

# Porous carbon–carbon composite replicated from a natural fibre†

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Highly porous carbon composites, suitable to be used as electrodes in electrochemical double layer capacitors, could be produced by pyrolysis of resorcinol–formaldehyde resins impregnated onto a natural fibre material (cellulosic fabric), without additional template agents or special drying of the polymer gels.

The carbonisation of phenol–formaldehyde resins produces solid compact glassy carbon.<sup>1</sup> However, the resins obtained by condensation of resorcinol with formaldehyde in aqueous media produce a highly porous gel, due to the formation of submicrometre sized clusters.<sup>2</sup> If the gel is dried in air, the porous structure collapses and the resulting material (xerogel) shows small open surface areas. To avoid collapsing, the gel could be dried using supercritical liquids (aerogels)<sup>3</sup> or with low surface tension solvents (ambigel).<sup>4</sup> In both cases, the small surface tension forces do not cause collapse of gel pores. Another way to preserve the porous structure involves sublimation of the water from the pores, by lyophilization of the gels (cryogels).<sup>5</sup> Alternatively, mesoporous inorganic matrices<sup>6</sup> or surfactant micelles<sup>7</sup> could be used to template the pores in the resin. Mesoporous carbon is especially suitable for use as an electrode material in supercapacitors and other energy storage devices<sup>8</sup> because mesopores can be wetted by solutions and the electrical double layer built inside the pores.<sup>9</sup> Since most porous carbons are produced as powders, sintering with other materials is required to produce solid electrodes whereas monolithic materials could be used without further processing. It has been demonstrated that reinforcing carbon aerogels with carbon cloth improves its mechanical properties.<sup>10</sup> While natural fibres microstructures have been replicated into inorganic microstructures,<sup>11</sup> to the best of our knowledge they have not been replicated in porous carbon structures.

In the present communication, it is shown that a carbon–carbon composite could be produced by pyrolysis of resorcinol–formaldehyde (RF) resins formed on a cellulosic fibre fabric. While the original purpose was to hold the resin with the fibre, to improve the mechanical properties, it was found that a highly porous composite material is formed without the use of templates or special drying procedures.

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Resorcinol and formaldehyde were polymerized by heating their aqueous solution, using  $\text{CO}_3\text{Na}_2$  as catalyst. First, the cellulosic fibre fabric was wetted by the solution and then the polymerization was performed by heating in a controlled humidity atmosphere. A brown gel was observed to form onto the fibres. The composite material was then dried in air. Complex shapes and extensive flat pieces could be easily assembled by the method (ESI†). The dry resins were pyrolyzed under a nitrogen stream at 800 °C.

The SEM micrographs of the pyrolyzed composite material looks quite similar (Fig. 1A) to the cellulosic fabric pyrolyzed in the same conditions (Fig. 1B), suggesting that the fibre morphology is replicated in the gel, as has been shown to occur with titania.<sup>12</sup>

The specific surface area of a typical composite ( $558 \pm 3 \text{ m}^2 \text{ g}^{-1}$ ) was calculated from the nitrogen adsorption ( $-196 \text{ }^\circ\text{C}$ ) isotherm (ESI†), using the BET method. The pore size distribution (Fig. 2) was calculated using the BJH method.<sup>13</sup> The profile suggests that,

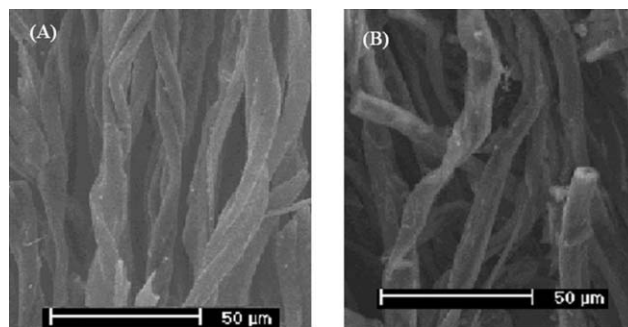


Fig. 1 SEM micrograph of the pyrolyzed composite material.

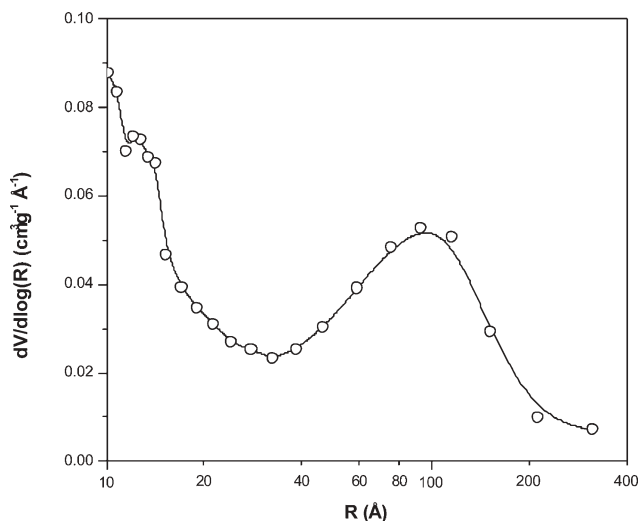


Fig. 2 Pore size distribution of a typical composite carbon.

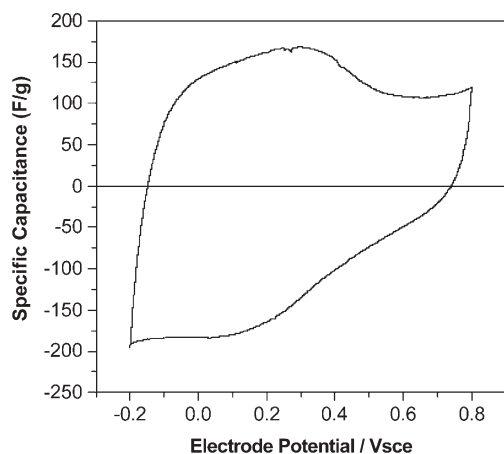
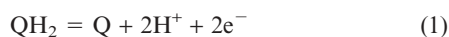


Fig. 3 Cyclic voltammogram of a composite electrode in 1 M H<sub>2</sub>SO<sub>4</sub>. Scan rate = 1 mV s<sup>-1</sup>.

while micropores contribute to the surface area, a significant portion of the pores have diameters in the range between 20 and 500 Å (mesopores). It is noteworthy that a resorcinol-formaldehyde resin, produced in the same conditions but in the absence of cellulosic fibres, shows a negligible surface area.<sup>14</sup> Additionally, the pyrolysis mechanism is different as can be seen in the thermogravimetric profiles (ESI†). The presence of fibres is also necessary since the carbon material obtained from RF resin deposited onto a cellulose film (cellophane®) shows quite different properties (ESI†).

The composite materials were tested as electrode materials for electrochemical supercapacitors. Small pieces of the material were cycled in aqueous solution (1 M H<sub>2</sub>SO<sub>4</sub>), in a conventional three electrode cell. The cyclic voltammetric response (Fig. 3) reveals a large specific capacitance with a broad wave around *ca.* 0.35 V<sub>sce</sub>. The wave observed is likely to be due to the oxidation/reduction of quinone-like functionalities (eqn (1)), present on the carbon surface.<sup>15</sup>



At low scan rates, maximum specific capacitances of up to 160 F g<sup>-1</sup> are measured. The mean specific capacitance in the complete potential window could be obtained by relating the voltammetric charge ( $\Delta Q$ ) with the potential window ( $\Delta E$ ). A value of the mean specific capacitance of 120 F g<sup>-1</sup> is determined in that way. On the other hand, cyclic voltammograms obtained in neutral media (ESI†), where quinones are inactive in this potential range, show mean specific capacitance values of 55 F g<sup>-1</sup>, nearly 50% of the total the value obtained in acid media. This result suggests that pseudocapacitance, related to the faradaic reaction in eqn (1), has an important contribution to the specific capacitance of the material.

The specific capacitance could be also measured using AC impedance. The profiles of AC impedance measurements with frequency and potential (ESI†) are different from those reported before for carbon aerogels.<sup>9</sup> The complex plane plots show constant resistance values, at low frequencies. Therefore, the specific capacitance could be calculated from the impedance values measured at low frequency, when most surface area of the pores is accessed. The specific capacitance (Fig. 4) depends on the electrode

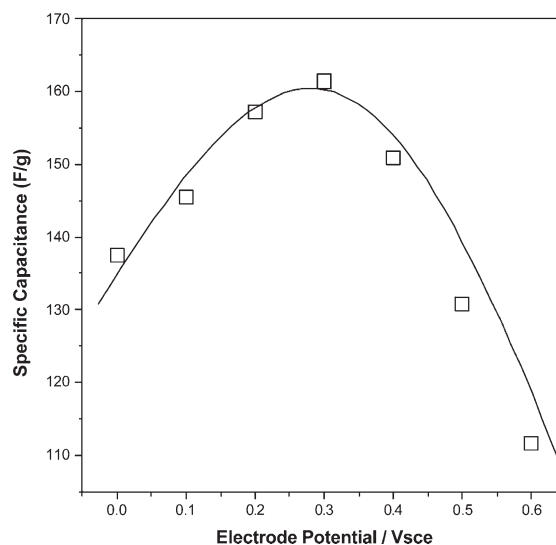


Fig. 4 Specific capacitance of a composite carbon electrode.

potential with a maximum value of *ca.* 160 F g<sup>-1</sup> at 0.3 V<sub>sce</sub>. The dependence of specific capacitance on potential is different from the one observed for carbon aerogels, where almost no dependence was observed in acid media.<sup>16</sup> The values are also higher than those measured with carbon aerogels, in the same media.<sup>17</sup>

An important question is the nature of the ions used up to compensate the for charge stored in the porous matrix. To find out, we used probe beam deflection (PBD) techniques.<sup>18</sup>

The cyclic deflectogram (Fig. 5) shows a negative deflection when the potential is scanned from negative to positive potentials, with a reverse response in the backward scan. The data suggest that ions (protons) are expelled from the material when more positive potentials are applied to the electrode. It is likely that the dominant ion exchange (protons) observed is related to the oxidation of quinone functionalities on the carbon surface (eqn (1)).<sup>19</sup> However, a counterflux of anions, related with population changes in the double layer, cannot be ruled out.<sup>20</sup>

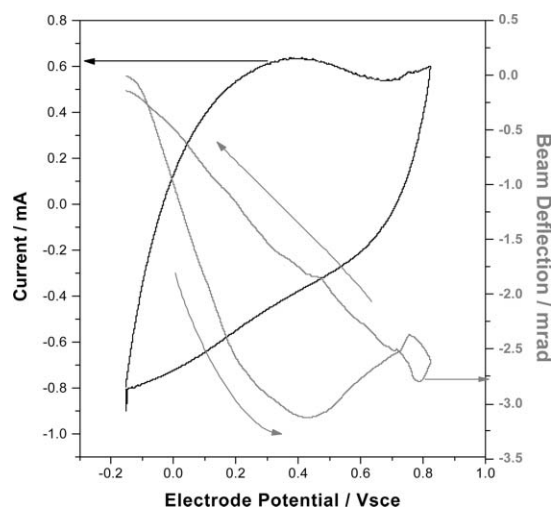
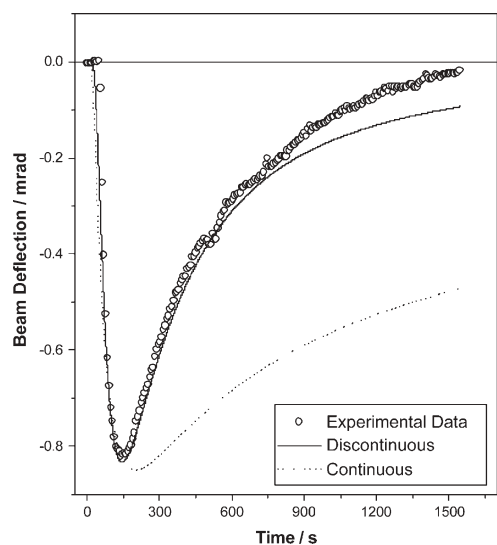


Fig. 5 Cyclic voltammogram (black line) and deflectogram (grey line) of a composite mesoporous carbon in 1 M H<sub>2</sub>SO<sub>4</sub>. Scan rate = 0.7 mV s<sup>-1</sup>. Beam-electrode distance = 1280 μm.



**Fig. 6** Chronodectometric response of a composite mesoporous carbon in aqueous media (0.5 M  $\text{KNO}_3$ ). The potential of the electrode is switched between 0.3 and 0.25  $V_{\text{sce}}$ . Beam electrode–distance = 1352  $\mu\text{m}$ .

It has been suggested, based on chronodectometric data, that ions are transferred continuously from the solution to compensate for the charge inside a carbon mesogel matrix.<sup>18</sup> That means that charge transport is slow inside the matrix. This is likely to be due to an electric potential distribution (transmission line) inside the pores.<sup>21</sup> The model predicts a continuous flux of ions, during the charging, with a  $t^{1/2}$  dependence. Such a model fits the behaviour of carbon mesogels well.<sup>18</sup> However, the chronodectometric data obtained with the composite electrode could not be fitted by a continuous flux of ions but agrees well with the simulation of a discontinuous process (Fig. 6).<sup>22</sup> The negative deflection in Fig. 6 corresponds to anion expulsion from the double layer, due to double layer discharging at potentials more positive than the potential of minimum charge of porous carbon ( $E_{\text{pmc}} = 0.09 V_{\text{sce}}$ ).<sup>9</sup>

Such behaviour is similar to that observed before in fibre supported aerogel materials.<sup>9</sup> By effectively shortening the pore length, it is possible to decrease the charge/discharge time of the porous matrix in fibre based porous materials, compared to monolithic porous carbon. If the pores are charged/discharged in a time negligible compared to the span of the measurement, the ion flux to the electrode occurs in a discontinuous pulse.<sup>23</sup> Therefore, fibre based porous materials show faster movement of mobile species, as seen here in the ion movement to/from an electrode.

The effect could influence the dynamic behaviour of adsorption pellets, deionization electrodes or controlled release devices. The free volume between the fibres could also be used as an electrolyte reservoir in the device.

It seems that fibres induce porosity by templating or stabilizing the gel, in that way maintaining a high surface area during drying. The presence of the fibres affects also the pyrolysis mechanism as can be seen by the different rate of mass loss (ESI†).

In summary, it is possible to produce porous composite materials by polymerizing resorcinol–formaldehyde onto a cellulosic fibre fabric. The porous composite resin, dried in air, is

pyrolyzed to give a carbon–carbon composite which has a surface area of more than 550  $\text{m}^2 \text{g}^{-1}$ , with a significant portion of the surface area in mesopores. The composite material could be used as a supercapacitor electrode in acid aqueous media (specific capacitance *ca.* 160  $\text{F g}^{-1}$ ) where the principal ion exchanged during charge/discharge of the electrode is proton. The synthetic procedure is simple and could be used to produce large pieces and complex shapes.

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- The samples (1 g) have surface areas that are below the lower limit of the measurement (1  $\text{m}^2$ ).
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- A clear hysteresis is present in the PBD signal, likely due to the large beam electrode distance (1280  $\mu\text{m}$ ), necessary to maintain the PBD signal in a linear range.
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- The simulation is performed using the binary diffusion coefficient of  $\text{NO}_3^- \text{K}^+$  ( $1.8 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ) and a beam–electrode distance of 1350  $\mu\text{m}$ . The fit does not improve by considering simultaneous flux of protons.
- Comparing the PBD profile in Fig. 6 with the one of carbon mesogel (Fig. 17 of ref. 18), taken at similar beam–electrode distances, it can be seen that the discharge process occurs in less than 100 s in the composite carbon (Fig. 6, a discontinuous process) while it lasts more than 1500 s in the carbon mesogel (a continuous process).