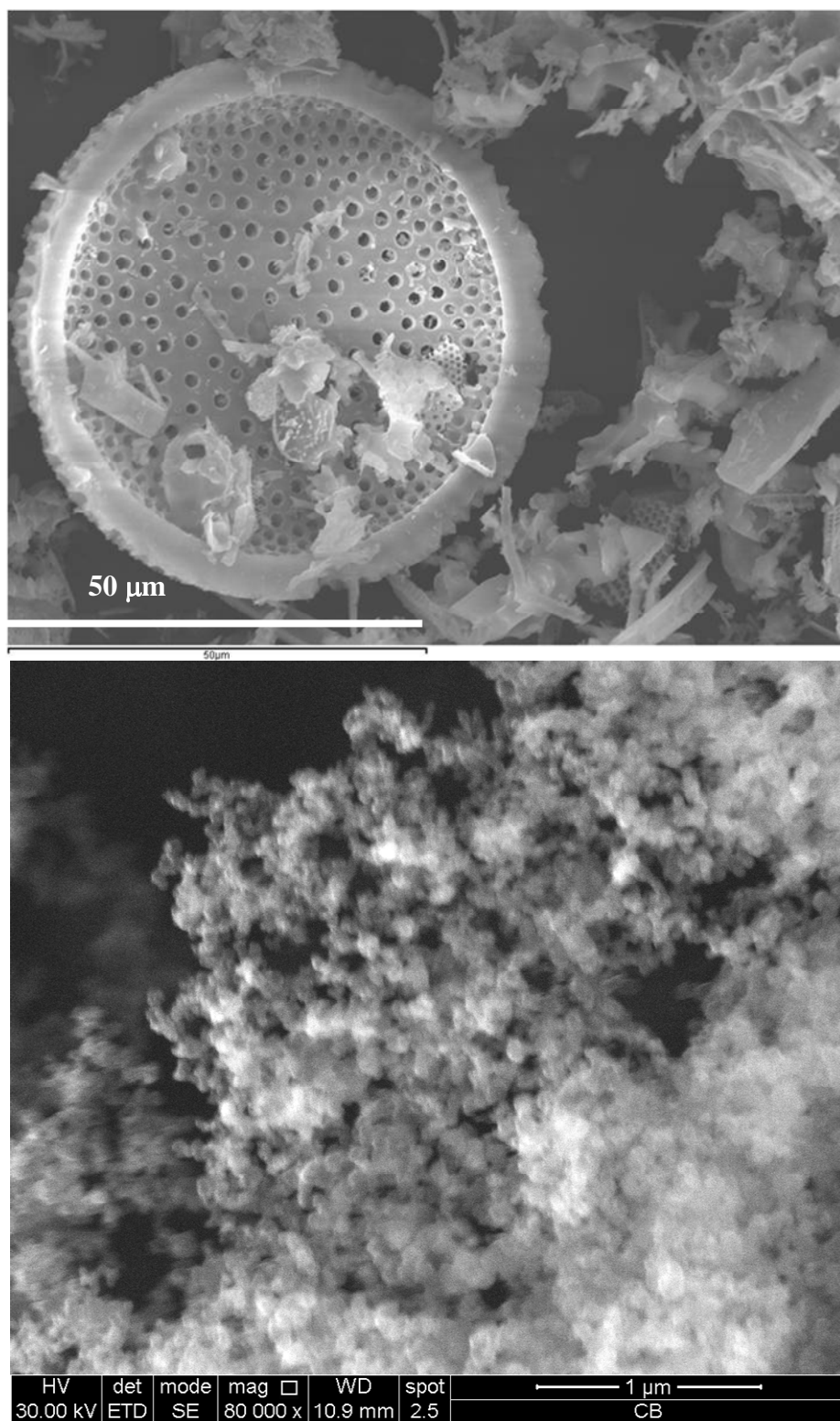


Figure S1. SEM images of the additives: diatomite (top) and carbon black (down).