Supporting Information

Activated carbon clothes for wide-voltage high-energy-density aqueous symmetric supercapacitors

Kwadwo Asare Owusu\textsuperscript{a}, Zhaoyang Wang\textsuperscript{a}, Longbing Qu\textsuperscript{b}, Zi'ang Liu\textsuperscript{a}, Jaafar Abdul-Aziz Mehrez\textsuperscript{a}, Qiulong Wei\textsuperscript{i}, Liang Zhou\textsuperscript{a, *}, Liqiang Mai\textsuperscript{a, *}

\textsuperscript{a}State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China
\textsuperscript{b}Department of Mechanical Engineering, The University of Melbourne, Parkville, VIC 3010, Australia.
\textsuperscript{i}Department of Materials Science and Engineering, University of California Los Angeles, CA 90095 – 1595, USA.

Experimental

Activation of carbon clothes

Activation of CCs. The CC was purchased from Shanghai Hesen Electric Co., Ltd. Before the activation process, the CC (4 × 5 \times 0.031 cm\textsuperscript{3}) was ultrasonicated in acetone, ethanol, and water respectively for 20 minutes to get rid of surface impurities. The activation process was carried out by calcining the CC at 400 °C for 6 hours with a ramp rate of 2 °C min\textsuperscript{-1} in air. The mass density of the activated CC is calculated to be 13 mg cm\textsuperscript{-2}. As control experiments, pristine CCs were calcined at different temperatures and time lengths (300 °C for 6 hours, 400 °C for 2 hours, and 500 °C for 6 hours) to study the influence of calcination conditions on the electrochemical performance.

Material characterization

Raman spectra were obtained using a Renishaw INVIA micro-Raman spectroscopy system with a laser power of 100 mW and a spot size of 1 µm. SEM images were collected with a JEOL-7100F microscope. TEM images were recorded using a JEM-2100F STEM/EDS microscope. The Brunauer–Emmett–Teller (BET) surface area was measured using a Tristar II 3020 instrument at 77 K. XPS measurements were performed using a VG Multi Lab 2000 instrument. The adsorption curves were analyzed using NLDFT models to obtain the pore-size...
distribution curves. The contact angle measurements were performed using an OCA Automatic contact angle measurement device.

**Electrochemical characterization**

All the electrochemical measurements were performed with an electrochemical workstation (CHI 760E). Electrochemical properties of the single electrodes were first measured in a three-electrode cell system in 1 M Na₂SO₄ aqueous electrolyte. As-prepared CC (1 cm²), platinum plate, and saturated calomel electrode were used as the working, counter and reference electrode, respectively. A symmetric electrochemical capacitor was fabricated using a coin cell with two activated carbon cloth electrodes separated by an NKK separator in 1 M Na₂SO₄ electrolyte and tested under a two-electrode system. Before fabrication, the activated carbon clothes were immersed in the aqueous electrolyte for an hour and 3 to 4 drops of electrolyte were dropped on the NKK separator. Electrochemical impedance spectroscopy was performed under a sinusoidal signal at open circuit potential over a frequency range from 0.01 to 10⁵ Hz with a magnitude of 10 mV. The constant float voltage method was carried out to test the stability of the fabricated carbon symmetric device using a battery test system (LAND CT2001A).

**Calculation methods**

*Calculation of Specific Areal and Volumetric Capacitances in a Three-Electrode System:*

The areal capacitances of the working electrodes were calculated from the cyclic voltammetry curves using the equation shown below:

$$C_A = \frac{\int I \, dV}{v\Delta V}$$  \hspace{1cm} (1)

where $C_A$ (mF cm⁻²) is the areal capacitance, $I$ (A) is the discharge current, $v$ is the scan rate and $\Delta V$ is the operating discharge potential range.

The areal capacitances of the working electrodes were calculated from the galvanostatic charge/discharge curves using the equation shown below.

$$C_A = \frac{I\Delta t}{s\Delta V}$$  \hspace{1cm} (2)
\[ C_V = \frac{I\Delta t}{V\Delta V} \]  

where \( C_A \) (mF cm\(^{-2}\)) is the specific capacitance, \( I \) (A) is the discharge current, \( \Delta t \) (s) is the discharge time, \( S \) is the surface area (1 cm\(^2\)) of the carbon cloth electrode, \( \Delta V \) is the operating voltage (obtained from the discharge curves excluding the potential drop) and \( V \) is the volume (0.031 cm\(^3\)) of the carbon cloth electrode.

**Calculation of Specific gravimetric, areal and volumetric capacitance in a two-electrode system:** The gravimetric, areal and volumetric capacitances of the single electrode in a two-electrode system were calculated using the equations shown below.

\[
C_S \left( \text{F g}^{-1} \right) = \frac{2I\Delta t}{m\Delta V} \tag{4}
\]

\[
C_A \left( \text{F cm}^{-2} \right) = \frac{2I\Delta t}{S\Delta V} \tag{5}
\]

\[
C_V \left( \text{F cm}^{-3} \right) = \frac{2I\Delta t}{V\Delta V} \tag{6}
\]

where \( C_S \) (F g\(^{-1}\)) is the gravimetric capacitance, \( C_A \) (F cm\(^2\)) is the areal capacitance, \( C_V \) (F cm\(^3\)) is the volumetric capacitance, \( I \) (A) is the discharge current, \( \Delta t \) (s) is the discharge time, \( m \) is the mass of the carbon clothes, \( S \) is the surface area (1 cm\(^2\)) of the carbon cloth electrode, \( \Delta V \) is the operating voltage (obtained from the discharge curves excluding the potential drop) and \( V \) is the volume of the carbon cloth electrode.

**Calculation of Specific gravimetric, areal and volumetric capacitance of the supercapacitor device:** The specific capacitance of the assembled symmetric supercapacitor cell was evaluated using the equations shown below:

\[
C_{ST} \left( \text{F g}^{-1} \right) = \frac{C_S}{4} \tag{7}
\]

\[
C_{AT} \left( \text{F cm}^{-2} \right) = \frac{C_A}{4} \tag{8}
\]

\[
C_{VT} \left( \text{F cm}^{-3} \right) = \frac{C_V}{4} \tag{9}
\]

where \( C_S \) and \( C_{ST} \) (F g\(^{-1}\)) are the gravimetric capacitance of the electrode and assembled symmetric supercapacitor, respectively, \( C_A \) and \( C_{AT} \) (F cm\(^2\)) are the areal capacitance of the electrode and assembled symmetric supercapacitor, respectively and \( C_V \) and \( C_{VT} \) (F cm\(^3\)) are the volumetric capacitance of the electrode and assembled symmetric supercapacitor, respectively.

**Calculation of energy and power density of the supercapacitor device:** The energy and power density of the assembled symmetric supercapacitor were calculated using the equations shown below:

\[
E_T(Wh \text{ kg}^{-1}; Wh \text{ cm}^{-3}; Wh \text{ cm}^{-2}) = 0.5C_TV^2 \tag{10}
\]

\[
P_T(W \text{ kg}^{-1}; W \text{ cm}^{-3}; W \text{ cm}^{-2}) = \frac{3600E_T}{\Delta t} \tag{11}
\]
where $E_T (Wh \ cm^{-3}; Wh \ cm^{-2}; Wh \ kg^{-1})$ is the energy density, $P_T (W \ cm^{-3}; W \ cm^{-2}; W \ kg^{-1})$ is the power density, $C_T (F \ cm^{-3}; F \ cm^{-2}; F \ g^{-1})$ is the capacitance of the symmetric supercapacitor device, $V$ is the operating potential window of the supercapacitor and $\Delta t$ (s) is the discharge time.

*Calculation of resistance from the voltage drop:* The resistance was calculated from the galvanostatic discharge curves by dividing the voltage drop using the formula shown below:

$$ R = \frac{V_{\text{drop}}}{2I} \quad (12) $$

*Float Voltage Test:* The constant float voltage method was carried out to test the stability of the fabricated carbon symmetric device using a battery test system (LAND CT2001A). In brief, a constant voltage of 2 V was applied to an assembled supercapacitor device with the CC-400 °C-6h electrodes and 1 M Na$_2$SO$_4$ electrolyte. Charge/discharge cycles from 0.1 to 2.0 V were performed at a constant current density of 2 mA cm$^{-2}$ every 10 hours to quantify the corresponding retaining areal capacitance. The total test time was 300 hours.
**Fig. S1.** (a) Optical photo of CC-400 °C-6h. (b) SEM image of CC-300 °C-6h. (c) SEM image of CC-400 °C-2h. (d) Optical photo of shriveled CC-500 °C-6h.

**Fig. S2.** HRTEM image of the activated CC.
Fig. S3. TEM image of the pristine CC
Fig. S4. N₂ adsorption-desorption isotherms of CC-300 °C-6h and CC-400 °C-2h.
Fig. S5. (a) Deconvolution of the C 1s spectrum of the CC-300 °C-6h. (b) Deconvolution of the O 1s spectrum of the CC-300 °C-6h. (c) Deconvolution of the C 1s spectrum of the CC-400 °C-2h. (d) Deconvolution of the O 1s spectrum of the CC-400 °C-2h.
Fig. S6. Raman Spectra of the different carbon clothes showing the D and G bands.
Fig. S7. (a) Areal capacitance of the CC-400 °C-6h negative electrode at different scan rates. (b) Areal capacitance of the CC-400 °C-6h positive electrode at different scan rates.
Fig. S8. (a) Charge/discharge curves of CC-400 °C-6h at different current densities in a -1.2 – 0 V potential window. (b) Charge/discharge curves of CC-400 °C-6h at different current densities in a 0 – 0.85 V potential window. (c) Areal and volumetric capacitances of the activated CC negative electrode at different current densities. (d) Areal and volumetric capacitances of the activated CC positive electrode as a function of current density.
Fig. S9. (a) Cyclic voltammetry curves of pristine CC, CC-300 °C-6h, CC-400 °C-2h, and CC-400 °C-6h negative electrodes at 5 mV s⁻¹. (b) Areal capacitances of pristine CC, CC-300 °C-6h, CC-400 °C-2h, and CC-400 °C-6h negative electrodes at 1 mA cm⁻². (c) Cyclic voltammetry curves of pristine CC, CC-300 °C-6h, CC-400 °C-2h, and CC-400 °C-6h positive electrodes at 5 mV s⁻¹. (d) Areal capacitances of pristine CC, CC-300 °C-6h, CC-400 °C-2h, and CC-400 °C-6h positive electrodes at 1 mA cm⁻².
Fig. S10. Nyquist plot of the activated CC at high frequencies.

Fig. S11. Specific gravimetric capacitance of the CC-400 °C-6h-based symmetric supercapacitor at different current densities.
Fig. S12. Float voltage test in 1 M Na$_2$SO$_4$ electrolyte.

Fig. S13. Nyquist plot of the activated CC based symmetric electrochemical capacitor.
**Fig. S14.** The areal and gravimetric energy densities of the activated CC-based aqueous symmetric supercapacitor at different areal and gravimetric power densities.

**Fig. S15.** Dynamic water contact angle measurement for pristine CC.
Study of the water splitting capabilities of the CC-400 °C-6h in the 1 M Na₂SO₄ electrolyte

Fig. S16. (a) CV curves of the CC–400 °C–6h electrode in increasing potentials up to -1.3 V. (b) Linear sweep voltammetry (LSV) analysis at 2 mV s⁻¹ to study the hydrogen evolution. (c) CV curves of the CC–400 °C–6h electrode in increasing potentials up to 0.9 V. (d) LSV analysis at 2 mV s⁻¹ to study the oxygen evolution.

The potentials for hydrogen and oxygen evolution are pH-dependent and can be determined from the equations shown below [1]:

\[ E_{\text{red}} = -0.059 \text{pH} - 0.244 \text{ vs. SCE} \]  \hspace{1cm} (1)
\[ E_{\text{oxid}} = 1.23 - 0.059 \text{pH} - 0.244 \text{ vs. SCE} \]  \hspace{1cm} (2)

The CV curves tested at a scan rate of 5 mV s⁻¹ with gradual shift to more negative (Fig. S16 a) and positive potentials (Fig. S16 c) shows that the activated CC is stable beyond the theoretical onset potentials for hydrogen and oxygen evolutions (indicated by a dotted line). The extended potential window is a result of the large hydrogen and oxygen overpotentials of the activated CC in 1 M Na₂SO₄ electrolyte, as confirmed from the LSV curves (Fig. S16 b and d).
The 1 M Na$_2$SO$_4$ electrolyte has a neutral pH value close to 7, hence a little amount of hydroxyl (OH$^-$) anions generated from the water reduction is able to cause an increase of the pH inside the pores of the CC–400 °C–6h to much higher values and this results in a higher overpotential for di-hydrogen evolution [2, 3]. On the other hand, oxygen evolution reactions (OER) are kinetically sluggish processes which involves multi-step redox reactions between the electrolyte and the oxygen functional groups on the carbon material surface. The sluggish nature of these reactions in the CC–400 °C–6h electrode results in a large overpotential which suppresses the oxygen evolution beyond the theoretical onset potential (0.606 V vs. SCE). The LSV curves show that the hydrogen and oxygen evolution start beyond -1.2 and 0.85 V vs. SCE, respectively, hence, it is safe to cycle the symmetric electrochemical capacitor device in the wide 2.0 V potential window.
**Table S1** Comparison of the XPS elemental composition of the CC-400 °C-6h electrodes as well as the control samples.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Carbon (at %)</th>
<th>Oxygen (at %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine CC</td>
<td>95.14</td>
<td>4.86</td>
</tr>
<tr>
<td>CC-360 °C-6h</td>
<td>95.29</td>
<td>4.71</td>
</tr>
<tr>
<td>CC-400 °C-2h</td>
<td>93.97</td>
<td>6.03</td>
</tr>
<tr>
<td>CC-400 °C-6h</td>
<td>87.89</td>
<td>12.11</td>
</tr>
</tbody>
</table>

**Table S2** Percentages of oxygen functional groups derived from the deconvoluted O 1s peak.

<table>
<thead>
<tr>
<th>Carbon Textile Material</th>
<th>C-OH (%)</th>
<th>O-C=O (%)</th>
<th>COOH (%)</th>
<th>C=O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine CC</td>
<td>48.03</td>
<td>29.51</td>
<td>22.46</td>
<td>–</td>
</tr>
<tr>
<td>CC-300 °C-6h</td>
<td>49.68</td>
<td>28.15</td>
<td>22.16</td>
<td>–</td>
</tr>
<tr>
<td>CC-400 °C-2h</td>
<td>25.3</td>
<td>30.87</td>
<td>21.81</td>
<td>21.86</td>
</tr>
<tr>
<td>CC-400 °C-6h</td>
<td>29.04</td>
<td>26.79</td>
<td>17.91</td>
<td>26.27</td>
</tr>
</tbody>
</table>
Table S3 Comparison of the electrochemical performance of the CC-400 °C-6h electrodes and other carbon textile-based electrodes.

<table>
<thead>
<tr>
<th>Carbon Textile Material</th>
<th>Electrolyte</th>
<th>Voltage Range (V)</th>
<th>Capacitance (mF cm$^{-2}$)</th>
<th>Capacitance Retention</th>
<th>Cycling Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemically activated carbon clothes [4]</td>
<td>1 M H$_2$SO$_4$</td>
<td>0 – 1.0 V</td>
<td>88 (10 mV s$^{-1}$)</td>
<td>73 % retention at 1000 mV s$^{-1}$</td>
<td>97 % after 20000 cycles</td>
</tr>
<tr>
<td>Electrochemically activated carbon clothes [5]</td>
<td>1 M LiCl</td>
<td>-1.0 – 0 V</td>
<td>756 (6 mA cm$^{-2}$)</td>
<td>65.2 % retention at 20 mA cm$^{-2}$</td>
<td>Stable cycling up to 30000 cycles</td>
</tr>
<tr>
<td>Paper + CNT + MnO$_2$ [6]</td>
<td>6 M KOH</td>
<td>0 – 1.0 V</td>
<td>123 (1 mA cm$^{-2}$)</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Activated carbon clothes [7]</td>
<td>1 M H$_2$SO$_4$</td>
<td>0 – 1.0 V</td>
<td>482.04 (1 mA cm$^{-2}$)</td>
<td>89.7 % retention at 60 mA cm$^{-2}$</td>
<td>129 % after 30000 cycles</td>
</tr>
<tr>
<td>Activated carbon clothes [8]</td>
<td>1 M H$_2$SO$_4$</td>
<td>0 – 1.0 V</td>
<td>505 (6 mA cm$^{-2}$)</td>
<td>88 % retention at 48 mA cm$^{-2}$</td>
<td>97 % after 30000 cycles</td>
</tr>
<tr>
<td>Functionalized carbon fabric [9]</td>
<td>0.5 M Na$_2$SO$_4$</td>
<td>0 – 0.8 V</td>
<td>143.4 (1 mA cm$^{-2}$)</td>
<td>91.63 % and 88.5 % retention at 20 mA cm$^{-2}$</td>
<td>–</td>
</tr>
<tr>
<td>Hydrothermally activated graphene fiber fabric [10]</td>
<td>1 M H$_2$SO$_4$</td>
<td>–</td>
<td>1060 (1 mA cm$^{-2}$)</td>
<td>68 % retention at 100 mA cm$^{-2}$</td>
<td>Stable up to 50000 cycles</td>
</tr>
<tr>
<td>Carbonized cotton mat [11]</td>
<td>1 M Na$_2$SO$_4$</td>
<td>0 – 0.8 V</td>
<td>0.7 (0.0112 mA cm$^{-2}$)</td>
<td>92 % retention at 0.112 mA cm$^{-2}$</td>
<td>–</td>
</tr>
<tr>
<td>Graphene cellulose paper [12]</td>
<td>1 M H$_2$SO$_4$</td>
<td>0 – 0.8 V</td>
<td>81 (1 mV s$^{-1}$)</td>
<td>–</td>
<td>Stable up to 50000 cycles</td>
</tr>
<tr>
<td>Activated carbon cloth [13]</td>
<td>6 M KOH</td>
<td>0 – 1 V</td>
<td>1136.7 (2 mV s$^{-1}$)</td>
<td>–</td>
<td>Stable cycling up to 50000 cycles</td>
</tr>
<tr>
<td>Activated porous carbon fiber textile [14]</td>
<td>5 M LiCl</td>
<td>-1 – 0 V</td>
<td>1200 (4 mA cm$^{-2}$)</td>
<td>59 % at 80 mA cm$^{-2}$</td>
<td>Stable cycling up to 25000 cycles</td>
</tr>
<tr>
<td>CC-400 °C-6h [This work]</td>
<td>1 M Na$_2$SO$_4$</td>
<td>0 – 2 V</td>
<td>1700 (1 mA cm$^{-2}$)</td>
<td>66 % at 65 mA cm$^{-2}$</td>
<td>Stable cycling up to 20000 cycles</td>
</tr>
</tbody>
</table>
Table S4 Carbon yield after activation.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Before</th>
<th>After</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine CC</td>
<td>~14.5 mg cm$^{-2}$</td>
<td>-</td>
</tr>
<tr>
<td>CC-360 °C-6h</td>
<td>~14.5 mg cm$^{-2}$</td>
<td>~14.4 mg cm$^{-2}$</td>
</tr>
<tr>
<td>CC-400 °C-2h</td>
<td>~14.5 mg cm$^{-2}$</td>
<td>~13.85 mg cm$^{-2}$</td>
</tr>
<tr>
<td>CC-400 °C-6h</td>
<td>~14.5 mg cm$^{-2}$</td>
<td>~13 mg cm$^{-2}$</td>
</tr>
<tr>
<td>CC-500 °C-6h</td>
<td>~14.5 mg cm$^{-2}$</td>
<td>~0.16 mg cm$^{-2}$</td>
</tr>
</tbody>
</table>

References