**Tailoring the Textural Properties of Hierarchical Porous Carbons
using DESs**

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Abstract

Soft-template approaches have been frequently applied for the preparation of porous carbons. Most of these processes proved highly effective for the preparation of mesoporous carbons with pore diameters below 10 nm but less explored has been the preparation of carbons with mesopores larger than 10 nm. The lack of syntheses providing large and well-interconnected mesopores is by no means a trivial issue because limits the achievement of materials suitable for applications where pore surface accessibility is crucial – e.g. electrodes in supercapacitors or adsorbents in flow-through systems, among others. In this work, we have used deep eutectic solvents (DESs, a sort of ionic liquids that are obtained by complexation of quaternary ammonium salts with hydrogen-bond donors) composed of resorcinol, urea and choline chloride for the preparation – via formaldehyde polycondensation and subsequent carbonization – of hierarchical porous carbons with micropores and large mesopores within the 10 to 20 nm range. The formation of large mesopores took place at the polycondensation stage via a spinodal decomposition process where part of the components forming the DES acted as precursors of the polymer phase, while the other one was segregated into

the polymer depleted phase. Thus, the ultimate dimensions of the mesopores was controlled by the mass ratio between the segregated and condensed phase, and this by the molar ratio of the components forming the original DES. We have finally demonstrated that carbons with larger mesopores exhibited better performance as electrodes in supercapacitor cells.

Graphical abstract

Introduction

Template syntheses have been frequently applied for the preparation of many porous materials. Among others, carbonaceous materials with well define porous structures have been obtained using both hard and soft templates. In the former case, zeolites, alumina membranes, opals and porous silicas have been widely used to obtain carbon replicas.^{1, 2, 3} In the latter case, block copolymers (e.g., pluronics) have typically been the structure directing agents (SDAs) of choice to obtain well-ordered mesoporous carbons.^{4, 5} Moreover, both hard and soft approaches have also allowed the production of 3D hierarchical carbon monoliths with porous structures that ranged from the micro- to the meso- up to the macropore.^{5, 6, 7, 8} Interestingly, the mesopore diameter was in most of cases below 10 nm and there have been less works dealing with synthetic methods that allow the preparation of carbons with larger mesopores – e.g. within the 10-60 nm range.⁹ Within this context, it is worth noting that the achievement of ultra-large and well-interconnected mesopores – rather than isolated ones¹⁰ – is quite interesting in practical terms – e.g. either as electrodes in supercapacitors or as adsorbents of gases and different pollutants – because they provide accessibility to the pore surface. Both hard and soft templates can be used for this purpose as well. Thus, mesocellular carbons have been prepared with the aid of silica as hard template^{11, 12} while with regard to soft templates, pluronics have not been capable by themselves to obtain large mesopores so typical approaches are based on either the addition of a pore expander to them^{13, 14} or their full replacement by other block copolymers like PS-*b*-P4PV, PEO-*b*-PS, or PEO-*b*-PMMA, among others.^{15, 16, 17, 18}

Ionic liquids (ILs) have also received great attention as precursors of porous carbons.^{19, 20, 21} For instance, their negligible vapor pressure and high thermal stability reduce mass loss before the beginning of the decomposition process, are favourable for carbonization processes without applied pressure, and allow the achievement of carbon materials by direct carbonization, thus reducing the preparation time and cost. Moreover, the structural and compositional diversity of ILs – e.g. from the originally described by Paraknowitsch et al. based on 1-ethyl-3-methylimidazolium or 3-methyl-1-butylpyridine and dicyanamide to those described by Antonietti and coworkers and formed with natural compounds (e.g. namely the most familiar nucleobases; adenine, guanine, cytosine, thymine and uracil) up to those recently described by Watanabe and coworkers and based on protic ionic liquids and salts, among others^{22, 23, 24, 25, 26, 27, 28} – allows controlling the structures and properties of the resulting carbon materials. Within the context of this work, it is worth noting how ILs proved highly suitable for the preparation of porous carbons with pores at the micro-to-the-small-mesopore range whereas the design of macropore and/or large mesopore structures has been reported in just

some few cases – e.g. carbonaceous polymers with up to 12 nm in pore diameter,²⁹ nitrogen-doped carbons made from ILs and nucleobases with up to 7.4 nm,³⁰ and ILs composed of bis-imidazolium cations linked to aliphatic groups³¹ – unless additional templates are used.³² Actually, papers describing the use of ILs in the preparation of hierarchical structures with macropores and/or large mesopores are rare not only for carbonaceous polymers but also for other IL-based polymers.^{33, 34}

At this stage, it is worth mentioning a sort of ILs that are obtained by complexation of quaternary ammonium salts with hydrogen-bond donors and were first described as deep eutectic solvents (DESs) by Abbott and coworkers in 2003.³⁵ DESs have been widely used in different processes,^{36, 37, 38, 39} including certain polymerizations reported by our group.^{40, 41} In particular, we have demonstrated that the use of DESs containing resorcinol (R) as carbon precursors allows the preparation of monolithic carbons consisting of highly cross-linked clusters that aggregated and assembled into a stiff and interconnected hierarchical structure with either micro and macropores, or micro and large mesopores.^{42, 43, 44, 45, 46, 47, 48, 49} The bicontinuous porous structure was obtained via a spinodal decomposition process⁵⁰ where part of the components forming the DES acted as precursors of the polymer phase, while the other one was segregated into the polymer depleted phase. Within the context of this work, it is particularly interesting the work describing the use of DESs composed of either R and choline chloride (C) or R, urea (U) and C for the formation of carbons with large mesopores – e.g. of 10 nm in the former case, and 23 nm in the latter one. In this latter case, urea seemed to play a role tailoring the structural features of the resulting carbons at the large-mesopore range.⁴³ Elucidating this role is challenging and by no means trivial considering the above-described limited number of soft-templates that are capable to tailor this particular sort of pores.

In this work, we have prepared DESs based on R and C, and with different molar ratios of U. The eutectic mixtures were studied by ¹H NMR spectroscopy and differential scanning calorimetry (DSC). These DESs were used for the preparation of porous carbons via polycondensation with formaldehyde and a basic catalyst (Na₂CO₃), and subsequent carbonization. The polymers resulting after polycondensation were studied by ¹³C NMR and FTIR spectroscopies to assess the degree of condensation and the U incorporation to the polymer network. The morphology of the carbons obtained after carbonization were studied by scanning and transmission electron microscopies, and their textural properties by N₂ and CO₂ adsorption/desorption isotherms, and Hg porosimetry. The role played by mesoporosity in the capability of these carbons as electrodes in supercapacitor cells was assessed upon assembling two samples – either in monolithic form with 1 mm in thickness or in powdered form and mixed with PVDF – in a two-electrode Swagelok type cell and using H₂SO₄ 2M as electrolyte.

Experimental Section

Materials: Resorcinol (R), urea (U), choline chloride (C), formaldehyde (F) 37 wt% in aqueous solution, sodium carbonate (Na_2CO_3) and polyvinylidene difluoride (PVDF) were purchased from Sigma-Aldrich and used as received. Water was distilled and deionized.

Preparation of carbons: DESs were obtained by physical mixing of the individual components and posterior thermal treatment at 90 °C for 1 hour. Different DESs were prepared varying R, U and C molar ratios. The R to C molar ratio was 3.5:0:1 for the preparation of RU00C sample, while the R, U and C molar ratios were 3.5:0.5:1, 3.5:1:1 and 3.5:2:1 for the preparation of RU05C-DES, RU10C-DES and RU20C-DES respectively. Gels – e.g. RU00C-G, RU05C-G, RU10C-G and RU20C-G – were obtained from their respective DESs following the procedure described in previous works.⁴³ Briefly, a F aqueous solution (37 % wt.) was added to each DES at F to R molar ratio of 2:1. After homogenizing the mixture by gently stirring it, a 140 mg/ml Na_2CO_3 solution was added as RF polycondensation catalyst (Cat) at R to Cat molar ratio of 50:1. Afterward, samples were thermally treated for 6 h at 60 °C and then for 4 days at 90 °C. Every gel was repeatedly washed with deionized water and pyrolysed at 800 °C over 4 hours (the heating ramp was 1.0 °C/min) and under a nitrogen atmosphere to finally obtain their respective carbon monoliths – e.g. RU00C-C, RU05C-C, RU10C-C and RU20C-C.

Samples characterization: DESs and diluted DESs were studied by ^1H NMR spectroscopy using a Bruker spectrometer DRX-500 and deuterated water – D_2O – as solvent. Samples were placed in capillary tubes, using deuterated chloroform – CDCl_3 – as an external reference. Gels were washed and freeze-dried, and the resulting residues were also analysed by ^1H NMR spectroscopy. In this case, samples were diluted in D_2O , placed in capillary tubes, and analysed using deuterated dimethyl sulfoxide (DMSO-d_6) as an external reference. The viscosity of the DESs was measured with a Brookfield Digital Rheometer DV-III+ at 22 °C. Differential scanning calorimetry (DSC) was performed with a TA Instruments Model DSC Q-100 system, under a nitrogen atmosphere. The samples were run in an aluminum pan in a sealed furnace, stabilized for 30 min at 50 °C, and then cooled to –90 °C before heating at rates of 1 and 10 °C/min. Thermogravimetical analysis (TGA) of the samples were carried out in a TA Instruments TGA Q500. Samples were heated at 10 °C/min from 25 °C to 1000 °C under a N_2 atmosphere. Fourier transform infrared (FTIR) spectroscopy of the gels was performed in a FTIR spectrometer (Bruker Model IFS60v). Solid-state ^{13}C CPMAS NMR spectra of the RF gels were obtained using a Bruker Model AV- 400-WB spectrometer, by applying a standard cross-polarization pulse sequence. X-Ray Photoelectron spectroscopy (XPS) surface analysis of the resins was performed in a VG ESCALAB 200R electron spectrometer equipped with a hemispherical electron analyser and an Al $\text{K}\alpha$ ($h\nu=1486.6$ eV, 1 eV= $1.6302\cdot 10^{-19}$ J) 120 watts X-ray source. Elemental chemical analysis of the resins was performed in an LECO Elemental Analyzer CHNS-932.

The morphology of the different carbons was studied via scanning electron microscopy (SEM), using a SEM Hitachi S-3000N system and via transmission electron microscopy (TEM), using a JEOL-2000 system operating at 200 keV. Nitrogen adsorption/desorption isotherms were conducted using a volumetric instrument (ASAP 2010, Micromeritics) on samples previously outgassed under dynamic conditions (ca. 10^{-5} Torr) at 100 °C for 6 h. Brunauer-Emmett-Teller (BET) theory was used to calculate the specific surface area (S_{BET}) of the materials. The total pore volume was determined from the nitrogen adsorption isotherms at $p/p_0 \sim 0.99$, and the micropore volume was calculated using the Dubinin–Radushkevich (DR) equation. The narrow microporosity (volume and average diameter) was further assessed by CO_2 adsorption isotherms at 0 °C. The PSD analysis of the N_2 adsorption/desorption isotherms was performed using the Barrett–Joyner–Halenda model (BJH), the density functional theory model (DFT) and the new non-local DFT model (2D-NLDFT-HS) for carbons that assumes energetic heterogeneity and geometrically corrugated pores.⁵¹

Cyclic voltammetry and chrono-potentiometry were performed at room temperature using a potentiostat/galvanostat PGSTAT30 Voltalab. Measurements were carried out in a two-electrode Swagelok type electrochemical cell. The monolithic carbons originally obtained from the synthesis were polished to obtain plane-parallel cylindrical monoliths with a thickness of 1.1 mm and a diameter of 9 mm, so the aspect ratio – diameter vs. thickness – was ca. 8. Two of these monoliths – with an identical mass of ca. 22 mg per cm^2 of current collector – were assembled in the cell separated by polyvinylidene difluoride (PVdF) paper using H_2SO_4 2 M solution as electrolyte. Samples of ground carbon were also prepared by physical mixing powered carbon with PVdF at 5 wt% and subsequent suspension in N-methyl-2-pyrrolidone under ultrasound agitation. Drops of each suspension were cast on tantalum sheet obtaining a final load of ca. 22 mg per cm^2 of current collector. In this case, the electrodes thickness was ca. 100 μm , so the aspect ratio was 90.

The specific capacitance was obtained from the galvanostatic plots recorded at different current densities, I , using the voltage range V , the discharge time, t_d , and the mass of the active material, m_c , for the calculation:

$$C = \frac{I \cdot t_d}{V \cdot m_c}$$

The power density – P – and the energy density – E – were obtained using the following expressions:

$$E = \frac{C \cdot V^2}{2}$$

$$P = \frac{I \cdot V}{4 \cdot m_c}$$

where R_s was the series resistance of the material. Volumetric results were obtained multiplying gravimetric ones by the density of the materials – e.g. 0.9 g/cm^3 .

Results and discussion

As mentioned in the introduction, we prepared eutectic mixtures of R, U and C with different molar ratios to obtain RU00C-, RU05C-, RU10C- and RU20C-DES (Table 1). It is worth noting that, just for sake of simplicity, we have named the binary DES composed of R and C as a ternary one where the U content is nil. Every DES was simply obtained by thermally treating (at 90 °C) the physical mixture of the components. The formation of eutectic mixtures was first revealed by the liquid nature of the mixtures at room temperature despite the melting points of the individual components were 110 °C for R, 133 °C for U and 302 °C for C (Figure 1). DES formation was further assessed by DSC (Figure 2). RU05C and RU20C displayed both melting point (T_m) and a vitrification (T_c) temperatures, whereas neither T_m nor T_c were displayed in the DSC trace of RU10C-DES. The lack of T_m and T_c revealed the not-easily crystallizable features of the mixtures with intermediate U contents. In this regard, the behaviour of RU00C could seem anomalous but, as mentioned above, this DES was a binary mixture so its physicochemical features differed from those of ternary ones. Finally, one could observe the inverse correspondence between the glass transition temperatures (T_g) of every DES and their respective viscosities (Table 1). The formation of hydrogen bond complexes between the DES components was also confirmed by ^1H NMR spectroscopy. In particular, the chemical shifts of the signals ascribed to R, U and C in the different DESs were up-field shifted as compared to those of the individual components (Figure S1 and Table S1).

Polycondensation was promoted for every DES by addition of an aqueous solution of F and Na_2CO_3 . It is worth noting that the ^1H NMR spectra of DESs diluted in D_2O with similar DES contents to those reached upon F addition – e.g. 56 wt% for RU00C-DES, 60 wt% for RU05C-DES, 61 wt% for RU10C-DES, and 63 wt% for RU20C-DES – exhibited chemical shifts that were in between those depicted in Table S1 for the components in neat DESs and for the individual components, thus revealing a partial rupture of the hydrogen bond complexes that made some R molecules available to initiate the polycondensation (Figure S2 and Table S1). In previous works, we hypothesized that polycondensation evolves via a spinodal decomposition process where some of the DESs components form the polymer phase, while the remaining ones are segregated into a polymer depleted phase that ultimately results in the formation of a bicontinuous structure. The most simple case illustrating this mechanism would be RU00C, with R forming the polymer phase upon polycondensation and C being segregated. C segregation was actually confirmed by washing the resin resulting after polycondensation with abundant water and analysing the residue obtained after freeze-drying by ^1H NMR spectroscopy (Figure S3). Meanwhile, the residue obtained from resins prepared with urea-based DESs – e.g. RU05C-G, RU10C-G and RU20C-G – contained not only C but also U, the content of which in the residue increased along with the U content in the original DES

(see data obtained by elemental chemical analysis in Table S2). Interestingly, the chemical analyses also indicated that the molar ratio of U to C in the residue was well below that in the original DES, so it seems that part of U was incorporated to the polymer network. Actually, the TGA analyses of the different gels revealed mass losses that increased along with the U content in the original DESs – i.e. RU00C-G < RU05C-G < RU10C-G < RU20C-G (Figure 3).

The incorporation of U to the polymer network was also confirmed by the presence of peaks at ca. 161 ppm and 1634 cm^{-1} ascribed to carbonyl groups of partially substituted U in, respectively, the solid-state ^{13}C NMR and FTIR spectra of the different polymers obtained after polycondensation (Figures 4 and 5).^{52, 53} With regard to RUC samples, the peak at 40 ppm in the ^{13}C NMR spectra – ascribed to methylene groups in amides⁵⁴ – as well as the bands at 1720 cm^{-1} and 1560 cm^{-1} in the FTIR spectra – ascribed to the presence of imide I and to imide II functional groups – provided further insights about the incorporation of U to the polymer network.⁵³ Moreover, the chemical analyses and XPS spectra of the resulting polymers revealed that the nitrogen content increased along with the U content in the DES originally used for polycondensation – e.g. RU05C-G < RU10C-G < RU20C-G (Table 2). The N1s deconvolution of the XPS spectra of the polymers also revealed the nature of the nitrogen incorporated after polycondensation in every case – i.e. amide-N, ester-N or imide-N at 399.5 ± 0.3 eV, pyrrolic-N or pyridone-N at 400.3 ± 0.3 eV and N-alkylammonium at 402.0 ± 0.5 eV (Figure 6).^{55, 56, 57} Interestingly, the increase of the U content in the original DES favoured the formation of pyrrolic-N rather than pyridinic-N groups whereas played no role in the fraction of N-alkylammonium ones. The C1s spectra also provided interesting information. Thus, spectra deconvolution revealed the presence of three main types of carbons in every carbon – i.e. aromatic and aliphatic C-C and C-H bonds at 284.8 eV, aromatic carbon linked to nitrogen or oxygen (C-N/C-O/C-OH) at 286.3 eV and carbon in carboxylic groups (C=O) at 287.8 eV,⁵⁵ regardless of the U content in the original DES. Interestingly, the O1s spectra provided the first insights about the occurrence of polycondensation, by the presence of both methylene ether and ether bridges at 532 and 531 eV, respectively.⁵⁸

N_2 and CO_2 adsorption–desorption isotherms were also useful to reveal certain insights about the U incorporation into the polymer network (Figures 7a and 7b). Since the seminal work by R. W. Pekala,⁵⁹ it is widely accepted that the synthesis and drying steps determine the pore size distribution at the mesopore and macropore levels, while the microporosity is mostly developed during the pyrolysis step because of the burnout of organic groups that leads to the creation of new pores or voids in the gel.^{60, 61, 62} Nonetheless, one should also consider that, regardless of the increase in micropore volume from carbonization, the original microporosity also depends on the synthesis conditions.^{63, 64} In particular, the pH and the concentration of reagents are the two most influential factors that determine polycondensation and sol-to-gel transition kinetics in a first stage, then the

size of the colloidal clusters that form the xerogels and ultimately the final porous properties of the gels. In all of our syntheses, we used Na_2CO_3 as the catalyst (Cat), the molar ratios of R/F and R/Cat were, respectively, 0.5 and 50, and the pH of every sol was ca. 7. Thus, the only difference among the samples was the molar ratio of U at the DESs used in the starting sols, from nil for RU00C-DES, to 0.5 for RU05C-DES, to 1.0 for RU10C-DES, up to 2.0 for RU20C-DES. Interestingly, the micropore volume of the polymers resulting after polycondensation decreased as the U molar ratio increased (Figures 7a and 7b, and Table 3). This trend was observed for the micropore volumes obtained from both the N_2 and CO_2 adsorption isotherms, indicating that it affects the whole microporosity (i.e., medium-sized and narrow micropores). One may wonder if this difference in the textural properties could be ascribed to slight pH fluctuations eventually coming from the presence of different U concentrations at the starting solutions or to certain underestimation of the surface area because of the somehow impeded N_2 adsorption on the urea-functionalized porous surface. As mentioned above, the pH of the different sols was similar so the former occurrence must be disregarded. Moreover, sols with different pHs typically result in gels with colloidal clusters exhibiting different sizes, and this was not the case as revealed the TEM micrographs of the resulting carbons (see below RU00C-C, RU05C-C, RU10C-C, and RU20C-C in Figure 8). Based on this and considering the above-described solid-state ^{13}C NMR, FTIR and XPS results, we ascribed the micropore volume evolution to the urea-functionalization – in form of carbamate groups – of the porous surface.

Interestingly, the porosity at the mesopore range also followed a certain tendency with the U content. In every case, the nitrogen adsorption-desorption isotherms were type IV and exhibited a marked type H1 hysteresis loop that shifted to higher relative pressures from RU05C-G to RU20C-G. This increase in the pore size was confirmed by the pore size distributions (PSDs) obtained from the analysis of the isotherms. PSDs were determined using classical methods based on thermodynamic assumptions – e.g. Barrett–Joyner–Halenda (BJH) – and non-classical ones based on statistical mechanics – e.g. density functional theory (DFT) – that take into account that the shape of the adsorption isotherm depends not only on the texture of the porous material, but also on the difference of thermodynamic states between the confined fluid and bulk fluid phase – e.g. non-local density functional theory (NLDFT).⁶⁵ Any of these methods allow the analysis of pores in the mesopore range in which we are particularly interested – being the NLDFT method the most suitable one according to the latest IUPAC technical report.⁶⁶ In any case, the PSDs obtained from all of them – BJH, DFT and NLDFT – revealed how the pore-diameter tends to increase from RU05C-G to RU20C-G (Figure 9, Table 3). We further explored the validity of these results by measuring mercury (Hg) porosimetry (Figure S4, Table 3).

We further explore the validity of these results by measuring mercury (Hg) porosimetry (Figure S4, Table 2). In this case, the average mesopore size evolved contrary to what we observed at the

PSDs obtained from BJH, DFT and NLDFT analysis. One may wonder whether this discrepancy can be ascribed to the presence of ink-bottle pores, the neck width of which may determine the achievement of different figures of mesopore size depending on the source of data –e.g., adsorption/desorption branch of N₂ isotherms or Hg intrusion –used for the calculation.^{69,70} However, it is worth remembering at this stage that the increase of the mesopore size from RU05C-G to RU20C-G was observed at the N₂ adsorption isotherms themselves –by the shifting of the hysteresis loops to higher relative pressures-where pore geometry assumptions were yet out of consideration.^{66,67} Moreover, the evolution of the mesopore size obtained from Hg porosimetry changed in carbonized samples, concurring now with the evolution reflected by the N₂ adsorption isotherms- and, obviously, with that reflected by the PSD obtained from BJH, DFT and NLDFT analysis (see further explanations below, Figures 9, S4 and Table 4). Based on this, we attributed the above-discussed disagreement in the evolution of the average mesopore size of RUC-G samples to the tendency of Hg porosimetry to underestimate the pore size when functional groups are grafted on the material's surface – i.e. the larger functionalization the larger the underestimation.^{70,67} Actually, the micropore volume obtained from Dubinin–Radushkevich analysis of both N₂ and CO₂ isotherms also exhibited a similar evolution because of the urea-functionalization – in form of carbamate groups – of the porous surface (Figures 7a and 7b, and Table 3).

Based on these results, we could discuss now about the mechanism governing the formation of the bicontinuous structure in our materials. As mentioned in the introduction of this work, the bicontinuous structure was formed at the polycondensation stage via a spinodal decomposition process where some of the DES components form the polymer phase, while the remaining ones are segregated into a polymer depleted phase. As confirmed above by the chemical analyses of the residues obtained after through full washing of RUC-G samples, part of U was segregated besides C and its content increased along with its original content at the DESs. Thus, the pore-diameter increase described above revealed how the higher the neat amount of matter segregated to the polymer depleted phase, the larger the dimensions of the pore network. It is worth noting that RU00C samples followed a different trend and exhibited an intermediate value of pore diameter rather than the lowest one of the set of samples according to the segregation of just C. However, one should also consider in this case whether U plays a role in the affinity of the phases that are ultimately segregated.

Both ¹³C NMR and FTIR spectroscopies also provided information about the efficiency of the chemical make up of the polymers.^{43, 52} In the ¹³C NMR spectra of RUC samples, the intensity of peaks assigned to methylene at 20-40 ppm and to methylene ether groups at 59 ppm were indicative of a significant number of linkages between R rings (Figure 4).⁴³ This was also the case in the FTIR spectra of RUC samples, with the intensity of bands assigned to methylene and methylene ether groups –

e.g. CH₂ groups at ca. 2920 and 1470 cm⁻¹ and C-O benzyl ether groups at 1220 and 1100 cm⁻¹ in Figure 5. The degree of polycondensation reached in the different samples can be estimated from the integration of the signal at 152 ppm versus the sum of the signals at 20-40 ppm plus that at 59 ppm. Looking at the resulting figures, one could see how similar was the degree of condensation for the different RUC-Gs.

The thermal treatment of the polymers at 800 °C in a nitrogen atmosphere produced non-nitrogen-doped porous carbons – with conversions of ca. 80% for all the samples – as consequence of the removal of the nitrogen functional groups during carbonization. SEM and TEM micrographs revealed the formation of a bicontinuous porous structure with an aggregates-of-particle-like morphology in every carbon⁶⁸ that is typical of DES-assisted polycondensation processes (Figure 8). The textural properties of the different carbons were studied by gas adsorption – N₂ at –196 °C and CO₂ at 0 °C – and Hg porosimetry. Nitrogen adsorption–desorption isotherms were type IV with a sharp increase in adsorption at low relative pressures – characteristic of microporous materials – and a hysteresis loop at relative pressures close to unity – typically ascribed to capillar condensation in large mesopores (Figure 7c). CO₂ adsorption–desorption isotherms also confirmed the presence of a narrow microporous network throughout the RUC-Cs (Figures 7d). Table 4 summarizes the Brunauer-Emmett-Teller surface area, the micropore volume and the mesopore diameter – the latter calculated as described above for RUC-Gs, this is applying BJH, DFT, and NLDFT methods to the N₂ isotherms, as well as from Hg porosimetry (see also Figures 9 and S4). First of all, it is worth noting that, after the pyrolysis step where the burnout of organic groups leads to the creation of new pores or voids in the gels, microporosity developed further in carbons coming from resins containing U than in the carbon coming from the urea-depleted one. Moreover and considering only those carbons coming from resins containing U, the micropore volume development was typically in correspondence with the U incorporated to the polymer network during polycondensation – i.e. the larger the U content, the larger the micropore volume development. Carbonization also caused an interesting evolution of the mesopore diameter. Thus, all of the PSDs – regardless the method applied to obtain them – revealed a decrease in the mesopore diameter of RU00C-C most likely due to the occurrence of some shrinkage during pyrolysis. Meanwhile, the mesopore diameter of all the samples containing U remained basically unmodified (Table 4), indicating a certain compensation between those processes leading to a mesopore diameter decrease – e.g. shrinkage – and those leading to a mesopore diameter increase – e.g. the release of urea-groups originally grafted to the surface. Interestingly, in all cases the mesopore diameters exhibited a linear increase from RU00C-C to RU20C-C (Figures 9 and S4, and Table 4). It is worth noting that the average mesopore diameters obtained from Hg porosimetry for RUC-Cs – where all the urea-based functional groups were cleaned

off from the porous surface by carbonization – agreed well with those provided by the analysis of the gas adsorption data (Table 4).

After demonstrating the capability of DESs containing U for controlling some textural features of the carbons resulting after polycondensation and pyrolysis, we evaluated the role played by the mesopore diameter of some certain carbons in their performance as electrodes in a supercapacitor cell. For this purpose, the micropore volumes of the studied carbons should be as close as possible to minimize further contributions coming from any additional parameter. Among the above-studied RUC-Cs, we selected RU10C-C and RU20C-C as the samples of choice. According to Table 4, the former carbon exhibited a mesopore diameter narrower than the latter one while the micropore volume remained quite similar in both cases – e.g. $0.27 \text{ cm}^3/\text{g}$ from the CO_2 isotherms. As in some of our previous works on supercapacitors, we used the samples in form of monoliths that we directly assembled – without any further processing, such as using polyvinylidene fluoride (PVDF) as a binder to form pellets and/or adding carbon black to improve the electrode electrical conductivity – into the supercapacitor cell. Prior to their assembly, monoliths of ca. 9.5 mm in diameter were polished to obtain 1.1 mm in height cylinders with parallel plane circular faces that favoured the electrical contact with the current collectors of the supercapacitor cell. The performance of these monoliths as supercapacitor electrodes was evaluated by voltammetry and galvanostatic measurements using H_2SO_4 (2 M in water) as electrolyte. The voltammograms exhibited a rectangular shape characteristic of the electric double-layer (EDL) mechanism (Figure 10a). The specific capacitances of RU10C- and RU20C-C were similar, above 200 F/g in both cases and reaching a maximum of 214 F/g for RU20C-C in agreement with their respective micropore volumes (Figure 10b). Meanwhile, mesoporosity is widely accepted that play a capital role in the retention of the capacity at high current densities, where charge and discharge processes occurring at high rates demand an efficient electrolyte replacement. For this purpose, large mesopores provide “highways” through which electrolyte diffuse efficiently and gain accessibility to the micropore surface. This is why the sample with wider mesopores – e.g. RU20C – exhibited better capacity retentions at high current densities than the sample with narrower mesopores – e.g. RU10C (Figure 10b).

Nonetheless, one may see that capacitance could only be measured at relatively low current densities – e.g. $8 \text{ mA}/\text{cm}^2$ for RU10C-C and $30 \text{ mA}/\text{cm}^2$ for RU20C-C – as compared to those typically exhibited by other carbon-based electrodes. This was indeed reflected in the power density depicted at the Ragone plot for both RU10C- and RU20C-C (Figure 10c), well below the data typically reported for similar carbons. Nonetheless, it is widely accepted that the electrode performance in terms of power density is strongly dependent on the geometrical aspect of the electrode – e.g. thickness versus contact area with the current collector, this is the electrode mass loading per area of the current collector.⁶⁹ Interestingly, this figure is below $3\text{-}5 \text{ mg}/\text{cm}^2$ in most of the works published to

date on supercapacitors,⁷⁰ within the 5-10 mg/cm² range in just some few ones,⁷¹ and quite rarely above 10 mg/cm².⁷² However, the critical work published by Gogotsi and Simon indicated that extrapolation from lab results to real applications is only valid for electrodes weighing (at least) 10 mg per cm² of current collector. In our monoliths, the mass loading per area of the current collector was ca. 92 mg/cm². The processing of RU20C-C in form of pellets of 9 mm in diameter and 0.2 mm in thickness – upon the grinding the monoliths and the subsequent mixing of the resulting fine powder with PVDF 5 wt% as binder – provided an electrode with a mass loading per area of the current collector of ca. 22 mg/cm². In this case, the energy density experienced a significant decrease as compared to that found for the same sample in form of monolith because of the incorporation of non-active compounds to the electrode. However, the power density delivered by these electrodes reached remarkable figures as compared to the heavier and thicker original monoliths (Figure 10c).

Conclusions

We have prepared different DESs – based on resorcinol, urea and choline chloride or resorcinol and choline chloride – to be used in the preparation of porous carbon monoliths and to control their textural properties. We had previously demonstrated that DES-assisted syntheses promoted the formation of a bicontinuous structure via spinodal decomposition process where some of the DES components form the polymer phase, while the remaining ones are segregated into a polymer depleted phase. In this paper, we found that the increase of the urea content in the original DES provided an easy way to tailor the pore dimensions of the resulting carbons in the large-mesopore range – for mesopore diameters above 10 nm. The combination of large mesopore diameters and high surface areas make these carbons suitable as electrodes in supercapacitor cells. We compared the performance of two of these carbons – e.g. RU10C- and RU20C-C – as electrodes using them either in form of monoliths or in powdered form. In monolithic form, the specific capacitance of both RU10C- and RU20C-C reached remarkable values of ca. 200 F/g in both cases while capacitance retentions were better for the sample with higher mesopore diameter. Nonetheless, the power energy delivered by both samples was quite poor. Interestingly, when RU20C-C was powdered and mixed with PVDF, the specific capacitance experienced a slight decrease because of the PVDF lacking of EDL features, but there was a significant enhancement of the performance in terms of power density – more than 100-fold as compared to that of the monolith – because of the change of the sample geometrical aspect.

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Table 1 – Molar ratios and physicochemical features – e.g. viscosities measured at 20 °C and glass transition temperatures, T_g – of the different DESs used in this work.

DESs	R:U:C molar ratio	T_g (°C)	Viscosity (cP)
RU00C-DES	3.5 : 0 : 1	-57	705
RU05C-DES	3.5 : 0.5 : 1	-50	2377
RU10C-DES	3.5 : 1 : 1	-47	2617
RU20C-DES	3.5 : 2 : 1	-42	2696

Table 2 – Ratio of nitrogen versus carbon content – in wt%, from both chemical analysis (a) and XPS (b) – of the gels resulting after polycondensation. The ratio of oxygen versus carbon content – in wt% – obtained from XPS is also included.

Gels	N/C ^a	N/C ^b	O/C ^b
RU00C-G	0.014	0.06	0.32
RU05C-G	0.05	0.10	0.32
RU10C-G	0.08	0.12	0.32
RU20C-G	0.15	0.06	0.34

Table 3 - Summary of data obtained from N₂ and CO₂ adsorption/desorption isotherms – at -196 and 0 °C, respectively – for the different gels prepared in this work.

Carbons	S_{BET} (m ² /g) ^a	Total Volume (cm ³ /g) ^b	Micropore Volume (N ₂) cm ³ /g) ^c	Micropore Volume (CO ₂) cm ³ /g) ^d	L (nm) ^e	Mean Pore Diameter (nm)			
						BJH ^f	DFT ^g	2D-NLDFT-HS ^h	Hg ⁱ
RU00C-G	264	0.64	0.094	0.110	0.59	23.2	27.7	12.6	29.1 - 18.3
RU05C-G	247	0.50	0.095	0.102	0.57	12.2	15.9	8.3	24.9 - 12.6
RU10C-G	186	0.52	0.067	0.087	0.56	18.3	20.1	11.1	21.9 - 13.7
RU20C-G	106	0.39	0.042	0.060	0.56	15.8	25.5	12.8	17.2 - ~10

^a Applying BET equation to the N₂ adsorption isotherms; ^b Determined at $p/p_0 \sim 0.99$; ^c Determined using the Dubinin–Radushkevich equation applied to the N₂ adsorption data; ^d Determined using the Dubinin–Radushkevich equation applied to the CO₂ adsorption data; ^e Average narrow micropore size determined applying the Stoeckli-Ballerini equation to the CO₂ adsorption data; ^f From BJH method; ^g From DFT method; ^h From 2D-NLDFT-HS method; ⁱ From Hg porosimetry.

Table 4 - Summary of data obtained from N₂ and CO₂ adsorption/desorption isotherms – at -196 and 0 °C, respectively – and from Hg porosimetry for the different carbons prepared in this work.

Carbons	S_{BET} (m ² /g) ^a	Total Volume (cm ³ /g) ^b	Micropore Volume (N ₂) (cm ³ /g) ^c	Micropore Volume (CO ₂) (cm ³ /g) ^d	L (nm) ^e	Mean Pore Diameter (nm)			
						BJH ^f	DFT ^g	2D-NLDFT-HS ^h	Hg ⁱ
RU00C-C	692	0.72	0.27	0.22	0.60	12.8	10.4	9.71	8.3
RU05C-C	690	0.68	0.27	0.24	0.57	13.6	17.2	9.26	13.8
RU10C-C	708	0.72	0.26	0.27	0.57	13.5	17.2	9.93	14.2
RU20C-C	631	0.64	0.23	0.27	0.57	15.9	25.5	11.01	18.8

^a Applying BET equation to the N₂ adsorption/desorption isotherms; ^b Determined at $p/p_0 \sim 0.99$; ^c Determined using the Dubinin–Radushkevich equation applied to the N₂ adsorption data; ^d Determined using the Dubinin–Radushkevich equation applied to the CO₂ adsorption data; ^e Average narrow micropore size determined applying the Stoeckli-Ballerini equation to the CO₂ adsorption data; ^f From BJH method; ^g From DFT method; ^h From 2D-NLDFT-HS method; ⁱ From Hg porosimetry .

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Figure 1 – Pictures of RU00C-DES and RU20C-DES (top panel) and RU00C-G, RU05C-G, RU10C-G and RU20C-G (from left to right, bottom panel).

Figure 2 – DSC traces of RU00C-DES, RU05C-DES, RU10C-DES and RU20C-DES.

Figure 3 – TGA curves of RU00C-G, RU05C-G, RU10C -G and RU20C-G in a N₂ atmosphere.

Figure 4 – Solid ^{13}C NMR spectra of (from top to bottom) RU00C-G, RU05C-G, RU10C-G and RU20C-G.

Figure 5 – FTIR spectra of RU00C-G (a), RU05C-G (b), RU10C-G (c) and RU20C-G (d).

Figure 6 – XPS C1s, O1s and N1s spectra of RU00C-G, RU05C-G, RU10C-G and RU20C-G. The the as-acquired-spectra are represented as solid black lines, the spectra of the components resulting from deconvolution as the solid lines with circles in blue, and the fitting curves resulting from the addition of every contribution as solid circles in black.

Figure 7 – Left panel: N₂ adsorption/desorption isotherms at 77 K (a) and CO₂ adsorption/desorption isotherms at 273 K (b) of RU00C-G, RU05C-G, RU10C-G and RU20C-G. Right panel: N₂ adsorption/desorption isotherms at 77 K (c) and CO₂ adsorption/desorption isotherms at 273 K (d) of RU00C-C, RU05C-C, RU10C-C and RU20C-C.

Figure 8 – SEM (left panel) and TEM (right panel) micrographs of RU00C-C (A), RU05C-C (B), RU10C-C (C), and RU20C-C (D). Scale bar is 2 μm in SEM micrographs and 30 nm in TEM ones.

Figure 9 – BJH, DFT and 2D-NLDFT-HS pore size distributions of the different resins and carbons.

Figure 10 – (a) Cyclic voltammetry measured at 0.5 mV/s using RU10C (grey) and RU20C (blue) monoliths as electrodes. (b) Plot of specific capacitance (F/g) vs. current density (mA/cm^2) obtained using RUC10C-C ($\bullet$) and RU20C-C ($\blacktriangledown$) monoliths of 1-mm-thickness as electrodes (see the inset for a picture of two representative RU10C monoliths), and RU20C-C after grounding and mixing with PVdF – 5wt% – as binder (∇). (c) Ragone plot representing the power and energy density – in volumetric terms – obtained for RU10C-C ($\bullet$) and RU20C-C ($\blacktriangledown$) monoliths, and for RU20C-C after grounding and mixing with PVdF – 5wt% – as binder (∇).

Electronic Supporting Information

of the paper entitled

Tailoring the Large Mesoporosity of Hierarchical Porous Carbons with DESs

by

N. López-Salas et al.

Figure S1 – ^1H NMR spectra (using CDCl_3 as external reference) of (A) RU00C-DES, (B) RU05C-DES, (C) RU10C-DES and (D) RU20C-DESs.

Figure S2 – ^1H NMR spectra (using CDCl_3 as external reference) of (A) RU00C-DES, (B) RU05C-DES, (C) RU10C-DES and (D) RU20C-DES diluted in water.

Figure S3 – ^1H NMR spectra (using DMSO as external reference and D_2O as solvent) of the residue obtained after thorough full washing of (A) RU00C-G, (B) RU05C-G, (C) RU10C-G and (D) RU20C-G and subsequent freeze-drying.

Table S1 - ^1H -NMR chemical shifts of RU00C-DES, RU05C-DES, RU10C-DES and RU20C-DES in neat and diluted form. The spectra were recorded using D_2O as solvent and CDCl_3 as the external reference. The chemical shifts of resorcinol (15 wt%), choline chloride (12 wt%) and urea (15 wt%) in D_2O solution are also included for comparison. The chemical shifts of the residues obtained after thorough full washing of RU00C-G, RU05C-G, RU10C-G and RU20C-G and subsequent freeze-drying are also included. In this case, the spectra were recorded using D_2O as solvent and DMSO as the external reference.

Sample	$\delta(\text{ppm})$						
	R			ChCl			U
	H at C5	H at C4 & C6	H at C2	H at C2	H at C1	H at CH_3	H at NH_2
R- CDCl_3	6.99 (1H)	6.34 (2H)	6.31 (1H)	-	-	-	-
C- CDCl_3	-	-	-	4.10 (2H)	3.56 (2H)	3.24 (9H)	-
C-DMSO				3.46 (2H)	2.56 (2H)	2.27 (9H)	
U- CDCl_3	-	-	-	-	-	-	5.5 (4H)
RU00C-DES	5.76 (3.5H)	5.63 (7H)	5.61 (3.5H)	2.74 (2H)	1.83 (2H)	1.52 (9H)	-
RU00C-DES diluted	6.78 (3.5H)	6.21 (7H)	6.26 (3.5H)	3.49 (2H)	2.70 (2H)	2.41 (9H)	-
RU00C-G extract	-	-	-	4.07 (2H)	3.53 (2H)	3.22 (9H)	-
RU05C-DES	6.10 (3.5H)	5.67 (7H)	5.83 (3.5H)	2.79 (2H)	1.87 (2H)	1.56 (9H)	4.89 (2H)
RU05C-DES diluted	6.78 (3.5H)	6.27 (7H)	6.22 (3.5H)	3.49 (2H)	2.69 (2H)	2.40 (9H)	5.48 (2H)*
RU05C-G extract	-	-	-	3.44 (2H)	2.95 (2H)	2.62 (9H)	-
RU10C-DES	6.10 (3.5H)	5.80 (7H)	5.65 (3.5H)	2.77 (2H)	1.85 (2H)	1.54 (9H)	4.89 (4H)
RU10C-DES diluted	6.80 (3.5H)	6.24 (7H)	6.28 (3.5H)	3.51 (2H)	2.72 (2H)	2.43 (9H)	5.50 (4H)*
RU10C-G extract	-	-	-	3.43 (2H)	2.94 (2H)	2.61 (9H)	-
RU20C-DES	6.13 (3.5H)	5.79 (7H)	5.66 (3.5H)	2.80 (2H)	1.91 (2H)	1.61 (9H)	4.94 (8H)
RU20C-DES diluted	6.82 (3.5H)	6.25 (7H)	6.29 (3.5H)	3.54 (2H)	2.76 (2H)	2.47 (9H)	5.52 (8H)*
RU20C-G extract	-	-	-	3.50 (2H)	2.97 (2H)	2.65 (9H)	-

Table S2 – Total mass and composition – in wt%, as obtained from chemical analyses – of residues obtained after thorough full washing of polymers with water and subsequent freeze-drying, and the molar ratios of urea versus ChCl in the residue calculated from the wt% of N and C. The molar ratios of urea versus ChCl in the original DES are also included for comparison.

Sample	Mass of residue (mg)	Elemental Composition			U/C molar ratio	
		C (wt%)	H (wt%)	N (wt%)	Residue	Original DES
RU05C	214.00	40.41	9.33	9.50	0.45	0.5
RU10C	228.10	37.79	9.21	9.11	0.72	1
RU20C	262.09	35.22	8.91	10.69	1.18	2

Table S3 – Summary of XPS data – binding energies and atomic ratios – found for RU00C-G, RU05C-G, RU10C-G and RU20C-G.

Sample	C1s	N1s	O1s	O/C at	N/C at	N _{CHN} wt. %	N _{max} wt. %*
RU00C-G	284.8 (52) 285.3 (4) 286.3 (35) 287.7 (9)		532.5	0.352	-	0.84	0
RU05C-G	284.8 (55) 286.2 (34) 287.7 (9) 289.3 (2)	399.4 (57) 400.6 (25) 402.3 (18)	530.8 (25) 532.4 (75)	0.351	0.059	2.93	4.09
RU10C-G	284.8 (56) 286.2 (30) 287.7 (10) 289.2 (4)	399.3 (62) 400.6 (27) 402.1 (11)	530.7 (31) 532.3 (69)	0.345	0.093	4.74	8.05
RU20C-G	284.8 (58) 286.2 (29) 287.7 (10) 289.2 (3)	399.3 (69) 400.6 (24) 402.2 (7)	530.7 (30) 532.3 (70)	0.386	0.174	7.93	15.5

Figure S4– Pore size distribution obtained by Hg porosimetry of resins (RUC-G, left) and carbons (RUC-C, right). Cumulative volume (line, left axis); derivative volume (symbols, right axis).