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Highly ordered macroporous woody biochar with ultra-high carbon content as supercapacitor electrodes

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Abstract

Woody biochar monolith with ultra-high carbon content and highly ordered macropores has been prepared via one-pot pyrolysis and carbonization of red cedar wood at 750 °C without the need of post-treatment. Energy-dispersive spectroscopy (EDX) and scanning electron microscope (SEM) studies show that the original biochar has a carbon content of 98 wt% with oxygen as the only detectable impurity and highly ordered macroporous texture characterized by alternating regular macroporous regions and narrow porous regions. Moreover, the hierarchically porous biochar monolith has a high BET specific surface area of approximately 400 m² g⁻¹. We have studied the monolith material as supercapacitor electrodes under acidic environment using electrochemical and surface characterization techniques. Electrochemical measurements show that the original biochar electrodes have a potential window of about 1.3 V and exhibit typical rectangular-shape voltammetric responses and fast charging-discharging behavior with a gravimetric capacitance of about 14 F g⁻¹. Simple activation of biochar in diluted nitric acid at room temperature leads to 7 times increase in the capacitance (115 F g⁻¹). Because the HNO₃-activation slightly decreases rather than increases the BET surface area of the biochar, an increase in the coverage of surface oxygen groups is the most likely origin of the substantial capacitance improvement. This is supported by EDX, X-ray photoelectron spectroscopy (XPS), and Raman measurements. Preliminary life-time studies show that biochar supercapacitors using the original and HNO₃-activated electrodes are stable over 5000 cycles without performance decays. These facts indicate that the use of woody biochar is promising for its low cost and it can be a good performance electrode with low environmental impacts for supercapacitor applications.

Keywords: Biochar electrode, supercapacitor, wood monolith, macroporous electrode, hierarchical pore network
1. Introduction

Supercapacitors are one of the most important developments in the field of energy storage and conversion. Currently, they are experiencing rapid annual growth because of their potentially broad applications in transportation, electric grid, renewable energy, consumer electronics, and industrial processes [1–4]. Due to the fact that electrostatic interactions occurring at the solid-electrolyte interface are far less detrimental to the integrity of the electrodes, supercapacitors can undergo 10^6 cycles of charge/discharge without significant performance decays [5]. The performance of a supercapacitor depends on several parameters, for instance, electrode materials, the nature of electrolyte and the electrode-electrolyte interface. To increase the interface, the size of the pores within the electrode should be larger than those of the ion size of the electrolyte [6]. Therefore controlling microstructures of the electrode is very critical in addition to the judicial of the electrolyte.

Carbon materials in different forms such as powders, fibers and sheets are the main electrode materials for supercapacitors because of their obvious advantages including low-cost, easy availability, environmental friendliness, and good stability over other materials [7]. For electric double-layer capacitance, activated carbons have received special recognition compared to other carbons because they have high surface areas along with controlled pore size distributions [8]. Theoretically, the higher the specific surface area of an activated carbon, the higher the specific capacitance should be expected. Practically, the situation is more complicated. Some activated carbons with smaller surface areas exhibit a larger specific capacitance than those with larger surface areas. The relation between the BET surface area, the total pore volume, the average pore size, and the pore size distribution of activated carbons and their electrochemical performance as electrodes for supercapacitors have been reviewed [9,10]. The reasons for the absence of proportionality between specific capacitance and surface area may include: (1) different types of carbons prepared from various precursors through different processes and subsequent treatment have different double-layer capacitance; (2) the accessibility of pores to electrolyte media is an important factor; and (3) surface reactions contribute to charge-discharge processes. In principle, the pores larger than 0.5 nm could be accessible electrochemically for aqueous solutions. Moreover, the mobility of ions inside the pores affects the rate of electrochemical accessibility. It
is generally considered that the movement of ions is more difficult in the small pores than in the large pores. For the practical applications, activated carbons with a large percentage of big pores are found to be more convenient as capacitor electrodes for high energy at high rate, although they can store less total energy. One further factor is the wettability of the carbon surface determined by the kind of surface functionality and the electrolyte medium used. It is expected that the porous texture of carbon can determine the ionic conductivity which relates to the mobility of ions inside the pores. Therefore, hierarchically porous activated carbon has been extensively studied as supercapacitor materials since a hierarchical pore network can improve the utilization of micro- and mesopores and decrease Ohmic and mass transport overpotentials [11,12].

Further factors influencing large-scale applications of carbon materials in supercapacitors include their cost and environmental impacts during the material preparation [5-8]. The major material costs for carbon/carbon capacitors are the carbon, the electrolyte medium, and the ion conductor. Among them, carbon is responsible for around 60% of total material cost. A key issue is the unit cost ($/kg) of the carbon in combination with its specific capacitance (F/g). The material cost of the capacitors can be expected to decrease markedly as the unit material costs become lower. For low-cost activated carbon ($5/kg), a total electrode material cost of less than 0.1 cent/F appears to be possible based on a specific capacitance of 50 F/g [8]. Therefore, developing lower cost carbon having good performance is obviously attractive. These costs must be further reduced if electrochemical capacitors are to be marketed in large volumes. Additionally, the sustainability of carbon materials with low environmental impacts has recently received great attention. Although a wide range of nanostructured carbons have been prepared and evaluated as supercapacitor materials, their high cost and secondary environmental pollution generated during their preparation will be potential hindrances to large-scale implementation of supercapacitors. Moreover, the functionalization of carbon surfaces and composites of carbon with redox-active compounds which is achieved by the use of toxic or corrosive chemicals has been extensively studied to improve supercapacitor performance [13,14]. However, the use of these chemicals must be at least limited or totally eliminated in order to mitigate the environmental impacts.
Biochar (BC) is the carbon-rich product produced when biomass (such as wood, manure or crop residues) is heated in a closed container with little or no available air. It can be made at promisingly low cost without negative environmental concerns via the gasification or pyrolysis of biomass materials. Raw BC materials are being considered as a potentially significant means of storing carbon for long periods to mitigate greenhouse gases [15]. It is possible to produce BC at a price of around $0.1/kg ($100/MT), close to the coal price ($116/MT) [16,17]. According to this price and an assumed specific capacitance of 10 F g\(^{-1}\), the total electrode material cost of 0.001 cent/F seems achievable. Therefore the use of low-cost BC in the supercapacitors has the potential to substantially reduce or even eliminate the cost of carbon materials. Furthermore, BC is a more sustainable material because it is nontoxic and can be easily disposed of. These attributes will be a huge boost to the implementation of supercapacitors for wide potential applications. Recently, the preparation and characterization of BC-based supercapacitor materials have attracted attention. Activated carbon prepared from cotton stalk exhibits a specific capacitance of 114 F g\(^{-1}\) [18] and that prepared from cotton mat presents excellent high-rate capacitive performance although its specific capacitance is limited to be about 14 F g\(^{-1}\) [19]. The specific capacitance of activated carbon prepared from a range of agricultural biomass wastes is in a wide range of around 10 to 200 F g\(^{-1}\), depending on the precursors and charge-discharge rate [20-22]. Hierarchical carbon with a high specific surface area of approximately 3000 m\(^2\) g\(^{-1}\) prepared from distiller dried grains with solubles reaches a capacitance of 260 F g\(^{-1}\) [23]. A porous wood carbon monolith shows a capacitance of 234 F g\(^{-1}\) in KOH after being activated in hot concentrated nitric acid [24]. However, these interesting performances have been obtained through complicated and/or caustic activation processes. Therefore, it is highly important to explore low-cost preparation of BC from abundant biomass precursors and the evaluation of their performance in supercapacitors without or with milder activation processes.

In this work, we have prepared BC with hierarchical porous texture and ultrahigh carbon content via direct carbonization of red cedar wood at 750 °C. We have further studied them as supercapacitor electrodes without introducing any binder in a half cell and in a single cell using cyclic voltammetry and chronopotentiometry. Original BC electrodes exhibit voltammetric responses similar to those of activated carbon under similar conditions and demonstrate fast charge-discharge behavior with a gravimetric capacitance of about 14 F g\(^{-1}\). Simple treatment of
BC in diluted nitric acid at room temperature increases the capacitance to 115 F g\(^{-1}\). We have attributed this remarkable capacitance increase to the introduction of surface oxygen groups. Preliminary life time studies show that the original and HNO\(_3\)-activated BC supercapacitors are stable over 5000 cycles. Based on the promisingly low-cost and good performance of BC materials, it is expected that the BC supercapacitors have the potential to meet the cost and performance targets required for broad applications of supercapacitors.

2. Experimental

2.1. Preparation of biochar and electrodes

BC was prepared through pyrolysis of a small chunk of red cedar wood in a N\(_2\) atmosphere by applying a temperature program to a MTI GSL-1100X tube furnace. The temperature was increased from room temperature to 200 °C and then held at this temperature for 1 hr to remove moisture. This was followed by increasing temperature to 750 °C at around 3 °C/min and dwelling at this temperature for 1 hr to remove volatile organics and to carbonize solid residues. The resulting BC chunk was removed from the furnace for characterization and evaluation after the temperature was cooled down to room temperature.

The BC chunk was cut into small monoliths. Those with weights of approximately 1 mg were directly used as supercapacitor electrodes without introducing any organic binder. This could facilitate fast evaluation of the intrinsic capacitance of BC materials under varying conditions without introducing considerable Ohmic overpotential.

2.2. Activation of BC electrodes

BC electrodes were further activated by immersing them into 0.5 mol dm\(^{-3}\) HNO\(_3\) solution at room temperature overnight to increase surface hydrophility and the coverage of surface oxygen groups. They were rinsed using deionized water (Nanopure\(^\circledR\), 18.2 Ω cm in resistivity) before use.

2.3. Physical characterization
Surface morphology and elemental composition of the electrodes were characterized using a Philips XL30 ESEM-FEG field-emission environmental scanning electron microscope operating at 15 keV equipped with a light-element energy-dispersive spectroscopy. BET surface areas of BC samples were measured using a Micromeritics Gemini VII 2390 V1.03 surface area/pore volume analyzer. Raman measurements were performed using a high-resolution research-grade Horiba LabRAM HR 3D-capable Raman spectroscopy imaging system that is optimized for the visible-to-NIR spectral range. A 532 nm wavelength laser was used in this study. X-ray photoelectron spectroscopy (XPS) measurements were conducted on the powders using a Kratos Axis Ultra DLD instrument. The XPS spectra were calibrated by the C1s signal at 284.6 eV. DC electrical conductivity of BC was determined from Ohmic resistance, cross-section area, length and porosity of a small monolith based on Pouillet's law. The Ohmic resistance corresponds to the slope of linear potential-current curve measured by applying potential scan to two ends of the monolith. A conductivity of around 2 S cm\(^{-1}\) was obtained.

2.4. Electrochemical measurements

All electrochemical measurements were performed using an Autolab general purpose electrochemical instrument PGSTAT 30 (Metrohm USA). Voltammetric and constant-current charge-discharge studies of a single BC electrode were carried out in 0.5 mol dm\(^{-3}\) H\(_2\)SO\(_4\) solution with a coil of 1 mm diameter Pt wire and a silver/silver chloride (Ag/AgCl) as the counter electrode and the reference electrode, respectively. The electrical contact of a BC electrode was obtained by wrapping fine gold wire around the monolith to minimize contact resistance. The geometric surface area is around 0.08 cm\(^2\) with 2 mm in width and 4 mm in length. The capacitive behavior of a BC supercapacitor constructed by putting two BC electrodes in similar size separated by a sheet of glassy filter-paper in 0.5 mol dm\(^{-3}\) H\(_2\)SO\(_4\) was evaluated by cyclic voltammetry and chronopotentiometry. Their preliminary durability was evaluated via successive potential cycling.

3. Results and discussion

3.1. Characterization of BC
Macroporous structures of a BC micro-monolith were studied by SEM. The SEM images corresponding to its end view and side view are shown in Fig. 1(A) to (C) and Fig. 1(D) to (E), respectively. In these images, light regions correspond to carbon walls and black regions correspond to pores. Its end view presents two alternative porous zones. One is characteristic of regular distorted hexagonal-shape pores whose center-to-center distance is about 20 μm, separated by very thin carbon wall of around 4 μm in thickness. Another zone shows squeezed olive-shape pores of average 5 μm height and 12 μm width which are separated by about 5 μm thickness carbon walls. Fig. 1(A) shows that the large porous stripes of approximately 400 μm width and the denser porous stripes of around 50 μm in width are alternated. Its side-view images show that these pores are developed in parallel, and separated by thin carbon walls. However, these tubular pores are interconnected through smaller array pores of around 4 μm in diameter across the thin carbon walls. This interconnection between tubular pores is useful to increase the utilization of micropore surfaces inside BC.

The microporous/mesoporous structures of BC samples were studied by the BET method. The adsorption isotherms and the pore size distribution curves for the original and activated samples are shown in Fig. 2(A) and (B). The similarity of their isotherms indicates that N₂ adsorption on the samples may follow similar kinetics. Their pore size distribution curves show that they have hierarchical micro/mesoporous textures, characteristic of slow pore volume increase at the pore diameter larger than 2.8 nm and multipeaks in the smaller pore diameter range. The original BC exhibits pore volume increase when the pore diameter is smaller than 2 nm. This suggests that the original BC has a higher percentage of micropores than the activated BC. The pore parameters of the two samples are summarized in Table 1. The values of BET specific surface area are 433 and 317 m² g⁻¹ for original and activated BC, respectively. The average pore size of the sample decreased from 4.4 to 3.8 nm after the HNO₃-activation. These changes clearly indicate that the activation decreases the specific surface area and average pore size. This is in agreement with literature results on porous structure changes of several carbon materials caused by the HNO₃ activation [13,24]. The introduction of oxygen groups onto pore surfaces and oxidation-induced pore structure collapse are considered to be responsible for the decrease in the specific surface area and pore size, especially the percentage of micropores.
Fig. 3 shows EDX spectra of original and activated BC samples. Only a major C K\(\alpha\) pattern and a minor O K\(\alpha\) pattern were observed. No other patterns associated with typical ash components such as silicon, calcium and potassium were noticeable. The elemental compositions of the two samples are listed in Table 2. The carbon content of the original BC was as high as 97.5 wt% or 98.3 at%. The activation of BC slightly decreased these values to 92.5 wt% and 94.3 at%. These values are obviously higher than those of regular BC which has a high value of around 80 wt% [25]. Therefore, the BC with ultrahigh carbon content and zero ash will be interesting material for supercapacitor applications. Moreover, the presence of oxygen in BC is also an important benefit since surface oxygen groups can be involved in the charge-discharge processes, leading to increased pseudo-capacitance.

Raman spectroscopy has been a sensitive probe of oxygen-functional-group-induced changes of electronic structure and defects in carbon materials. Fig. 4 presents Raman spectra of original and activated BC samples. The most important features observed are the graphite band at 1530-1610 cm\(^{-1}\) (G band) and the disorder-induced D band at 1320-1370 cm\(^{-1}\). Second-order weak bands also occur at 2680-2690 cm\(^{-1}\) (D\(^*\)) and 2910-3220 cm\(^{-1}\) (D+G). Usually the ratio between the intensity of the D band and the G band (I\(_D\)/I\(_G\)) is taken as a measure of defect concentration [26-28]. An increase in I\(_D\)/I\(_G\) corresponds to a higher proportion of \(sp^3\) carbon, which is generally attributed to the presence of more structural defects. In our case, the values of I\(_D\)/I\(_G\) increased from 1.05 to 1.18 after the BC is activated using HNO\(_3\). This can be interpreted to be that the introduction of oxygen-containing functional groups onto carbon surfaces through surface oxidation increased the number of \(sp^3\) hybridized carbon, leading to increased surface disorders. It has been reported that surface C=O groups can be enriched on glassy carbon by hot HNO\(_3\) treatment [27]. Additionally, the acid treatment may lead to the intercalation of acid molecules inside the carbon lattice [29]. This will exert pressure on the \(sp^2\) structure and extraction of electrons.

The changes of BC surfaces after the HNO\(_3\) activation were further studied by XPS. Fig. 5 shows XPS data collected in the regions of C 1s, N 1s and O 1s for the original and HNO\(_3\)-treated samples. In Fig. 5(A), a sharp peak at 284.6 eV assigned to C-C and C=C was clearly observed, and the wave-like feature observed at around 290 eV is normally caused by \(\pi\rightarrow\pi^*\) shake-up and plasmon [30,31]. An interesting change occurred in the range of approximately 286
to 290 eV when the sample was treated by HNO$_3$. The fitting of C 1s peak shown in Fig. 5(B) suggests that the introduction of two surface oxygen groups, hydroxyl (C-OH) and carbonyl (C=O), is the most likely origin. Their total surface coverage is around 15%. This is supported by the changes of O 1s peak in the range of 530 to 535 eV, as shown in Fig. 5 (C). The intensity of the peak seen at 533.0 eV associated with hydroxyl and carboxyl oxygen is obviously increased. Therefore, the changes of the C 1s and O 1s spectra suggest that the HNO$_3$ activation promotes the formation of hydroxyl and carboxyl oxygen on BC surfaces. This is consistent with results reported in the literature [27]. The N 1s region displays very interesting changes, as shown in Fig. 5(B). No peaks were observed for the original sample. The HNO$_3$ activation produced two peaks. The one seen at 400 eV is related to C-N and another seen at 406 eV is assigned N-O [32,33]. This result strongly suggests that HNO$_3$ is bound to biochar surfaces rather than physically trapped inside the pores.

3.2. Electrochemistry of BC electrodes

Cyclic voltammograms for the original BC electrode in 0.5 mol dm$^{-3}$ H$_2$SO$_4$ at varying scan rates are shown in Fig. 6. The electrode possessed a potential window of around 1.3 V extending from -0.3 to 1.0 V versus the Ag/AgCl reference electrode. Within the window, a capacitive behavior and a couple of redox peaks were observed. Their current values increased with increased scan rate. Moreover, the potential shift of the redox peaks with the variation of scan rate was insignificant. These voltammetric characters are similar to those of commercial activated carbon [34]. The major difference is that the oxidation and reduction peaks are stronger for activated carbon than for the original BC electrode.

Fig. 7 shows the variations of electrode potential with galvanostatic polarization time at varying current. Typical capacitive responses were obtained. The potential linearly increased with increasing time during the discharge, and it decreased with increasing time during the discharge. The deviations from the linear behaviors observed at switching potentials are normally caused by Ohmic resistance and pseudo-reversibility of surface redox reactions [35,36]. We also observed that the charge-discharge responses were very reproducible. There are no obvious changes for the first five cycles at three varied currents. Specific capacitance ($C$) of the
BC electrode is calculated from the reciprocal \( (b) \) of the slope of linear potential-time section as follows [37]:

\[
C = \frac{I \Delta t}{\Delta E} = I \times b
\]  

(1)

where \( I \) is current in \( \text{A g}^{-1} \). The current dependence of the specific capacitance is shown in Fig. 8. The capacitance value decreased slightly from 15.1 \( \text{F g}^{-1} \) at 0.2 \( \text{A g}^{-1} \) to 12.5 \( \text{F g}^{-1} \) at 0.5 \( \text{A g}^{-1} \).

Cyclic voltammograms for the HNO\(_3\)-activated \( BC \) electrode in 0.5 mol dm\(^{-3}\) \( \text{H}_2\text{SO}_4 \) at different scan rates are shown in Fig. 9. Compared to those for the original BC electrode shown in Fig. 6, the voltammetric currents were significantly increased and different voltammetric characters were produced. First, the current values in the potential range of -0.3 to 0.4 V were much higher than those in the potential range of 0.4 to 1.0 V. Second, the redox peaks were stronger and their peak potentials are considerably dependent on the scan rate. The potential difference between the anodic and cathodic peaks was only at about 40 mV at 2 mV s\(^{-1}\). But it significantly increased to around 400 mV when the scan rate increased to 50 mV s\(^{-1}\). The unusual increase in the potential difference is less likely to be caused to the change of Ohmic resistance between the reference and the working electrode since the current values are limited to a few mA or lower in our case. In addition, the pore structures have no substantial changes after the HNO\(_3\) activation, for which parameters are shown in Table 1.

Analogous to activated carbon, there are difference oxygen groups on BC surfaces depending upon the nature of biomass precursors and their preparation [38,39]. They may include strongly carboxylic acid; weakly acidic groups with one or two oxygen atoms such as phenolic and hydroquinone; and non-acidic groups including quinone and carboxyl. These oxygen groups have different electrochemical activity and contribute surface charge-discharge processes in different patterns. In acidic solution, the electrochemical reduction of quinone and electrochemical oxidation of hydroquinone are rather reversible [35]. Therefore, increasing the coverage of surface quinone and hydroquinone groups on BC surface will be desirable. But this is challenging. It is generally considered that electrochemical reactivity of carboxylic acid groups is poor [40]. Its contribution to pseudo-capacitance would be small. Because our XPS results
showed that the HNO$_3$ activation promotes the formation of surface carboxyl (>C=O) and hydroxyl (>C-OH) groups, the most likely redox reactions could be simplified as follows [41]:

\[
>\text{C}=\text{O} + \text{H}^+ + e^- \leftrightarrow >\text{C}-\text{OH} \tag{I}
\]

\[
>\text{C}=\text{O} + e^- \leftrightarrow >\text{C}-\text{O}^- \tag{II}
\]

The kinetics of Reactions I and II will determine the capacitive characters of the electrode and their contribution to its capacitance. The significant potential shift of the redox peaks with increasing scan rate shown in Fig. 9 indicates that Reactions I and II are likely to be quasi-reversible rather than highly reversible.

Fig. 10 shows the variations of potential with galvanostatic polarization time for the activated BC electrode at different currents. Linear potential-time relation was produced in the charge and discharge branches and good cycling performance was also observed. The values of specific capacitance were similarly calculated according to Eq. (1) and presented in Fig. 8. They were less dependent upon the charge-discharge currents, indicating good high-rate response. Their average gravimetric capacitance was 115±5 F g$^{-1}$. The value was obviously much higher than that of the original BC electrode (14±1 F g$^{-1}$). We also observed that the immediate potential drops at switching potentials were not significant. In contrast, non-linear potential decays were observed at a transition section between the immediate potential drop section and linear potential-time section. This non-linear behavior should not be attributed to the contribution of Ohmic resistance within pores since its induced potential drops should be immediate at switching potentials.

It is well known that independent of its origin, texture, and pore size, a carbon material is characterized by more or less constant surface capacitance of about 10 µF cm$^{-2}$ [41,42]. Consequently, the double-layer capacitance should be limited to 30-40 F g$^{-1}$ for a pure material with a specific surface area of 300-400 m$^2$ g$^{-1}$, assuming 100% utilization of pore surfaces. Table 1 also shows that the BET specific surface area of BC material is decreased from 433 to 317 m$^2$ g$^{-1}$ after the HNO$_3$ activation. Therefore, the high capacitance of 115 F g$^{-1}$ for the activated BC electrode is not caused by the changes of electrode surface areas and the utilization degree of
pore surfaces. The increased contribution of pseudo-capacitance owing to the redox reactions of surface oxygen groups is the most likely origin. For hierarchically porous carbon materials, the total capacitance \( C \) collects the contribution of micropores \( C_{\text{micro}} \), mesopores \( C_{\text{meso}} \), macropores \( C_{\text{macro}} \) and surface faradaic reactions as follows:

\[
C = C_{\text{micro}} + C_{\text{meso}} + C_{\text{macro}} + \sum \frac{\Gamma n F A}{\Delta V}
\]

where \( n \) is the electron number transferred per molecular, \( \Gamma \) is surface concentration of oxygen group in mol cm\(^{-2}\), \( A \) the total surface area and \( \Delta V \) is the cell voltage. Normally the contribution of \( C_{\text{macro}} \) is very small since macropores contribute only a small portion of the total \( A \). The contribution of pseudo-capacitance to \( C \) is strongly dependent upon the concentration and reactivity of surface oxygen groups. In our case, around two-thirds of total \( C \) may come from this contribution, assuming 100% of pore surface utilization.

The specific capacitance of the activated BC electrode was comparable to those of other advanced carbon materials with a BET specific surface area of 1000-2000 m\(^2\) g\(^{-1}\) [43,44]. In sulfuric acid media, the capacitance values of single-wall and multiwall carbon nanotube were in the range of 100 to 200 F g\(^{-1}\). The performance of reduced graphite oxide falls within the same range. Those of activated carbon are widely varied, strongly depending on material types and experimental methods [43]. This indicates that high BET surface area is helpful for high performance carbon-based electrodes, but it may be not definitively required.

### 3.3. Evaluation of BC supercapacitors

The performance of BC supercapacitors comprised of either two similar original BC electrodes or two similar activated BC electrodes in sulfuric acid was evaluated by cyclic voltammetry and chronopotentiometry. Fig. 11(A) shows that an original BC supercapacitor exhibited typical rectangular voltammetric responses of a capacitor, even at high scan rates (100 mV s\(^{-1}\) and higher). This is a signature of good fast charge-discharge behavior. The dependence of cell voltage on polarization time at different currents for the capacitor is shown in Fig. 11(B). Pseudo linear voltage-time behavior was observed during the charge and discharge.
The voltammetric characters of the activated BC supercapacitor comprised of two activated BC electrodes slightly deviated from the typical rectangular responses of a capacitor, as shown in Fig. 12(A). Moreover, the degree of the deviation was dependent on the scan rate. The higher the scan rate was, the higher the deviation was. During the constant-current charge and discharge, obvious deviations from the linear voltage-time relation were also observed at high currents, as shown in Fig. 12(B). These deviations observed on the voltammograms and chronopotentiograms especially at high scan rates and high currents were mainly caused by quasi-reversible surface reactions responsible for the pseudo-capacitance.

The preliminary performance durability of the original and activated BC supercapacitors was evaluated by applying successive 5000 potential cycles between -0.65 and 0.65 V to the supercapacitors at 50 mV s\(^{-1}\). The inset to Fig. 13 shows no obvious changes in voltammetric responses over 5000 cycles for both the original and activated BC supercapacitors. Their gravimetric capacity values were stabilized at around 2 F g\(^{-1}\) and 24 F g\(^{-1}\) for the former and the latter, respectively, as shown in Fig. 13. This is indicative of promisingly high durability of the two BC supercapacitors.

4. Conclusions

A biochar material having unique hierarchically porous microstructures has been produced through a one-pot pyrolysis and carbonization of red cedar precursor at 750 °C. This BC has a carbon content as high as 98 wt% with oxygen as the only detectable impurity and a highly ordered macroporous network. Original BC electrodes exhibited voltammetric responses similar to those of activated carbon under similar conditions, and their corresponding supercapacitor demonstrated typical responses of an electrochemical double-layer capacitor and promising fast charge-discharge capability. Mild activation of the electrodes using dilute HNO\(_3\) at room temperature substantially increased the gravimetric capacitance to approximately 115 F g\(^{-1}\) which is comparable to those of advanced carbon materials. We have attributed the substantial capacitance increase to the pseudo-capacitance caused by redox reactions of carbonyl-type surface oxygen groups. Furthermore, the original and HNO\(_3\)-activated BC supercapacitors were stable over 5000 cycles without obvious performance decays. Considering there is still more space to further capacitance improvement, the combination of its potentially
low cost and demonstrated high performance suggests that the BC supercapacitors are a promising technology for potential expected applications of supercapacitors. We expect that woody biochars with high surface area, good conductivity and electrochemical stability, and unique hierarchical porous structures will be promising materials for a wide range of energy and environmental materials.

5. Acknowledgement

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References


**Figure captions**

Figure 1 SEM images for a BC micromonolith prepared from red cedar wood. (A-C): End view; (D-E): Side view.

Figure 2 Adsorption isotherm (A) and BJH adsorption plot (B) for original (black line) and HNO₃-activated (red line) BC samples.

Figure 3 EDX spectra for original (black line) and HNO₃-activated (red line) BC samples.

Figure 4 Raman spectra for original (black line) and HNO₃-treated (red line) BC samples.

Figure 5 XPS spectra collected in the regions of C 1s (A), C 1s fitting (B), N 1s (C) and O 1s (D) for original (black line) and HNO₃-treated (red line) BC samples.

Figure 6 Cyclic voltammograms measured at different scan rates for an original BC electrode in 0.5 mol dm⁻³ H₂SO₄.

Figure 7 Potential-time transients for an original BC electrode in 0.5 mol dm⁻³ H₂SO₄ upon applying a galvanostatic polarization of 30 s for five cycles.

Figure 8 Dependence of specific capacitance on charge-discharge current for original (black) and activated (red) BC electrode.

Figure 9 Cyclic voltammograms at varying scan rate for a HNO₃-activated BC electrode in 0.5 mol dm⁻³ H₂SO₄.

Figure 10 Potential-time transients for a HNO₃-activated electrode in 0.5 mol dm⁻³ H₂SO₄ upon applying a galvanostatic polarization of 30 s for five cycles.

Figure 11 Cyclic voltammograms at varying scan rate (A) and potential-time transients under different galvanostatic polarizations (B) for a BC supercapacitor comprising of two similar original BC electrodes in 0.5 mol dm⁻³ H₂SO₄.
Figure 12 Cyclic voltammograms at varying scan rate (A) and potential-time transients under different galvanostatic polarizations (B) for a BC supercapacitor comprising of two similar activated BC electrodes in 0.5 mol dm$^{-3}$ H$_2$SO$_4$.

Figure 13 Variation of specific capacitance as a function of cycle number for an original BC supercapacitor (black square) or an activated BC supercapacitor (red circle). Inset: Their corresponding cyclic voltammograms during 5000 potential cycles between -0.65 and 0.65 V.
Tables

Table 1 BET specific surface area, pore volume and pore size of original and activated BC samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET specific surface area (m² g⁻¹)</th>
<th>BJH pore volume (cm³ g⁻¹)</th>
<th>BJH adsorption average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original BC</td>
<td>433</td>
<td>0.17</td>
<td>4.4</td>
</tr>
<tr>
<td>Activated BC</td>
<td>317</td>
<td>0.10</td>
<td>3.8</td>
</tr>
</tbody>
</table>

Table 2 EDX analysis of original and HNO₃-treated BC monoliths prepared from red cedar wood.

<table>
<thead>
<tr>
<th>Element</th>
<th>Original BC</th>
<th>HNO₃-treated BC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wt% At%</td>
<td>Wt% At%</td>
</tr>
<tr>
<td>C Kα</td>
<td>97.5±0.1  98.3±0.1</td>
<td>92.5±0.3  94.3±0.2</td>
</tr>
<tr>
<td>O Kα</td>
<td>2.5±0.1  1.9±0.1</td>
<td>7.5±0.3  5.7±0.2</td>
</tr>
</tbody>
</table>
Figure 1
Figure 2
Figure 3
Figure 4
Figure 5
Figure 6
Figure 7
Figure 8

Gravimetric capacitance (F g\(^{-1}\))

Current (A g\(^{-1}\))

- Original BC
- HNO\(_3\)-activated BC
Figure 9
Figure 10
Figure 11
Figure 12
Figure 13