Achieving high volumetric EDLC carbons via hydrothermal carbonization and cyclic activation

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Abstract

A novel activation method involving hydrothermal carbonization (HTC) and a pressure-induced low temperature oxidation has been demonstrated for cellulose derived HTC char by using hydrogen peroxide as an active di-oxygen source. The optimized porosity versus gravimetric capacitance results from cellulose derived HTC char synthesized at 220 °C. Almost homogeneous and small particle size micro-ellipse/sphere, relatively high surface area and narrow pore size distributions lead to a high bulk density, i.e. 0.73 g cm$^{-3}$, of coating-type electrodes, which is much denser than those manufactured from steam-activated carbons for supercapacitor industry, i.e. 0.52 g cm$^{-3}$. The resulting carbon prepared herein achieves a relatively high volumetric capacitance in an organic electrolyte-based supercapacitor, reaching a competitive value of an industrial system with the features being environment-friendly, cost-effective as well as high yield, and less energy consumption.

Introduction

Fossil fuel’s combustion with emissions of predominately CO$_2$ presents the principal contributor to climate change [1, 2]. It has been reported that coal power plants release 1.5 billion tons/year of CO$_2$ in the United States alone, whereas emissions from developing countries are accelerating [3]. Hence, the development of low-carbon technologies, such as solar and wind energy as well as hybrid electric vehicles (HEVs) with low emissions which are crucial to save the planet. This requires significant advances in reliable and low-cost energy storage technologies [4].

To date, electrochemical energy storage (EES) plays a central role in various energy storage technologies [1]. The two key technologies in EES are energy devices (batteries) and power devices (supercapacitors) [5]. Numerous batteries have dominated the large-scale of stationary energy storage, grid stabilization, and hybrid electric vehicle applications, etc [6, 7], which store energy in chemical bonds and deliver a much larger energy density than supercapacitors. However, they simultaneously undergo a slow power delivery/uptake and volume changes in electrodes causes their limited cycle life [8]. On the other hand, supercapacitors physically store charges without a major volume change in the electrode texture, leading to fast charge/discharge rates and almost unlimited cycling stability [9]. As a consequence, supercapacitors are the promising choice for frequency regulation and the regenerative braking systems of light rail systems in the smart grid [10]. Nevertheless, their energy density, which is frequently expressed as watt-hours per kilogram (Wh kg$^{-1}$) named gravimetric energy density, is relatively low at about 10 Wh kg$^{-1}$ for commercial supercapacitors compared to ∼300 Wh kg$^{-1}$ for lithium-ion batteries [11, 12]. Therefore, the greatest challenges in supercapacitor research is improving the gravimetric energy density of supercapacitors, shifting it as close as possible to batteries [13].

Besides gravimetric energy density, the volumetric energy density (Wh l$^{-1}$ or Wh cm$^{-3}$), which is currently the main requirement of the supercapacitor industry, is of great interest for portable electronics and vehicles because of their restricted space [14]. Hence, the improvement of volumetric energy/capacitance is a very relevant parameter to evaluate the industrial potentiality of various carbon materials as supercapacitors’
electrodes [15, 16]. Since the capacitance of supercapacitors correlates proportionally with the accessible surface area, carbons play a central role because of their high surface area, low-cost, versatility of structural properties, and high electrical conductivity. Improvements in volumetric energy density could be essentially realized by increasing the volumetric capacitance, which depends on the inherent properties of the electrode materials such as the electrode density, the active surface area, porosity, etc [14, 17, 18]. Another common way to enhance the volumetric energy is to use carbon particles with an appropriate morphology to minimize the interparticle voids. For instance, porous carbon microspheres can achieve a large packing density of up to 74% of the sphere density which is much higher than the irregular-shaped carbon particles [19–21]. Various approaches have been employed for synthesizing carbon spheres [22]. Using a nano-casting approach and sacrificial template, Ferrero et al [19] reported that nitrogen-doped dense uniform carbon microspheres could deliver a packing density of 0.97 g cm⁻³. Since 2004, hydrothermal carbonization (HTC) has been extensively explored at relatively low temperatures to prepare carbon spheres [23–27], and a variety of carbons for supercapacitors have been obtained through HTC synthesis and further activation [26, 28, 29]. Meanwhile, most of traditional activation of nano-porous carbons are based on the partial gasification of a precursor in oxidative conditions, including CO₂, steam, chlorine, KOH and NaOH at high temperatures. All of them lead to an uncontrolled pore widening and not pore size specific. Therefore, novel activation methods are highly desirable to synthesize a narrow pore size distribution and dense carbons. In our previous work, micro-porous carbons, with a narrow pore size distribution and relative high surface area, have been prepared from cellulose based non-porous chars by cyclic activation in a highly porosity-controlled manner [30, 31]. Consequently, our carbons make significantly denser electrode (0.71 g cm⁻³) compared with standard steam-activated carbons (0.52 g cm⁻³) used in supercapacitor industry. From the foregoing, combination HTC treatments and cyclic activation could be a much better choice to realize dense carbon materials to achieve dense electrodes.

Here we report that the combination between HTC of microcrystalline cellulose and cyclic activation represents a suitable methodology to produce dense carbon materials to achieve dense electrodes. The resulting carbon spheres after the HTC treatment of the cellulose precursor helped to reach a high electrode bulk density and a large volumetric capacitance at the same time. An additional advantage is that cellulose is the most abundant and inexpensive saccharide available to date while the HTC represents an environmentally friendly and cost-effective process compared with other carbonization methods since it takes place at low temperature and in water with a favorable energy balance. Furthermore, our method simplifies and reduces the activation treatment processes to only one cyclic activation cycle.

**Experimental**

**Activated carbon preparation**

Hydrothermal carbonization (HTC) was carried out at 210 °C, 220 °C, 230 °C, and 250 °C. Microcrystalline cellulose (20 g, Sigma-Aldrich) was dispersed in water (250 ml) and stirred for 4 h in a closed stainless-steel autoclave (internal volume 600 cm³, Parr Instrumental Company, USA). The autoclave was heated up to the targeted temperatures and maintained for 2 h. The resulting solid was recovered by filtration with abundant distilled water and dried at 120 °C in an oven for 3 h. Pyrolysis was further performed with the obtained hydrochar materials at 1050 °C (5 °C min⁻¹) holding for 3 h under nitrogen flow (100 ml min⁻¹) in a horizontal tubular furnace (internal diameter 36 mm).

The obtained cellulose based non-porous carbons (4 g) were oxidized by 200 g of hydrogen peroxide (35 wt%, PO₂ = 136 bar) in a closed stainless-steel autoclave (internal volume 600 cm³, Parr Instrumental Company®, USA) at 200 °C and during 8 h with stir. After filtration and drying of the resultant material, the surface functionalities were desorbed via thermal treatment at 900 °C (10 °C min⁻¹) holding for 2 h under nitrogen flow (100 ml min⁻¹) in a horizontal tubular furnace (internal diameter 36 mm). One step of oxidation and desorption represents one cycle of cyclic activation. To investigate the temperature dependence in HTC and simplify the processes to cut cost, cellulose based non-porous carbons (2 g), obtained with different HTC temperatures and further pyrolysis at 1050 °C, were oxidized with hydrogen peroxide solutions (128.75 g, 35 wt%, PO₂ = 72 bar) in one cycle of cyclic activation. To control the highly exothermic carbon-oxygen reactions, 100 ml water has been added into the autoclave together with non-porous carbon and hydrogen peroxide solutions.

**Porosity parameters and morphology characterizations**

Nitrogen adsorption isotherms have been performed at 77 K with a Quantachrome Autosorb-1 instrument for relative pressure (P/P₀) = 10⁻⁶ ~ 1). The samples were vacuumed for 12 h at a temperature of 300 °C. The quenched solid density functional theory approach (QSDFT) has been employed to determine the pore size distribution, micropore (Vmicro) and mesopore (Vmeso) volumes. The average micropore width (L₀) and the
specific surface area \( (S_{DB}(N_2)) \) at relative pressure up to \( P/P_0 < 0.015 \) were calculated with the Dubinin–Radushkevich method. The \( CO_2 \) adsorption isotherms at 273 K were used to determine the ultra-micropore volume \( (V_{ultramicro}) \) and the specific surface area \( (S_{DB}(CO_2)) \) according to the Dubinin–Radushkevich equation. SEM images of the resulting carbons were collected by using a Hitachi S4500 microscope (Hitachi High-Tech, Japan).

Electrodes preparation and electrochemical testing

The working electrodes were prepared by mixing the carbon material with a carbon black additive (Pureblack®, Superior Graphite Co.) and a polyvinylidene fluoride binder according to the mass ratio of 80:10:10. The electrode mass was then pressed into pellets with a mass of 10–15 mg. Supercapacitor cells were assembled with a Teflon Swagelok® airtight system using two identical pellets (electrodes), titanium current collectors, a porous cellulose membrane separator with 1 mol l\(^{-1}\) TEABF\(_4\) in acetonitrile as electrolyte. Electrodes coated on a conductive substrate were prepared to evaluate the electrode density by using an aluminum foil current collector and slurry containing the resultant carbon. The slurry was a mixture of the obtained carbon (85 wt%), carbon black (Pureblack\(^\circledR\), 5 wt%) and a binder (10 wt%, polyvinylidene fluoride). The electrodes were obtained by coating a 30 \( \mu \)m aluminum foil with the slurry dissolved in N-methylpyrrolidone (NMP) using a doctor blade, then dried under atmosphere and vacuum. A disc type electrode (diameter 16 mm) was then pressed and dried at 120 °C overnight in a special dryer (Buchi) for a glove box. The ECC electrochemical cells (EL-CELL\(^\circledR\), Germany) were employed to characterize the performance of coating-type electrode with a porous membrane separator, 1 mol l\(^{-1}\) TEABF\(_4\) in acetonitrile as electrolyte.

The assembling was carried out under argon atmosphere in a glove box with \( O_2 \) and \( H_2O \) content controlled under 1 ppm. Electrochemical measurements were implemented through cyclic voltammetry (CV, 5 mV s\(^{-1}\)) and galvanostatic charge-discharge cycling (GA, 200 mA g\(^{-1}\) to 10 A g\(^{-1}\)) using MPG-2 multichannel generator (Biologic, France). The gravimetric capacitance \( C \) was calculated from galvanostatic discharge and expressed per electrode (F g\(^{-1}\)) from two-electrode cell data using the formula (1):

\[
C = \frac{2\pi I}{(dV / dt)m}
\]

where \( I \) is the current (A), \( dV / dt \) the slope of the discharge curve (V s\(^{-1}\)), \( m \) the mass of carbon in each electrode for symmetric capacitors (g).

Results and discussion

Porosity parameters and morphology characterizations

It is reported that the carbon material morphology partially depends on the HTC temperatures [25, 32]. To verify the temperature dependence of HTC treatments, cellulose based carbons have been prepared at temperatures ranging from 210 °C to 250 °C followed by a pyrolysis at 1050 °C and one cycle of oxidation/thermal desorption activation (CDHCs carbons). Figure 1(a) presents SEM images of the cellulose derived carbons obtained by a direct pyrolysis at 1050 °C, while figures 1(b)–(e) show the cellulose derived HTC carbons (CDHCs) obtained by varying the HTC temperatures before the pyrolysis and the activation. Figure 1(b) shows that the cellulose subjected to 210 °C hydrothermal treatment has a similar microcrystalline structure with the one obtained via direct pyrolysis of cellulose at 1050 °C (figure 1(a)), indicating that cellulose is not reacted by an HTC treatment at relatively low temperatures. However, there is an important morphological change when HTC temperature is increased to 210 °C–220 °C, suggesting that HTC reactions take place around 220 °C. Figures 1(c), (d) show that upon increasing the HTC temperatures from 220 °C to 250 °C, micro-ellipse or sphere-like particles with narrow particle size distributions are formed. Moreover, the smallest particle diameter and the larger bulk density are observed for the materials hydrothermally treated at 220 °C. Figure 1(e) shows that higher HTC temperatures result in relatively larger particles. The combination HTC treatments and pyrolysis harvest more uniform and smaller size particles compared with pyrolysis only at 1050 °C which results in an irregular morphology. Therefore, HTC treatments hold the promise of attaining higher packing densities electrodes.

To confirm that indeed the hydrothermal process has a significant effect on the morphology of the resulting carbonaceous materials and that this is independent of the subsequent pyrolysis, figure 2 shows the SEM images of an HTC treated cellulose before and after pyrolysis. It can be observed that the morphology is almost the same. Thus one could clearly see carbon sphere-like morphology is present only with HTC treatment (also see figure 1).
Table 1 lists the porosity parameters of the CDHCs carbon materials presented in figures 1(b)–(e). The specific surface area of CDHCs follows the order of CDHC-220 > CDHC-210 > CDHC-230 > CDHC-250. Furthermore, CDHC-220 shows the largest ultra-micropore (<0.7–0.8 nm) and micropore volume amongst all CDHCs. The pore size distribution presented in figure 3(a) confirms the highest proportion of ultra-micropores in CDHC-220. Therefore, one can predict that CDHC-220 will have the best electrochemical performance as the pores are in a range of diameters which should effectively trap the ions during the double layer formation [33, 34]. In particular, it is stressed that the maximal stored energy of porous carbons can be achieved via carbon materials with a narrow pore size distribution with sizes close to the dimensions of the electrolyte ions [35].

Figure 1. Scanning electron (SEM) microphotographs of cellulose derived carbons obtained with direct pyrolysis at 1050 °C under an inert atmosphere (a) and hydrothermally treatments (b)–(e) at different HTC temperatures: (b) 210 °C; (c) 220 °C; (d) 230 °C; (e) 250 °C.
Electrochemical performance of the HTC carbons

To check the capacitive performances of CDHCs, galvanostatic charge/discharge (GCD) has been tested with symmetric Swagelok cells operating at 2.7 V using 1 mol l$^{-1}$ TEABF$_4$/acetonitrile as electrolyte. It becomes obvious (figure 3(b)) that CDHC-220 shows the largest specific capacitance at whichever current density up to 10 A g$^{-1}$, which confirms our predictions after the porous texture characterization.

The gravimetric capacitance values are proportional to the $S_{DR}$ (N$_2$), i.e. CDHC-220 > CDHC-210 > CDHC-230 > CDHC-250. Although the CDHC-210 presents the highest mesopore volume (table 1 and figure 3(a)), it shows the most noticeable decrease of specific capacitance within the current density (from 5 to 10 A g$^{-1}$). Such results contrast with many other works suggesting that the presence of mesopores in carbons

Figure 2. SEM images of hydrothermal carbonized cellulose (a) and further thermal treatment at 1050 °C under nitrogen flow (b).

Table 1. Porosity characteristics of cellulose derived HTC carbons (CDHCs) obtained after one cycle of cyclic oxidation/desorption. The temperatures represent the HTC temperatures.

| Sample   | After desorption | $S_{DR}$ (N$_2$) (m$^2$ g$^{-1}$) | $S_{DR}$ (CO$_2$) (m$^2$ g$^{-1}$) | $V_{DIFF}$ micro$^b$ (cm$^3$ g$^{-1}$) | $V_{DIFF}$ meso$^c$ (cm$^3$ g$^{-1}$) |
|----------|------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| CDHC-210 |                  | 848                             | 603                             | 0.23                            | 0.27                            | 0.43                            |
| CDHC-220 |                  | 964                             | 948                             | 0.36                            | 0.36                            | 0.26                            |
| CDHC-230 |                  | 676                             | 817                             | 0.31                            | 0.24                            | 0.26                            |
| CDHC-250 |                  | 503                             | 520                             | 0.20                            | 0.16                            | 0.28                            |

$^a$ Pore diameter <0.7 nm;
$^b$ Pore diameter <2.0 nm;
$^c$ 2.0 nm < pore diameter <50 nm.

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improve the high rate performance [28]. Nevertheless, they confirm the weak interaction of ions in large pores [34, 35].

Most works on supercapacitors present the gravimetric capacitance (Farad per gram) and energy (watt-hours per kilogram), while the volumetric energy (watt-hours per volume) is a more reliable information from the application point of view [14, 15]. In fact, the size of supercapacitors is the most important parameter for their implementation in portable applications and vehicles because of their restricted space [36]. Volumetric performances of carbons essentially depend upon the electrode density or packing density of carbon coatings [14]. In this sense, it can be expected that CDHC-220 with its narrow pore size distribution and its dense bulk morphology (see figure 1) combined with its high gravimetric capacitance should achieve high volumetric values. Therefore, we were starting from the hydro-char obtained at 220 °C to produce coatings to further evaluate the volumetric energy. An increase in the O2 pressure increase from 72 to 136 bar and in the mass of the carbons from 2 to 4 g is optimal to prepare suitable slurries for coatings over Al current collectors. For comparison purposes, we have also prepared electrodes using carbon coatings obtained by direct pyrolysis of cellulose followed by activation in the same conditions as for the CDHC carbon, giving carbon named AC. Table 2 shows the textural characterization and the yield of the materials obtained via different synthetic routes. An interesting feature is that CDHC provides slightly higher yield than AC obtained without previous HTC treatments whilst both cases attain relatively high yield. This means that such protocol results in a higher yield, i.e. 76% of CDHC, than conventional KOH or NaOH activation [37]. In fact, since vapour-solid interactions are effectively the only source to form the char during the pyrolysis of pure cellulose [38], one could expect higher yields from HTG protocol in a closed autoclave instead of direct pyrolysis in an open crucible [27, 39]. On the other hand, as the yield of biomass charcoal at elevated pressures exceeds those
Table 2. The specific surface area and yield after one cyclic activation cycle, gravimetric capacitance \((F g^{-1})\), electrode density \((g cm^{-3})\) and volumetric capacitance \((F cm^{-3})\) of a cellulose derived HTC carbon (CDHC) and a cellulose derived carbon without HTC treatments (AC) obtained with a standard electrochemical testing cell-EL CELL operating at 2.7 V. The normalized capacitance \((C/S_{DFT}>0.67nm}\) is expressed as the gravimetric capacitance divided by the accessible surface area \((DFT\text{ surface area corresponding to pores larger than 0.67 nm, i.e. ion size of desolvated TEA}^+\)).

| Sample After desorption | \(S_{DR}(N_2)(m^2 g^{-1})\) | \(V_{DR}\) ultramicro\(^a\) \((cm^3 g^{-1})\) | \(V_{DFT}\) micro\(^b\) \((cm^3 g^{-1})\) | Yield (%) | \(C(F g^{-1})\) | \(C/S_{DFT}>0.67nm\) \((\mu F cm^{-2})\) | Density \((g cm^{-3})\) | \(C(F cm^{-3})\) |
|-------------------------|-----------------------------|---------------------------------|---------------------------------|-----------|----------------|--------------------|----------------|----------------|
| CDHC                    | 917                         | 0.31                            | 0.34                            | 76        | 83             | 16                 | 0.73           | 61             |
| AC                      | 1147                        | 0.41                            | 0.44                            | 73        | 93             | 15                 | 0.58           | 54             |

\(^a\) Pore diameter <0.7 nm;
\(^b\) Pore diameter <2.0 nm.
obtained at atmospheric conditions, oxidation under 136 bar during cyclic activation of both cases could enhance the yield \[30, 31\].

Regarding the electrochemical performances, GCD indicates ideal capacitive performance of coated electrodes, by showing symmetric triangular shape without a noticeable IR drop (figure 4). Determining the IR drop provides the total resistance of the system, and therefore one could conclude that the coatings give a good contact between carbon active materials and current collectors \[40\]. As a consequence, the gravimetric capacitance of CDHC—83 F g\(^{-1}\) (200 mA g\(^{-1}\)) is smaller than that of AC—93 F g\(^{-1}\) (200 mA g\(^{-1}\)) due to its higher specific surface area, larger volume of ultra-micropore of the latter (table 2). On the other hand, the Nyquist plots (figure 5) show a semicircle in the high frequency region which represents the resistive nature of supercapacitor system. The beginning of the semicircular line indicates the resistance of the electrolyte in contact with the current collector and electrode, while the termination of the semicircle represents the internal resistance of the electrode \[41\]. All those resistance shows slightly lower values for AC compared with CDHC, which makes the former a higher gravimetric capacitance.

Coating the active materials over Al current collectors obtained with CDHC exhibits a higher density than AC based coatings without HTC treatments, i.e. 0.73 g cm\(^{-3}\) for CDHC and 0.58 g cm\(^{-3}\) for AC coatings. Meanwhile, SEM images (figure 6) presented that CDHC coatings are more densely packed than that of AC based ones. The reasons for the better packing arise from the fact that carbon morphologies of CDHC and AC
are different. Figure 7 shows that those CDHC materials are denser and have smaller particle sizes than AC. Consequently, the HTC treatments enable the microcrystalline cellulose to form uniform and smaller dimension micro-ellipse or sphere leading to a denser aggregation among carbon particles. Furthermore, the electrodes prepared from the resultant carbons AC and CDHC are much denser than those produced from steam-activated carbons ($S_{O2} (N_2) = 1560 \text{ m}^2 \text{g}^{-1}; V_{ultramicro} = 0.58 \text{ cm}^3 \text{g}^{-1}; V_{micro} = 0.62 \text{ cm}^3 \text{g}^{-1}; V_{meso} = 0.21 \text{ cm}^3 \text{g}^{-1}$), i.e. 0.52 g cm$^{-3}$, optimized for supercapacitor industry [30], which can be traduced in a real improvement of the technology. Finally, higher density CDHC based coatings allow a volumetric capacitance of 61 F cm$^{-3}$ to be obtained, which is slightly larger than that of AC with 54 F cm$^{-3}$ and also comparable values with CDCs [42–44]. Currently activated carbons with a volumetric capacitance in the range of 30–60 F cm$^{-3}$ in organic medium remain the most common electrodes for the supercapacitor industry [45]. Therefore, the resultant carbons prepared herein can achieve a relatively high volumetric capacitance in organic electrolyte-based supercapacitors reaching a competitive value for the industrial system.

Long-term cycling stability has been further studied for assessing the reliability of our system to be further implemented in a commercial device. In this sense, figure 8 shows that EL-CELLs using AC and CDHC as electrode active materials present an excellent cycling stability at 2.7 V with a relatively high current density of 1 A g$^{-1}$. The capacitance retention ratio is as high as 94% and 92% after 2 000 cycles for CDHC and AC based system, respectively.

Conclusions

We have demonstrated a novel activation method involving hydrothermal carbonization and a pressure-induced low temperature oxidation of cellulose derived HTC char by using H$_2$O$_2$ as an active di-oxygen source. Under high di-oxygen pressures at low temperature, the main mechanism associated with the low burn-off values seems to be creating the narrow pores existing initially in the chars. In the experimental conditions used for this study, the optimized porosity versus gravimetric capacitance, results from cellulose derived HTC char synthesized at 220 °C. Almost homogeneous and small particle size micro-ellipse/sphere, relatively high surface area and narrow pore size distributions lead to a high bulk density, i.e. 0.73 g cm$^{-3}$. Hence, coating-type carbon electrodes on conductive substrates exhibit dense coatings compared with the those manufactured from steam-activated carbons for the supercapacitor industry. The resulting carbon herein can achieve a relatively high volumetric capacitance in the organic electrolyte-based supercapacitor reaching a competitive value for the
industrial system with the features of environment-friendly, economically competitive, high yield and less energy consumption. By optimizing the synthesis parameters and using different precursors, higher volumetric energy can be predicted with these new family carbons in the near future.

**Figure 7.** SEM images of cellulose derived HTC carbon (a), CDHC and cellulose derived carbon without HTC treatments (b), AC.

**Figure 8.** Long-term cycling stability obtained with charge/discharge at 2.7 V and 1 A g⁻¹ in symmetric two electrodes EL-CELL assembled with CDHC and AC. Electrolyte: 1 mol l⁻¹ TEABF₄ in acetonitrile.
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