Hierarchically nanoporous carbons derived from empty fruit bunches for high performance supercapacitors

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Abstract
Hierarchically porous, chemically activated carbon materials are readily derived from biomass using hydrothermal carbonization (HTC) and chemical activation processes. In this study, empty fruit bunches (EFB) were chosen as the carbon source due to their sustainability, high lignin-content, abundance, and low cost. The lignin content in the EFB was condensed and carbonized into a bulk non-porous solid via the HTC process, and then transformed into a hierarchical porous structure consisting of macro- and micropores by chemical activation. As confirmed by various characterization results, the optimum activation temperature for supercapacitor applications was determined to be 700°C. The enhanced capacitive performance is attributed to the textural property of the extremely high specific surface area of 2861.4 m² g⁻¹. The prepared material exhibited hierarchical porosity and surface features with oxygen functionalities, such as carboxyl and hydroxyl groups, suitable for pseudocapacitance. Finally, the as-optimized nanoporous carbons exhibited remarkable capacitive performance, with a specific capacitance of 402.3 F g⁻¹ at 0.5 A g⁻¹, a good rate capability of 79.8% at current densities from 0.5 A g⁻¹ to 10 A g⁻¹, and excellent life cycle behavior of 10,000 cycles with 96.5% capacitance retention at 20 A g⁻¹.

Keywords: porous carbon, activated carbon, hierarchical structure, biomass, supercapacitor

1. Introduction

The supercapacitor (SC) is considered an attractive energy storage device because it provides high power density, fast charge/discharge capability and a long life cycle [1-3]. The electrochemical double layer capacitor (EDLC), a representative kind of SC, stores charges at the interfaces of the electrodes and electrolyte in a non-faradaic manner [1,4,5]. To ensure fast energy-supplying performance and high power density, the accessibility of those electrode surfaces to the transport of ions is critical. Accordingly, carbon materials which have tailored textural and electrochemical properties are considered among the most promising electrode materials for EDLCs [2,5-8]. Activated carbons have been used as commercial electrode materials for decades for this reason. The specific capacitance of EDLCs can be dramatically improved by utilizing the full potential of activated carbons, including their large specific surface area (SSA) and reasonable electrical conductivity [1,8-10]. However, reducing the high cost of high-quality activated carbons, while improving their supercapacitive performance, remains a challenge [2,6,7,11,12].

Recently, biomass has been intensively investigated as a precursor for nanoporous carbons because of its sustainability, abundance, and low cost. Wood-based biomass is primarily obtained from the carbon-rich residues of plants such as shells, peels, seeds and straws [13-17]. Lignin, which is the main component of lignocellulosic biomass, is the second most abundant aromatic biopolymer in nature. This polymer is expected to be a cost-efficient sustainable source material for the synthesis of biochar activated carbons, due to its high carbon content and molecular structure, which is similar to bituminous coal [15,18-20]. How-
ever, at present, massive amounts of lignin are being treated as waste in global timber markets, because lignin is very difficult to isolate with high purity. Precisely controlling the porous structure of lignin-derived nanoporous carbons is also problematic, since their accurate chemical structure has not been defined yet [18,20].

To synthesize nanoporous carbons, the key activation chemistries used to create a porous structure with a large SSA can be classified into physical and chemical methods [15,20]. The physical activation processes are generally considered cost-efficient and environmentally friendly, but the SSA of the final product is typically not large enough to achieve the high specific capacitance needed for electrodes [21-23]. The chemical activation processes, which use alkali metal-based agents such as KOH, K$_2$CO$_3$, and ZnCl$_2$, are more suitable for synthesizing highly porous, nanostructured carbons with high quality. The chemical reactions produced by the activating agents can also remove impurities from the heterogeneous carbon sources of lignin [16,24-29].

Despite the advantages of chemical activation processes, the yield of lignin-derived carbons is often very low because the carbon precursors decompose under the harsh chemical activation conditions [15]. More importantly, the quality of the as-obtained lignin-derived carbons is generally not good; they typically exhibit low SSA and poor electrochemical properties, which are inferior to those of a commercialized activated carbon, which have SSAs higher than 2000 m$^2$ g$^{-1}$ [30-33].

Herein, we report the preparation of hierarchically nanoporous carbons for SC applications, derived from empty fruit bunches (EFB) that contain lignin, using hydrothermal carbonization (HTC) and chemical activation, where the porous structure is systematically controlled [34]. The EFB, which is an agricultural waste obtained from palm trees after harvesting palm fruits, basically contains materials with 10 to 36.6 wt% lignin [35,36].

The HTC method has advantages over conventional thermal methods. It allows the synthesis of strongly combined carbonized structures through the condensation and pyrolysis of carbon materials, including lignin content [37,38], while preventing excessive removal of the product by the violent activation etching reaction [38,39]. In this study, non-porous, bulk HTC-treated EFB (HEFB) solid was transformed into a hierarchical porous structure consisting of macro- and micropores by chemical activation [31]. The superiority of this unique nanoporous carbon was demonstrated by application as an SC electrode.

### 2. Experimental

#### 2.1. Preparation of HEFB

The HEFBs were prepared from raw EFB fragments by the HTC process. Five hundred milligrams of EFB fragments were soaked in 10 g of deionized (DI) water and stirred for a time to permit wetting. After the EFB was sufficiently wet, the resultant mixture was inserted into a 20 mL autoclave reactor and thermally treated at 200°C for 12 h for HTC. During the HTC process, the EFB was transformed into a carbonized material with a chemically reduced carbon surface and reduced impurities. After being transformed by the thermal treatment, the solid state carbonized samples were washed with DI water and freeze-dried for 72 h to obtain the HEFB.

#### 2.2. KOH activation for preparation of ACE samples

The HEFB samples obtained from the preceding HTC process were completely blended with KOH by grinding. The mass ratio of KOH to HEFB was 3:1. Then the mixture was thermally treated in a tube furnace at a heating rate of 2.5°C min$^{-1}$ up to the desired temperature (of 600, 700 and 800°C) and kept for 2 h under a nitrogen flow of 100 mL min$^{-1}$. After KOH activation, the activated samples were washed with DI water until the pH of the samples came to 7.0, and then were freeze-dried for 72 h to produce the final resultant samples, called ACES. The samples activated at 600, 700 and 800°C were designated AC600, AC700 and AC800, respectively.

#### 2.3. Fabrication of electrodes

To evaluate the electrochemical behaviors of the prepared samples in a three-electrode system, working electrodes were prepared as follows. A mixture of 70 wt% samples, 20 wt% polyvinylidene fluoride (PVDF) as binder and 10 wt% carbon black as conductive agent was ground with N-methyl-2-pyrrolidone (NMP) as solvent. Each uniformly mixed slurry of HEFB and ACE samples was manually coated on a titanium plate and dried at 80°C overnight. For a two-electrode system, a slurry prepared by the same method mentioned above was manually coated on circular copper foil with a diameter of 15 mm and dried at 80°C overnight. A cylindrical platinum rod and a saturated Ag/AgCl electrode were used as the counter electrode and reference electrode in the three-electrode system, respectively. Capacitive performance was tested using a 1 M H$_2$SO$_4$ aqueous solution as the electrolyte.

#### 2.4. Characterizations

Scanning electron microscopy (SEM) images were collected on a field emission SEM (FEI Sirion model, USA) equipped with an inhouse Schottky emitter with high stability. Transmission electron microscopy (TEM) images were obtained using a JEM-3010 high resolution TEM (HR-TEM; 300 kV, JEOL, Japan). N$_2$ adsorption/desorption isotherms were obtained by a Brunauer-Emmett-Teller apparatus (BELSORP-mini II; Microtracbel Corp., Japan). Before measurement, the samples were prepared under vacuum condition at 200°C overnight. To ensure the reproducibility of the data, we tested at least five samples prepared under the same experimental conditions. The Brunauer-Emmett-Teller (BET) method was used to calculate the SSA of the samples. The pore size distributions were derived using the Barrett-Joyner-Halenda (BJH) model. Raman spectra, X-ray diffraction (XRD) patterns and X-ray photoelectron spectroscopy (XPS) were prepared to determine the chemical structures and compositions of the samples. Raman spectra were obtained from 100 to 3000 cm$^{-1}$ at room temperature using a Raman spectroscope (Remishaw Raman Microscope, 785 nm; UK) equipped with a $\times$100 objective. The XRD data were collected.
on a Rigaku D/max III C (3 kW; Japan) with a 0/0 goniometer equipped with a CuKa radiation generator. XPS data were obtained using a Thermo MultiLab 2000 system (USA) with an Al Mg X-ray source at 200 W.

### 2.5. Electrochemical measurements

All of the electrochemical measurements of the prepared samples were conducted on an electrochemical work station (VSP; Bio Logic Science instrument, France). In order to evaluate the capacitive performances of each sample, cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) were performed. Both two- and three-electrode system tests were conducted in a 1 M H₂SO₄ aqueous solution as electrolyte. The EIS tests were implemented in a frequency range of 100 KHz to 0.01 Hz. The specific capacitance (C) was calculated by using a following equation:

\[ C = \frac{\int I \, dV}{\upsilon \times m \times \Delta V} \]

where I is the response current density (A cm⁻²), V is the potential (V), υ is the potential scan rate (mV s⁻¹), and m is the mass of the electroactive materials in the electrodes (g cm⁻²), respectively [40].

In the two-electrode system, the tests were carried out in a 2016-type coin cell configured with two electrodes of nearly equivalent weight and size. The specific capacitance of a single electrode was calculated by multiplying the result calculated by the previous equation by 4 [41].

### 3. Results and Discussion

In this study, the HTC process and chemical activation were used to synthesize hierarchical porous carbons derived from the lignin included in the EFB. The EFB was carbonized to become HEFB, which has a chemically reduced surface and reduced impurities compared with the raw biomass state. Before the activation step, the molecular weight of the EFB was increased via the HTC process [18,37]. This led to more condensed and carbonized compounds, derived from the pyrolysis of the carbon precursor [37,38]. The resulting bulk solid HEFB was then chemically activated with KOH at different temperatures to optimize the capacitive performance of the electrodes.

The morphologies of the HEFB and ACEs are shown in the SEM and TEM images in Fig. 1. The bulk non-porous structure of HEFB was reorganized into a hierarchical porous structure by the KOH activation. At low magnification SEM (Fig. 1a1), it can be seen that the morphology of the HEFB derived from the HTC process was strongly influenced by the original structure of the lignin-based component [37,42,43]. The high-magnification

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**Fig. 1.** Scanning electron microscopy (a1-d1, a2-d2, a3-d3), transmission electron microscopy (a4-d4) images of (a) HEFB, (b) ACE600, (c) ACE700, and (d) ACE800.
SEM images show a morphology consisting of coral-shaped, irregular forms on the porous surface (Fig. 1a2 and a3). These were speculated to have originated from the original structure of the cellulosic/lignocellulosic carbon materials, which were decomposed during the HTC process and became aggregated on the surface [43,44].

In comparison to the HEFB, the macroporous structures of all the activated samples (Fig. 1b1-d1) have several micrometer scales, but no regular macroporous structures can be observed. The SEM images of the ACEs (Fig. 1b2-d2) confirm that their hierarchical texture was successfully constructed by the chemical activation of HEFB with KOH. As shown in the high-magnification SEM images of the ACEs (Fig. 1b3 and d3), the pores became denser as the activation temperature was elevated. The ACE800 sample shows that the sizes of the macropores tended to excessively increase, resulting in high porosity (Fig. 1d1), because of the violent reaction between the surface defects and KOH. This harsh reaction also leads to a reduction in the yield of the final product.

As shown in the HR-TEM images of the HEFB and ACE samples (Fig. 1a4-d4), all the samples contained an amorphous phase resulting from the intrinsic characteristic of the biomass-derived carbon substance after the HTC process [45,46]. For the ACEs (Fig. 1b4-d4), the random disordered combinations of carbon atoms on the surface, which were produced by the etching reaction with the metallic potassium of KOH, led to the destruction of the aligned regions and mainly resulted in the presence of nanosheets with a disordered structure [47,48].

In addition to evaluating the effects of the HTC and the activation processes on the morphology, the textural properties of the HEFB and ACEs were characterized by nitrogen adsorption/desorption analysis using the BET and BJH models, as shown in Fig. 2. In other words, the mean pore sizes, SSAs and pore size distributions of the samples treated at different activation temperatures were measured.

The adsorption isotherms of the activated samples (Fig. 2a-c) are indicative of typical IUPAC type 1, corresponding to a Langmuir-type isotherm with a high N₂ adsorption plateau and the absence of hysteresis [49]. As shown in Table 1, the SSA of the HEFB was 3.5768 m² g⁻¹, while the SSA of the samples activated at 600, 700, and 800°C were 1824.3, 2861.4, and 2903.1 m² g⁻¹, respectively. The low SSA of the HEFB can be attributed to slender splintered cracks, which can provide a large amount of cavities, providing the KOH molecules easy access to deep inside the HEFB structure. The highly microporous structures produced by the KOH activation resulted in the prominent values of the ACEs.

This can be confirmed by the mean pore diameters of about 1.7 nm and the isotherm plots of type 1 [50]. The BJH plot (Fig. 2d) shows the pore size distributions of the activated samples, as well as that of the HEFB. Although the proportion of mesopores is much less than the micropores, the peaks located near 5 nm are apparently due to the presence of mesopores in the ACEs, which is beneficial for good accessibility of the electrolyte, and provides sufficiently wide pathways for ion transfer [51].

By comparing the SSAs of all the ACEs samples, it was determined that the KOH activation was carried out more efficiently at temperatures above 700°C than at 600°C, because the SSA of ACE700 and ACE800 were much higher than that of ACE600. In addition, the total pore volumes of ACE700 and ACE800 were also greater than 1.2 cm³ g⁻¹ which was larger than the 0.83 cm³ g⁻¹ of ACE600.

Fig. 3 displays the structure of the prepared samples as obtained by XRD and Raman spectroscopy. In Fig. 3a, a broad (002) peak at 2θ=23° can be attributed to the crystalline plane of the graphitic structure [47,52]. The carbonized solid derived from decomposition of the EFB during the HTC process should have a certain degree of crystallinity, with the morphology consisting of amorphous and crystalline phases. However, in the results, the peak of the (100) plane was found to be negligible, due to the low degree of graphitization [51]. Thus, the overall composition of HEFB was determined to be an amorphous structure rather than a graphitic structure, because the lignin-based carbon materials produced a disordered formation during the carboniza-

<table>
<thead>
<tr>
<th>Sample</th>
<th>EFB</th>
<th>HEFB</th>
<th>ACE600</th>
<th>ACE700</th>
<th>ACE800</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area (m² g⁻¹)</td>
<td>1.1425</td>
<td>3.5768</td>
<td>1824.3</td>
<td>2861.4</td>
<td>2903.1</td>
</tr>
<tr>
<td>Total pore volume (cm³ g⁻¹)</td>
<td>0.0044</td>
<td>0.0133</td>
<td>0.8315</td>
<td>1.2506</td>
<td>1.2402</td>
</tr>
<tr>
<td>Mean pore diameter (nm)</td>
<td>15.541</td>
<td>14.891</td>
<td>1.8231</td>
<td>1.7482</td>
<td>1.7089</td>
</tr>
</tbody>
</table>

BET, Brunauer-Emmett-Teller; EFB, empty fruit bunches; HEFB, hydrothermal carbonization-treated ACE.

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After KOH activation, the (002) peak in the ACEs had vanished. This was likely due to the intercalation of potassium compounds in the narrow cracks on the surface, which eroded the crystalline structure of the carbonized materials [55-57]. The Raman spectra for the HEFB and ACEs shown in Fig. 3b showed two peaks at 1362 and 1594 cm\(^{-1}\), corresponding to the D and G bands of the defective and graphitic carbon phases, respectively. The intensity ratio of the D/G bands \((I_d/I_G)\) demonstrated the degree of structural order [58]. The \(I_d/I_G\) value of 0.68 for the HEFB indicated that a graphitic structure evidently existed on the surface despite the substantial amount of defect sites. In contrast, the \(I_d/I_G\) values of ACE600, ACE700 and ACE800 were 0.95, 0.97 and 0.99, respectively. These values mean that the degree of graphitic ordering was lower, due to the formation of defective micropores, even though the ACEs were thermally reduced a little [59].

The results obtained from the HRTEM images, XRD patterns and Raman spectra confirm that the ACEs derived from EFB were typical of activated nanoporous carbons, with a highly amorphous structure.

The chemical composition and elemental analysis of the HEFB and ACEs as determined by XPS results were shown in Fig. 4 and Table 2. The chemical compositions of the prepared samples in this study were in a narrow range spectrum of C and O. Fig. 4a shows there was an increase in carbon and decrease in oxygen content at the elevated activation temperature. These results are considered to reflect the chemical reduction that occurred on the surface, indicating that the reduction reactions were proportional to the activation temperatures [60].

The deconvolution of the high-resolution C 1s spectra of the HEFB (Fig. 4b) and ACE700 (Fig. 4d) consist of five individual component peaks, corresponding to C-C (284.6 eV), C=C (284.8 eV), C-O (285.9 eV), C=O (287.5 eV), and O-C=O (289.2 eV), respectively [61,62]. Furthermore, the O 1s deconvolution spectra of the HEFB (Fig. 4c) and ACE700 (Fig. 4e) are composed of three individual peaks of C=O (531.7 eV), O-C-O (532.6 eV) and C-O (533.5 eV), respectively [61,62].

In the full range spectrum of the HEFB, the 19.5 at% oxygen content was mostly comprised of single bonds or double bonds between carbon and oxygen atoms, because the C 1s spectrum showed intensities of 43.7 at% and 20.8 at% for the peaks, i.e., for C-O and C=O, respectively. The O 1s spectrum of the HEFB (Fig. 4c) showed respective intensities of O-C-O of 48.2 at%, C-OH of 17.5 at% and C=O of 34.3 at% demonstrating that the major components of HEFB were from lignin-derived materials, including an amount of hydroxyl and ether groups.

After KOH activation, the intensities of the C-C, C=C, and O-C=O bonds in the high-resolution C 1s spectrum of ACE700 (Fig. 4d) increased to 21.8, 28.8, and 15.8 at% from the 9.1, 25.9, and 1.7 at% of the HEFB, respectively. In contrast, the intensities of the C-O and C=O decreased considerably to 30.3 and 3.2 at% from the 42.3 and 20.8 at% of the HEFB, respectively. Furthermore, the O 1s spectrum of the ACE700 (Fig. 4e) showed that the intensity of the hydroxyl groups highly increased to 41.1 at% from the 17.5 at% of the HEFB.

From these results, we determined the generation of hydroxyl and carbonyl groups, which were constructed by the breaking of C=O bonds by reactions with KOH during the activation process.
The ACE800 sample had a higher SSA than the ACE700 sample, even though the ACE700 sample had lower capacitance, which was attributed to its higher electrical conductivity, like that of the ACE800 sample. A smaller Rct and Rint were observed in the Nyquist plots of the ACEs, indicating better capacitive performance. However, the ACE600 sample had better performance as compared to the other ACEs.

Based on the above analysis, the electrochemical capacitive performance of the HEFB and ACEs was evaluated in a three-electrode system using a 1 M H2SO4 aqueous solution as the electrolyte. Measurement of the HEFB was conducted after thermal treatment at 700°C for accurate comparison with the other ACEs.

The CV experiment was conducted to understand the electrochemical behavior of the prepared samples at different potentials. Fig. 5a shows the CV curves of the HEFB and ACEs at a scan rate of 5 mV s\(^{-1}\). All the CV curves of the ACEs show an ideal double layer capacitor (EDLC) behavior. In addition, substantially projected broad redox peaks at high scan rates, recognized as the redox reactions of the oxygen functional groups, were evident.

The curves of the HEFB thermally treated at 700°C were recorded as a typical quasi-rectangular shape, but the scale of the results was too small to be exhibited in the same frame with the ACEs. The GCD curves at a current density of 1 A g\(^{-1}\) are presented in Fig. 5b. The specific capacitances were determined to be 2.6, 191.5, 356.5 and 307.6 F g\(^{-1}\) for the thermally treated HEFB, ACE600, ACE700 and ACE800, respectively. In comparison to the capacitance of thermal treated HEFB, the capacitive performances of the ACEs were dramatically improved after KOH activation. For obvious comparison of the capacitive performances, the specific capacitances, calculated at current densities of 0.5 and 5 A g\(^{-1}\), are listed in Table 3.

To investigate the capacitive behaviors further, EIS analyses of the HEFB and ACEs were performed at a frequency range from 100 kHz to 10 mHz, and displayed as Nyquist plots. In Fig. 5c, the Nyquist plot of the HEFB exhibits a steep vertical slope in the low frequency region, a small diameter semicircle in the high frequency region, and a small value of x-intercepts, which indicate the successful diffusion of electrolyte ions into the surfaces, low charge-transfer resistance (Rct) and internal resistance (Rint), respectively.

After KOH activation, all of the ACE samples showed similar degrees of vertical slopes, Rct and Rint. Among them, the ACE700 exhibited a reduction in all types of resistance, including a smaller x-intercept, a tiny semicircle and an almost perpendicular vertical slope angle, demonstrating remarkable conductivity for better capacitive performance. However, ACE600 had better Rct than those of the HEFB and other ACEs. This was caused by a smaller x-intercept and almost vertical slopes, close to those of an ideal double layer capacitor, leading to the outstanding rate capability shown in Fig. 5d.

Nonetheless, even though the ACE600 rate capability was high, because of its electrical conductivity, like that of the ACE700, it had lower capacitance, which was attributed to ACE600 having a lower SSA than ACE700. Even though ACE800 had a high SSA of 2900 m\(^2\) g\(^{-1}\), its drastic decrease in rate capability was ascribed to the enhanced overpotential arising from defective sites and small pores with the increase in current density. This result could also be observed in the impedance data, which showed a large Rct and relatively inclined slope due to the low electronic conductivity of the defects, which originated from the severe activation reaction, and the very small micropores sizes, which hinder rapid ion diffusion at higher current densities [70,71]. Compared to the ACEs, the HEFB had EIS measurement results suitable for SCs applications, but the extremely low SSA produced poor capacitive performance.
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Table 3. Capacitive performances of thermally treated HEBF and ACEs prepared in a three-electrode system, using a 1 M H$_2$SO$_4$ aqueous solution as electrolyte.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific capacitance (F g$^{-1}$ @ 0.5 A g$^{-1}$)</th>
<th>Specific capacitance (F g$^{-1}$ @ 5 A g$^{-1}$)</th>
<th>Capacitance retention over 5000 cycles (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEBF (thermal treated)</td>
<td>3.3</td>
<td>1.7</td>
<td>21</td>
</tr>
<tr>
<td>ACE600</td>
<td>216.7</td>
<td>160.7</td>
<td>92</td>
</tr>
<tr>
<td>ACE700</td>
<td>402.3</td>
<td>290.9</td>
<td>98</td>
</tr>
<tr>
<td>ACE800</td>
<td>439.1</td>
<td>206.4</td>
<td>79</td>
</tr>
</tbody>
</table>

Fig. 6. Electrochemical performance of ACE700 measured in a two-electrode system using a 1 M H$_2$SO$_4$ aqueous solution as the electrolyte. (a) Cyclic voltammetry curves at a different scan rates from 1 to 100 mV s$^{-1}$, (b) galvanostatic charge-discharge curves at different current densities from 0.5 to 10 A g$^{-1}$, (c) rate capability for varying current densities from 0.5 to 15 A g$^{-1}$, and (d) capacitive retention performance at a current density of 20 A g$^{-1}$ over 10,000 cycles; and an optical image of the electrochemical coin type cell photographed by a digital camera.

Fig. 6b were 365.9, 355.7, 339.9, 315.8 and 292.0 F g$^{-1}$ at current densities of 0.5, 1, 2, 5 and 10 A g$^{-1}$, respectively. A superior rate capability of 79.8% was measured at varying current densities from 0.5 A g$^{-1}$ to 10 A g$^{-1}$. The cycle retention performance was also a remarkable level of 96.5% after 10,000 cycles. The results confirmed the excellent capacitive performances of ACE700 in a two-electrode full configuration.

A detailed evaluation of ACE700 was conducted, since it demonstrated the best electrochemical performances from among all the samples prepared for this study. In Fig. 5e, the CV curves from tests at scan rates from 1 mV s$^{-1}$ to 100 mV s$^{-1}$ show a rectangular shape, with redox peaks resulting from oxygen functional groups. The GCD curves of ACE700 over the range of current densities from 0.5 A g$^{-1}$ to 10 A g$^{-1}$ (Fig. 5f) also displayed an almost symmetrical shape.

The specific capacitance of ACE700 was calculated to be 402.3 F g$^{-1}$ at a low current density of 0.5 A g$^{-1}$, and remained at 268.3 F g$^{-1}$ at a current density of 10 A g$^{-1}$. Fig. 5g shows the cycle capacitive performances of the thermally treated HEFB and ACEs at a current density of 20 A g$^{-1}$. As shown in the figure, the ACE700 sample showed a capacitance retention of 98% of the initial capacitance after 5000 GCD cycles. In comparison with the other ACEs, ACE700 demonstrated excellent potential for application as an electrode material for SCs.

Next, to investigate the actual device performances of ACE700, a two-electrode symmetrical SC cell was fabricated with a 1 M H$_2$SO$_4$ aqueous electrolyte and measured. Fig. 6 shows the capacitive performance of the ACE700 cell device at potentials ranging from 0 V to 0.8 V. In Fig. 6a, the CV curves obtained at scan rates from 1 mV s$^{-1}$ to 100 mV s$^{-1}$ show the typical quasi-rectangular shape. The forms of the CV curves exhibited stable behavior with less resistance during changes of voltage.

The specific capacitances calculated from the GCD curves in Fig. 6b were 365.9, 355.7, 339.9, 315.8 and 292.0 F g$^{-1}$ at current densities of 0.5, 1, 2, 5 and 10 A g$^{-1}$, respectively. A superior rate capability of 79.8% was measured at varying current densities from 0.5 A g$^{-1}$ to 10 A g$^{-1}$. The cycle retention performance was also a remarkable level of 96.5% after 10,000 cycles. The results confirmed the excellent capacitive performances of ACE700 in a two-electrode full configuration.

4. Conclusions

Hierarchical porous carbon materials with exceptionally high SSAs composed of microporous structures and superior electrical conductivities were synthesized from EFB biomass by a facile method using the HTC process and KOH activation. In this study, we used a biomass of EFB, which has a substantial degree of lignin material among its components, to make a carbon precursor for the activation process. HTC processing of the EFB produced a strong structure with a lignin-based carbon substrate, HEFB. Then, following activation of the HEFB, measurements demonstrated the generation of hierarchically porous structures with an SSA of about 2900 m$^2$ g$^{-1}$. These properties are obviously beneficial for capacitive performance.

Based on those advantages, the activated carbon was optimized at a temperature of 700°C and subsequently exhibited the remarkable specific capacitance of 402.3 F g$^{-1}$ and a long life cycle behavior of 5000 cycles with 98% capacitance retention. The excellent results were due to the HTC process and the KOH activation. The HTC promoted the reorganization of components, such as the lignin- and cellulose-based materials, and assisted in the creation of structural cracks with an SSA of 3.6 m$^2$ g$^{-1}$, further facilitating the access of KOH into the core of the bulk material. Oxygen-containing structures on the surface acted as good reaction sites for the KOH, and their characteristics ensured the carbonized samples would be a good carbon precursor for KOH activation.

One aspect of this study was to investigate the effective use of biomass containing lignin-based components. This work confirmed that using the HTC process on a biomass carbon precursor before chemical activation is an attractive way to produce an activated carbon with a high SSA and electrical conductivity for application in SCs. The electrochemical capacitive performance of the final product showed a great improvement in the development of a biomass-derived activated carbon and energy storage system. In conclusion, this study will be valuable to the further commercialization of SCs.
Conflicts of interest

No potential conflict of interest relevant to this article was reported.

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