



Successful application of a commercial cationic surfactant mixture (benzalkonium chloride) as porosity stabilizer in porous carbons fabrication



L.H. Tamborini^a, M.E. Casco^b, M.P. Militello^a, J. Silvestre-Albero^b, C.A. Barbero^{a,*}, D.F. Acevedo^{a,c,*}

^a Departamento de Química, Facultad de Ciencias Exactas, Físicoquímicas y Naturales, CONICET, Universidad Nacional de Río Cuarto, 5800, Río Cuarto, Argentina

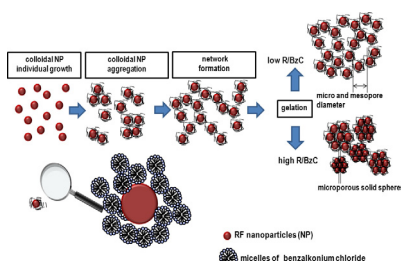
^b Laboratorio de Materiales Avanzados, Departamento de Química Inorgánica, Universidad de Alicante, Apartado 99, E-03080 Alicante, Spain

^c Departamento de Tecnología Química, Facultad de Ingeniería, Universidad Nacional de Río Cuarto, 5800, Río Cuarto, Argentina

HIGHLIGHTS

- Porous carbons are obtained using commercial surfactant mixtures.
- Porous carbons are produced in an economical way.
- Commercial surfactant mixtures as a soft template are used in the synthesis.
- The presence of the surfactant avoids the collapse of the wet gel during drying.
- Carbons have a specific capacitance of 165 F/g and high specific surface area 645 m²/g.

GRAPHICAL ABSTRACT



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ABSTRACT

Porous carbons (BSPCs) were obtained by carbonization of resorcinol-formaldehyde gels in the presence of cationic surfactants mixture (benzalkonium chloride) which act as porosity stabilizer. The application of an inexpensive industrial grade surfactant mixture as porosity stabilizer permits obtaining porous carbons with well-developed micro and mesoporosity at low cost. The stabilizing effect on the sol-gel nanostructure allows maintaining the gels porosity during conventional air drying, simplifying the production of porous carbon by making unnecessary complex drying procedures (e.g. supercritical drying), cumbersome solvent exchanges, and long curing times. The carbonization process of BSPCs studied by TGA shows that the stabilizer and non-carbon elements (hydrogen and oxygen) are only eliminated during pyrolysis at temperature above 600 °C. The BSPCs morphological and textural properties were studied by scanning electron microscopy and nitrogen physisorption isotherms. The BSPCs present large specific surface areas (up to 645 m²/g) containing mesopores and micropores. Furthermore, the pore distribution and morphology depend on the monomer (resorcinol) to stabilizer (benzalkonium chloride) ratio. Cyclic voltammetry and electrochemical impedance spectroscopy were employed to study the electrochemical properties of the carbon materials. The BSPCs exhibit a large specific capacitance (up to 179 F/g at 2.8 mHz in 1 M H₂SO₄). The results suggest that porosity stabilization of resorcinol/formaldehyde gels could be performed using different cationic surfactants, even commercial mixtures like benzalkonium chloride.

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* Corresponding authors at: Departamento de Química, Facultad de Ciencias Exactas, Físicoquímicas y Naturales, CONICET, Universidad Nacional de Río Cuarto, 5800, Río Cuarto, Argentina.

E-mail addresses: cbarbero@exa.unrc.edu.ar (C.A. Barbero), dacevedo@ing.unrc.edu.ar (D.F. Acevedo).

1. Introduction

Porous carbon materials such as activated carbons, carbon nanotubes and nanofibres, and recently novel structured carbons have been widely used in a variety of applications [1]. In this sense several studies have shown that different carbon materials: activated carbons [2–4] (powder or fiber cloths), carbon nanotubes [5], carbon aerogels [6,7], carbon cryogels [8,9] and ordered mesoporous carbons can be successfully employed in technological application such as catalyst [10], supercapacitors [11], as electrodes [12]. The use of carbon materials is based on their excellent chemical stability, thermal conductivity, high specific surface areas, large pore volumes and good mechanical stability. Several of these materials are synthesized by pyrolysis of resorcinol-formaldehyde (RF) gels [13,14,11]. While the wet RF gel is highly porous, due to the nanostructure obtained from the sol–gel synthesis process, upon drying the pore structure collapses and the resulting material has a smaller surface area [15]. Therefore, various strategies have been explored towards stabilizing the pore structure in order to avoid the shrinkage of the gel, especially in the critical stage of drying and/or carbonization of the gel [16–18]. Another important consideration for new synthetic strategies concerns the cost associated with the synthesis of the material, i.e. supercritical and freeze drying processes must be avoided without any sacrifice of the porosity in the final material. Bell et al. and Lee et al. used a cationic surfactant as a template in the polymerization reaction [19,20]. Surfactant molecules in the synthesis generate spherical micelles in aqueous solution and act as templates for the sol-gel polymerization. Bell considers that the gel polymerization is carried out around the micelles, whereas Lee proposed that the spherical aggregates, in the order of nanometers, would be formed within the micelles, which then would interconnect three-dimensionally by a crosslinking reaction. As a result, interstitial sites would generate the pores of the material. Moreover, it is known that the surfactant adsorbs on the pores walls after the reaction, making the surface tension of the liquid/vapour interface decreases, allowing minimizing the pore collapse during drying stages. Subsequently, it has been proposed to stabilize microemulsions cationic surfactants which result in the porous structure [21]. In other work, N. Nishiyama et al. reported a new synthetic method to produce microporous carbons using surfactants [22]. Bruno et al. proposed that cationic micelles of cetyltrimethylammonium chloride (CTAB) stabilize RF nanoparticles and maintain the gel porosity during drying [11]. Taking into account the results these authors proposed the use of cationic polyelectrolytes to stabilize the pores [23]. The use of cationic polyelectrolytes in the synthesis of the gel allows varying its concentration over a wide range; and consequently, the concentration is not limited to a minimum value as surfactants form micelles.

The aim of this work is to obtain porous carbons with good performance using inexpensive reactants which could be used in large-scale synthesis at industrial scale. The use of industrial grade benzalkonium chloride (BzC), which is composed of a mixture of related cationic surfactants, to generate porous carbons is proposed. The BzC is produced by the reaction of benzylamine with a mixture of several long chain halides. Those halides are themselves made by nucleophilic substitution on the long chain alcohol prepared by reduction of fatty acids. These acids are prepared by hydrolysis of triglycerides from animal fat or vegetal oil. Taking into account the uses of the benzalkonium chloride (disinfectants, fabric softeners, etc.), a cationic surfactant mixture is useful to achieve these tasks and is not necessary employing a pure compound. In this work, BzC is used as surfactant in order to stabilize the structure of the RF gels. Nevertheless, the use of a mixture of surfactants with different chain length will produce micelles of different sizes. It is demonstrated that the stabilizing

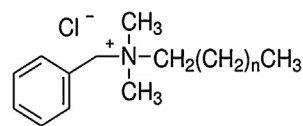


Fig. 1. Composition of Benzal 80[®]. R = C12 (40%), C14 (50%), C16 (10%).

effect of RF nanoparticles is not highly affected by the micelle size. It is shown the synthesis of porous carbon varying the molar ratio of resorcinol/benzalkonium chloride (R/BzC) from 0.03 to 0.12. The porous materials obtained using different R/BzC ratios allows estimating the surfactant concentration that produces resins, and then carbons, with well-developed porosity. Those highly porous carbons could facilitate the electrochemical charging/discharging through the fast ion transport in the pores. The morphological and textural properties of the BSPCs were studied by scanning electron microscopy (SEM) and nitrogen physisorption isotherms. Thermogravimetric analysis (TGA) shows that the stabilizer and non-carbon elements (hydrogen and oxygen) are only eliminated during pyrolysis at temperature above 600 °C. The scanning electron microscopy (SEM) images show that the carbons are formed by aggregation of primary particles. The nitrogen physisorption isotherms were employed to evaluate the surface area and the pore distribution and morphology. Based on the results it is possible to conclude that the carbon presents large specific surface area (up to 645 m²/g) and that the porosity strongly depends on the resorcinol to BzC ratio. Cyclic voltammetry and electrochemical impedance spectroscopy were employed to understand the role of the pore size and distribution on the electrochemical performance. The BSPCs exhibit a large specific capacitance (up to 165 F/g) with low charge transfer resistance due to the pores. In the best of our knowledge, there are no reports dealing with the use of cetyltrimethylammonium chloride in the fabrication of porous carbon materials. Additionally, since benzalkonium chloride is an industrial mixture of biomass originated cationic surfactant, its use have environmental and economic advantages and suggests that micelles of different sizes, as those originated from a mixture of surfactant, are effective as pore stabilizer.

2. Experimental

2.1. Synthesis of resorcinol-formaldehyde-benzalkonium chloride materials

Monolithic porous carbons were synthesized by polycondensation of resorcinol (R) (Fluka) with formaldehyde (F) (Cicarelli) in the presence of a Benzal 80[®] (B) as pore stabilizer and sodium carbonate (C) (Cicarelli) as basic catalyst. Benzal[®] 80 is a solution (80% p/v) of benzalkonium chloride. The benzalkonium chloride in Benzal[®] 80 is composed of a mixture of quaternary ammonium salts (structure depicted in Fig. 1).

The molar ratio of resorcinol to formaldehyde (37% wt. in an aqueous solution) (R/F) and the ratio of resorcinol to water (R/W) were fixed at 0.5. Furthermore, the R/C ratio was kept constant at 200 [24]. In order to study the influence of the BzC on the porous structure of the synthesized carbons, the molar ratio to R/BzC was varied from 0.03 to 0.12. All components were mixed and stirred for 10 min. Then the samples were polymerized by heating at 70 °C, in a closed system, for 24 h to obtain a porous organic gel. The organic gel was dried at 70 °C in air for 6 h. Finally, porous carbons materials stabilized by BzC (BSPCs) were obtained by pyrolysis of the dried monolithic gels at 800 °C for 1 h under an argon atmosphere with a heating rate of 40 °C/h. The samples obtained were denoted as BSPCx, where x represents the molar ratio R/BzC (0.03, 0.06 and 0.12).

2.2. Carbonization process evaluated by TGA and TGA/MS measurements

The carbonization process was evaluated by TGA analysis (under flowing N₂), with a Mettler Toledo model TGA/SDTA851e/SF/1100 instrument coupled to a mass spectrometer Pfeiffer Vacuum brand model Thermostar GSD301T. The heating rate was 10 °C/min and the temperature range of 25 to 1000 °C.

2.3. Structural and morphological characterization

The study of the morphology of the carbon samples was performed using Carl Zeiss EVO equipment MA10. The textural properties of the synthesized carbons were evaluated by nitrogen adsorption measurements at –196 °C using homemade automatic manometric equipment designed and constructed by the Advanced Materials Group (LMA), now commercialized as N₂Gsorb-G (Gas to Materials Technologies (www.g2mtech.com)). Before the adsorption experiments, the samples were degassed for 8 h at 250 °C. Apparent surface area (SBET) was calculated by application of the B.E.T. equation to the nitrogen adsorption data [25]. The Dubinin–Radushkevich equation was used to calculate the micropores volume (V₀) and narrow micropores volume (V_n) from the nitrogen (–196 °C) and carbon dioxide (0 °C) adsorption data, respectively [26]. As already described in the literature, V₀ corresponds to the total micropore volume, whereas V_n provides the volume of micropores below 0.7–0.8 nm [27]. The mesopores volume (V_{meso}) was deduced from the N₂ adsorption isotherm, by subtracting the value V₀ (N₂) from the total amount adsorbed at P/P₀ = 0.98 [28]. The mesopores size distribution was estimated by application of the Barrett–Joyner–Halenda (BJH) method to the desorption branch of the nitrogen isotherm [29].

2.4. Preparation of electrodes and electrochemical measurements

The electrochemical characterization was performed by cyclic voltammetry (CV) with Autolab Eco-Chemie potentiostat/galvanostat instrument, and the electrochemical impedance spectroscopy (EIS) measurements were performed using a PC4 potentiostat/galvanostat–ZRA (Gamry Instruments, Inc.). The cyclic voltammetry measurements were performed in a typical three-electrode cell, where a mesoporous carbon and a silver/silver chloride electrode (saturated KCl) were used as a counter and a reference electrode, respectively. A sulfuric acid (1 M) aqueous solution was used as an electrolyte. Before the measurements, the carbon samples were milled and sieved to obtain powdered BSPCs down to 0.210 mm size. The working electrodes were prepared by coating Nafion-carbon ink onto a vitreous carbon electrode in order to obtain a film-coated electrode, as described before [21]. Carbon inks were prepared mixing 10 mg of powdered BSPCs with 0.25 mL ethanol, 0.25 mL of deionized water and 0.15 mL of Nafion solution (5 wt.%, DuPont). These mixtures were ultrasonicated for 60 min to form a homogeneous ink. Then, 15 µL of the resulting ink was deposited by drop-coating on a glassy carbon electrode (1.5 cm²) and dried at 50 °C for 5 min. The procedure has been used before [21], and gives results comparable with measurement of monolithic samples where no binder or additional current collector is present [11]. The presence of Nafion® allows the stabilization of the colloidal dispersions of carbon microparticles [30]. The dispersions are stable for months but are treated with ultrasound before use. The amount of active material (porous carbon) is calculated from the deposition volume. Weighing with a microbalance (Precisa 262 SMA-FR, 0.01 mg precision) gives the same mass values within 1% error. While the amount of mass is small, both mass and capacitance values are reproducible and are larger or in the order

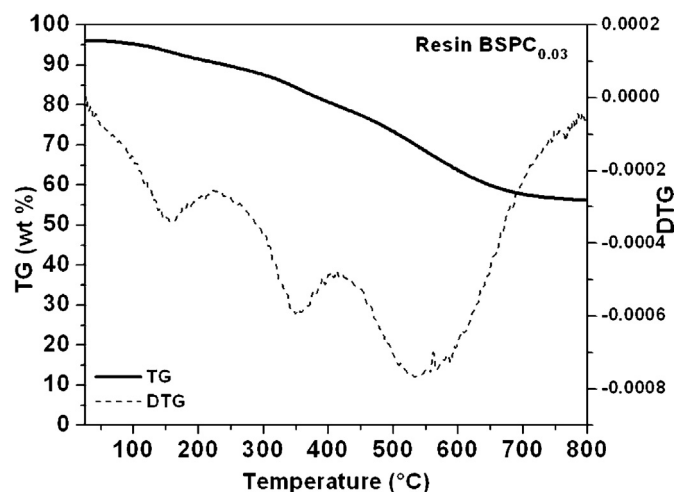


Fig. 2. TG weight loss curves and d(M)/dT for resin BSPC0.03.

of similar studies of the intrinsic properties of carbon materials [31,32].

The specific capacitance obtained by electrochemical impedance spectroscopy (CEIS) was calculated from the data at the lowest frequency (f), and evaluated using Eq. (1):

$$C_{\text{EIS}} = \frac{-1}{2\pi f Z'' m} \quad (1)$$

where f is the measurement frequency, Z'' is the frequency imaginary part value and m is the active material mass. EIS measurements were performed from 1×10^4 to 2.8×10^{-3} Hz with sinusoidal perturbation of 1 mV of amplitude and 10 points per decade change in frequency. A resting time of at least 15 min at each potential was used before measuring the electrochemical impedance.

The measured values are the intrinsic specific capacitance of the materials. On the other hand, the measurement of actual electrodes requires other constraints in the electrode formation to allow extrapolation of the measured parameters to commercial devices [33].

3. Results and discussion

The porous carbons are obtained by pyrolysis of the porous resin produced by reaction of resorcinol and formaldehyde in the presence of a cationic surfactant (benzalkonium chloride). The mechanism proposed before for the role of another cationic surfactant (cetyltrimethyl ammonium bromide, CTAB) involves the interaction of cationic micelles with negatively charged resin nanoparticles avoiding the interparticle pore collapse during drying [11]. Therefore, the surfactant cannot be removed before drying. A relevant question involves the removal of the surfactant during pyrolysis. Therefore, we monitored the release of volatiles during heating using thermogravimetric analysis TGA alone and coupled with mass spectroscopy (TGA-MS).

3.1. TGA and TGA/MS measurements

Fig. 2 shows the thermogravimetric analysis of the resin BSPC0.03, performed under nitrogen with a scan rate of 10 °C/min. The results are expressed in% of mass loss and its derivative (DTG) in function of temperature is shown, which goes from 25 to 800 °C.

Through the thermogravimetric analysis, the resin weight loss value during carbonization process calculated is c.a. 40%. The analysis of the derivative shows two zones, the first until 150 °C can be

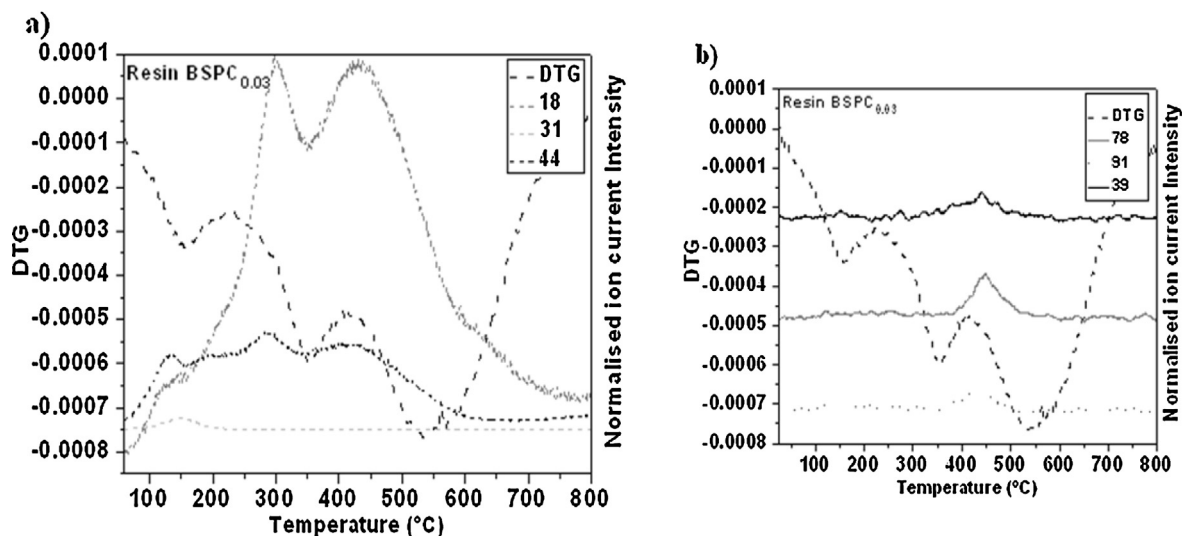


Fig. 3. Normalized $d(M)/dT$ profile and profile of species during thermal carbonization of RFB resin in N_2 atmosphere a) $m/z = 18, 31, 44$ and b) $m/z = 78, 91, 39$.

attributed to the moisture loose and the second zone, from 150 to 550 °C, corresponds to the thermal decomposition of the functional groups in the resin, which were determined by a thermogravimetric analysis coupled to a mass detector. Fig. 3(a and b) shows the derivative and intensity variations in the mass spectra as a function of the temperature of selected m/z fragments obtained during carbonization of the resin BSPC_{0.03}.

The evolution of water and carbon dioxide due to the pyrolysis of the sample is clearly appreciated in the thermogravimetric analysis (Fig. 3 a) up to about 550 °C, as evidenced by mass fragments $m/z = 18$ and $m/z = 44$. Furthermore, thermal decomposition fragments at $m/z = 31$ and 39 are observed (Fig. 3a and b) due to the curing of the resin, and resulting in the formation of methylene bridges in the polymer network. In Fig. 3 b, the fragments $m/z = 78$ and 91 are observed and can be attributed to the thermal decomposition of benzalkonium chloride.

From this study, it is reasonable to conclude that for such materials the resin carbonization temperature must be above 600 °C because at lower temperatures there are still some remnants of benzalkonium chloride. Additionally, up to 600 °C water and carbon dioxide are produced by pyrolysis of the resin, suggesting that the materials carbonized below 600 °C contain significant amount of hydrogen and oxygen, besides carbon. The presence of chemical groups bearing hydrogen and oxygen could involve differences in the structure and morphology of the carbons.

While other m/z fragments are also detected the one shown were chosen according to previous results [11] under the assumption that the presence of the different surfactant does not change the pyrolysis mechanism of the RF dry resin.

3.2. Morphology and textural properties of BSPC

Xerogels precursors of BSPC were obtained from the sol-gel polycondensation of resorcinol and formaldehyde using benzalkonium chloride as pore stabilizer and dried in air at 70 °C for 6 h. The dried porous gels were then carbonized by heating at 800 °C in an argon atmosphere. SEM images of the carbons materials are shown in Fig. 4 at different magnifications.

Fig. 4 shows that the carbons are formed by aggregation of primary particles, typical of resorcinol-formaldehyde gels [29,34–37], which form aggregates and it is possible to observe empty space between the primary particles. The cavities between the aggregates produce mesopores and/or macropores in the carbon material. It

is known that the RF primary particles or clusters are negatively charged in a basic media due to the presence of phenolic groups [38]. Thus, BzC micelles can stabilize the nanoparticles minimizing aggregation. The pore size variation observed in the micrographs could be explained as follows: the positively charged BzC forms micelles which interact electrostatically with negatively charged RF particles, initiating the self-assembly processes that results in RF-particles/BzC clusters. At large R/BzC ratio, the cationic surfactant induces the formation of small clusters increasing the aggregation of the particles, which generates solid spheres containing micropores. On the contrary, at low R/BzC ratio, the larger amount of surfactant promotes the electrostatic interaction between positively charged surfactant chains and RF particles, thus generating carbon materials containing micro and mesopores (BSPC_{0.03}).

Nitrogen adsorption-desorption measurements and pore size distribution of BSPCs prepared with different R/BzC ratios are shown in Fig. 5. The physical parameters deduced from the nitrogen adsorption data are listed in Table 1.

All samples show a type I isotherm characteristic of microporous samples with a small hysteresis loop at higher relative pressures, indicating the additional presence of certain mesoporosity in the carbon material. Moreover, the isotherms of sample BSPC_{0.03} present an inflection point at very high relative pressures due to the condensation in the interparticle space and/or the presence of macroporosity. All isotherms exhibit a sharp knee at low relative pressures $P/P_0 = 0.01$ indicating the presence of narrow micropores. The BSPC_{0.06} sample exhibits the highest BET surface area of 645 m²/g.

In Fig. 6 it can be seen the variation in surface area (BET) and pore volume of the BSPCs based on the molar ratio (R/BzC).

The results in Fig. 6 show that the lower molar ratio R/BzC favors the development of mesoporosity with an appropriate development of microporosity. This effect is very desirable since the presence of mesopores should improve the mass transport of chemical species (reactants, products, ions) while the surface area is large.

3.3. Electrochemical behavior of BSPC carbon materials electrodes

Cycling voltammetry measurements were carried out in order to examine the BSPCs electrochemical properties. In Fig. 7 are shown the cyclic voltammograms of different BSPCs in 1 M H₂SO₄ at 50 mV/s.

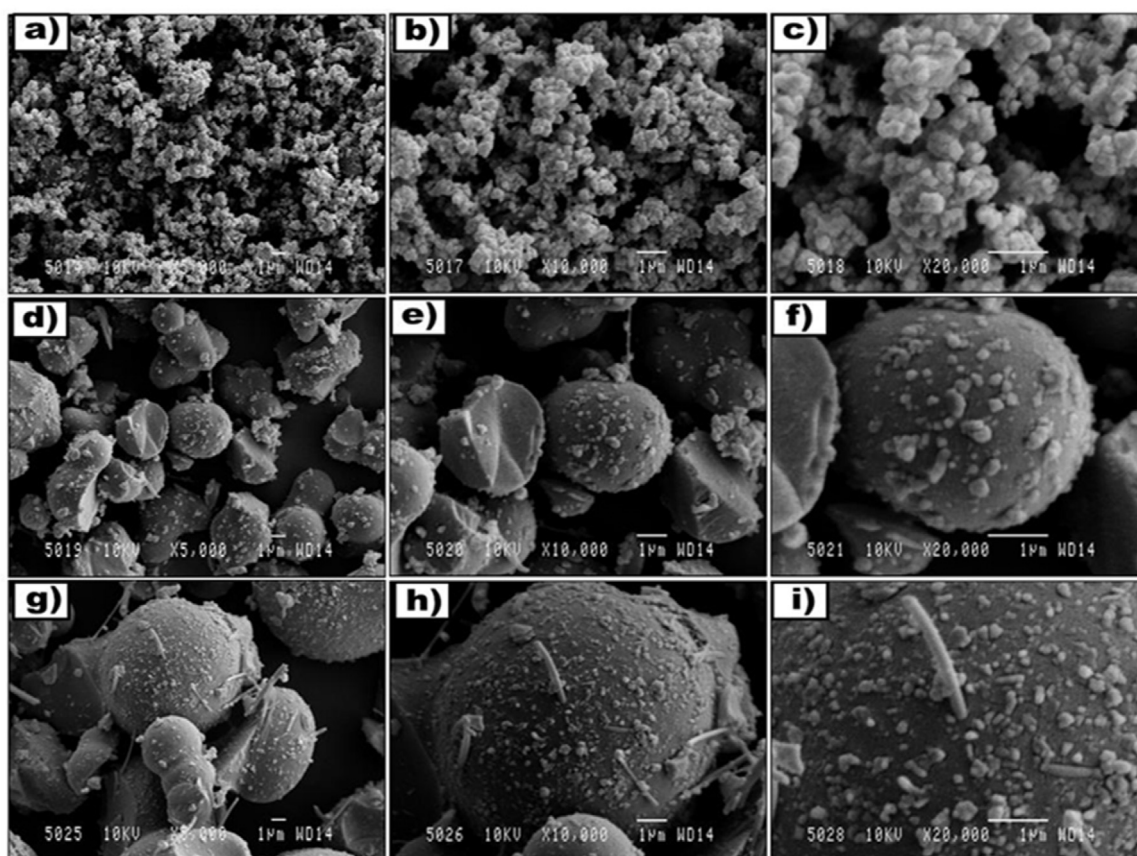


Fig. 4. SEM images obtained by scanning electron microscopy of a-c) BSPC_{0.03}; d-f) BSPC_{0.06}; g-i) BSPC_{0.12} at different magnifications.

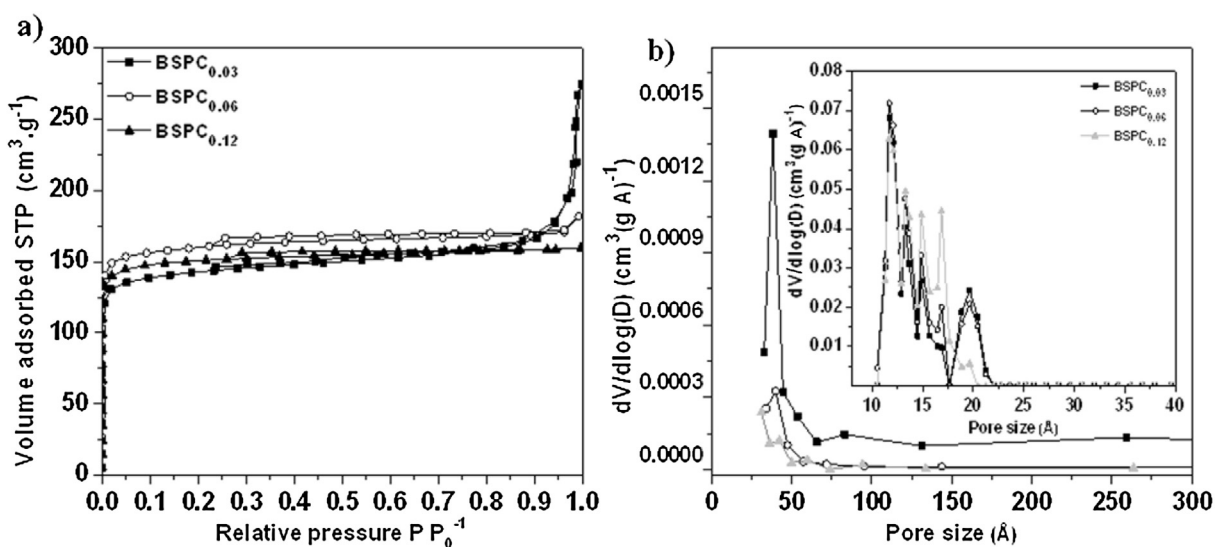


Fig. 5. a) Nitrogen adsorption isotherms of BSPCs prepared with different R/B ratios. b) Pore size distribution obtained after application of BJH and NLDFT (inset) methods.

Table 1

Textural properties of BSPCs obtained at different R/BzC ratio.

Samples	Specific surface area ^a (m ² /g)	V ₀ ^b (cm ³ /g)	V _{meso} (cm ³ /g)	V _t ^c (cm ³ /g)	D _p ^d (nm)	D _p ^e (nm)
BSPC _{0.03}	535	0.22	0.20	0.42	4	2
BSPC _{0.06}	645	0.25	0.03	0.28	4	1
BSPC _{0.12}	590	0.23	0.01	0.25	3	1

^a Determined from BET theory.

^b Determined from Dubinin-Radushkevich.

^c Volume adsorbed at p/p_0 of 0.98.

^d Determined after application of the BJH method to the desorption branch.

^e Determined after application of the NLDFT method (slit/cylinder pore, equilibrium model).

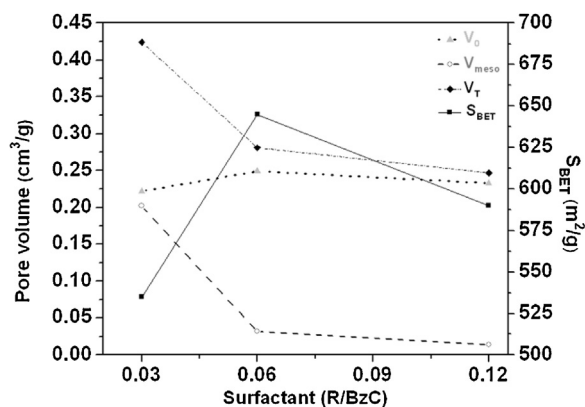


Fig. 6. (Right) BET surface areas of BSPCs as a function of R/BzC molar ratio (Left) Micro-meso and total pore volume for the different samples.

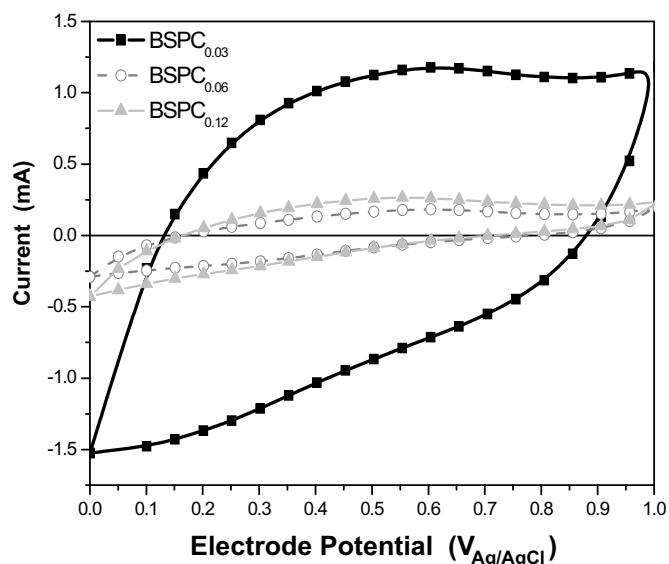


Fig. 7. Cyclic voltammogram of a carbon BSPCs electrode in 1 M H₂SO₄. Scan rate: 50 mV/s.

The shape of the cyclic voltammogram indicates that the BSPCs electrical charge and discharge response are reversible and only small indications of the presence of pseudocapacitive peaks are detected.

The specific capacitance was quantitatively measured using electrochemical impedance spectroscopy. In Fig. 8 the experimental results are shown in Nyquist plots.

The Nyquist plots of BSPc (Fig. 8) exhibits a capacitive behavior in the low frequency range which involves not a vertical dependence of the imaginary part, as expected for pure capacitive behavior but a skewed line which could be related with the existence of a semicircle with a centre at very low frequencies (beyond the minimum frequency available in our instrument set-up). A similar behavior has been observed before [21]. However, the resistance changes weakly with the frequency and the behavior tends to approach that of a pure capacitance, allowing to use the value at the lowest frequency as the maximum capacitance. The specific capacitances data obtained at the lowest frequency are summarized in Table 2.

As it can be seen, the specific capacitance value is weakly affected by the stabilizer/monomer ratio, in agreement with the similar values of surfaces areas obtained by measuring the textural properties.

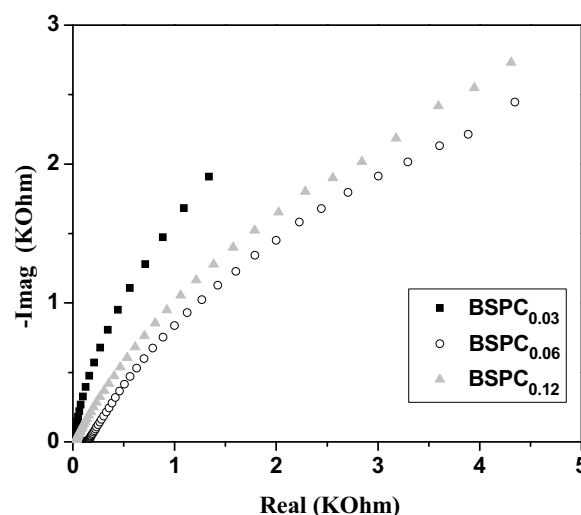


Fig. 8. Impedance plot measured from 1×10^4 to 2.8×10^{-3} Hz of BSPCs. Measurement potential = 0.5 V vs Ag/AgCl. The insert shows the magnification of the high frequency range.

Table 2

Specific capacitance of BSPCs obtained by cyclic voltammetry and electrochemical impedance spectroscopy.

Material	Specific capacitance (F/g) C_{EIS}
BSPC _{0.03}	179
BSPC _{0.06}	140
BSPC _{0.12}	125

Specific capacitance obtained at 0.25 V and at a frequency 0.0028 Hz.

As can be observed the values of specific capacitance, for BSPC_{0.03} obtained using BzC are larger in comparison with other methods such as supercritical drying [39,40] or freeze drying [41,42].

The results suggest that the mechanism previously proposed before for porosity stabilization [11], is general and could be applied using other cationic surfactants, besides CTAB, and even mixtures like the benzalkonium chloride. The mechanism for cationic micelles to stabilize the gel nanoparticles is described in Fig. 9.

During the first stage of gelation, each nanoparticle grows individually and it is dispersed in the solution. Later on, these particles are added together to form the interconnected structure and finally the cross-linked structure is formed. When the relative benzalkonium chloride concentration is high (R/BzC low), the micelles act directly as a template and stabilize the dispersion of the polymeric nanoparticles, thus preventing the pore collapse during the drying step. At low surfactant concentration (R/BzC high) an aggregation of the nanoparticles occurs and microporous areas are generated in the structure, accompanied by a more pronounced pore collapse during drying of the resin.

4. Conclusions

The use of industrial quality cationic surfactants (benzalkonium chloride) to act as stabilizer of a resorcinol-formaldehyde gel nanoporous structure is demonstrated. Using this surfactant, the production cost of carbon materials could be strongly diminished. The presence of the cationic surfactant avoids the collapse of the wet gel during the air drying. The thermal behavior of the resin during the carbonization step was analyzed by thermogravimetric measurement, the results show a mass loss of about 40%.

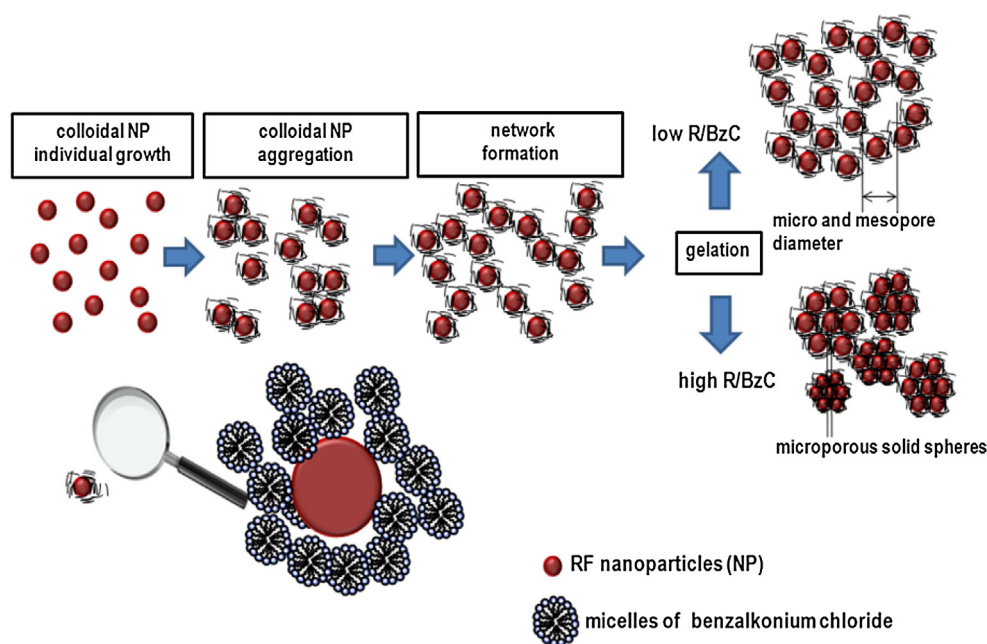


Fig. 9. A schematic representation of the porous resin formation mechanism.

The method proposed here simplifies greatly the production of porous carbon by making unnecessary to use complex drying procedures, cumbersome solvent exchange and long curing times. In addition, organic solvents are not utilized in our approach, reducing the overall environmental impact preparing such novel materials. The surfactant is still retained in the RF matrix after drying and it is released during pyrolysis at a temperature about to 600 °C. The BSPC material with the better porosity was synthesized at a molar ratio R/BzC of 0.03. The materials synthesized in this condition achieve larger surface area 535 m²/g, including both micro and mesopores. The increment of molar ratio R/BzC shifts the pore size distribution to lower size diameters, generating microporous solid spheres.

The BSPCs present specific capacitances in the range 125–179 F/g (measured by electrochemical impedance spectroscopy at 2.8 mHz).

The results suggest that the role of cationic surfactant micelles, previously proposed [11], is general of cationic surfactants and not a special effect of cetyltrimethylammonium bromide (CTAB). Such result is relevant since, in the best of our knowledge, only CTAB has been previously used as surfactant to stabilize porosity of RF resins. Moreover, since benzalkonium chloride is a mixture of surfactants, the successful stabilization of gel porosity during drying suggests that micelles of different sizes can stabilize the nanoparticle structure.

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