Hierarchical porous graphitic carbon for high-performance supercapacitors at high temperature†


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Electrochemical measurement

Carbon product (80 wt%), acetylene black (15 wt%) and polytetrafluoroethylene (PTFE) binder (5 wt%) were mixed in ethanol, then coated onto nickel-foam current collectors (1×1 cm²), and dried at 120 °C for 12 h. The mass loading of the active materials in each working electrode was ~1.5 mg cm⁻². For the three-electrode system, Pt foil and Hg/HgO electrode were used as the counter and reference electrodes, respectively. The electrochemical performance was tested in 6 mol L⁻¹ KOH electrolyte. For the two-electrode system (2032 stainless steel coin cell, PTFE as insulation), both 6 mol L⁻¹ KOH and EMIMBF₄ were used as the electrolyte, respectively. The dried electrodes (~1.5 mg cm⁻², 0.2 mm in thickness) were symmetrically assembled with glassy paper as the separator in a glove box filled with argon. The cyclic voltammetry (CV), galvanostatic charge-discharge, and electrochemical impedance spectroscopy (EIS) measurements were carried out using an electrochemical workstation (CHI660E, ChenHua Instruments Co. Ltd., Shanghai).

For the three-electrode system, the specific capacitance derived from galvanostatic tests were calculated by the following equations:

\[ C_{sp} = \frac{I \Delta t}{m \Delta V} \]

(1)

in which \( C \) (F g⁻¹) is the specific capacitance; \( I \) (A) is the discharge current; \( \Delta t \) (s) is the discharge time; \( \Delta V \) (V) is the potential window; and \( m \) (g) is the mass of the active materials.

\[ \rho = \frac{1}{V_{total}} + \frac{1}{\rho_{carbon}} \]

(2)

in which \( \rho \) (g cm⁻³) is the density of electrode materials; \( V_{total} \) (cm³ g⁻¹) is the total pore volume of active material measured by nitrogen isotherm; and \( \rho_{carbon} \) is the density of carbon (2 g cm⁻³).

\[ C_v = C \rho \]

(3)

in which \( C_v \) (F cm⁻³) is the volumetric capacitance; \( C \) (F g⁻¹) is the specific capacitance; and \( \rho \) (g cm⁻³) is the density of electrode materials.

For the two-electrode system, the specific (or gravimetric) capacitances \( C \) (F g⁻¹) were calculated using equation 4 for galvanostatic charge-discharge method and equation 5 for cyclic voltammetry data:

\[ C_{sp} = \frac{4I \Delta t}{m \Delta V} \]

(4)

\[ C = \frac{2}{m v (V_b - V_a)} \int_{V_a}^{V_b} I dV \]

(5)

in which \( I \) (A) is the discharge current, \( \Delta t \) (s) is the discharge time, \( \Delta V \) (V) is the potential window, \( v \) (V s⁻¹) is the scan rate, \( V_b \) and \( V_a \) (V) are the high and low potential limit of the CV tests; and \( m \) (g) is the total mass of the active materials.

To construct the Ragone plot, the energy density \( E \) (Wh kg⁻¹) and \( P \) (W kg⁻¹) based on the electrode were calculated by the following equations:

\[ E = \frac{1}{8} C_{sp} (\Delta V)^2 \left( \frac{1000}{3600} \right) \]

(6)

\[ P = 3600 \frac{E}{\Delta t} \]

(7)

in which \( C \) (F g⁻¹) is the specific capacitance, and \( \Delta V \) (V) is the potential window, and \( \Delta t \) (s) is the discharge time.
The SSA was measured by nitrogen adsorption-desorption isotherms (BeiShiDe Instrument-S&T 3H-2000PS1) after vacuum drying at 120 °C for 1 h. The Brunauer-Emmett-Teller (BET) method was used for calculating the specific surface area, and the Barrett-Joyner-Halenda (BJH) model was used for estimating the pore size distribution. Nitrogen adsorption–desorption isotherm (with the pore size distribution in the inset) of (a) ‘GC-Mg/ZA’, (b) ‘GC-1Mg/U’, (c) ‘GC-3Mg/U’, and (d) ‘GC-5Mg/U’.
Fig. S2 (a) XPS survey, (b) C1s, (c) O1s and (d) N1s spectra of the ‘GC-3Mg/U’ sample.

Fig. S3 The urea and zinc acetate dehydrate mixture at the same conditions.
**Fig. S4** Electrochemical performance of all samples measured in a three-electrode system using 6 mol L\(^{-1}\) KOH electrolyte. (a) CV curves at a scan rate of 50 mV s\(^{-1}\). (b) Charge–discharge curves at a current density of 1 A g\(^{-1}\). (c) Gravimetric capacitances at different current densities from 1 to 40 A·g\(^{-1}\). (d) Volumetric capacitances at different current densities.

**Table S1** Comparison of the specific capacitances of previously fabricated hierarchical porous carbons using three-electrode systems.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Electrolyte</th>
<th>Current Density</th>
<th>Specific Capacitance (F·g(^{-1}))</th>
<th>Ref. No.</th>
</tr>
</thead>
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<tr>
<td>Hierarchical porous graphitic carbon</td>
<td>6 M KOH</td>
<td>1 A·g(^{-1})</td>
<td>320</td>
<td>This work</td>
</tr>
<tr>
<td>Hierarchical porous carbon fibers</td>
<td>3 M KOH</td>
<td>1 A·g(^{-1})</td>
<td>189.7</td>
<td>[1]</td>
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<tr>
<td>Three-dimensional beehive-like hierarchical porous carbons</td>
<td>6 M KOH</td>
<td>1 A·g(^{-1})</td>
<td>287</td>
<td>[2]</td>
</tr>
<tr>
<td>Hierarchical hollow porous carbon spheres</td>
<td>6 M KOH</td>
<td>1 A·g(^{-1})</td>
<td>303.9</td>
<td>[3]</td>
</tr>
<tr>
<td>Hierarchical porous carbons</td>
<td>6 M KOH</td>
<td>0.2 A·g(^{-1})</td>
<td>283.4</td>
<td>[4]</td>
</tr>
<tr>
<td>Porous carbon through hard–soft dual templates</td>
<td>6 M KOH</td>
<td>1 A·g(^{-1})</td>
<td>153</td>
<td>[5]</td>
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<tr>
<td>Hierarchical porous carbons</td>
<td>6 M KOH</td>
<td>1 A·g(^{-1})</td>
<td>190</td>
<td>[6]</td>
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<td>Nitrogen-doped porous carbon nanofibers</td>
<td>6 M KOH</td>
<td>1 A·g(^{-1})</td>
<td>202</td>
<td>[7]</td>
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<td>Nitrogen and sulfur codoped porous carbon microsphere</td>
<td>6 M KOH</td>
<td>0.1 A·g(^{-1})</td>
<td>295</td>
<td>[8]</td>
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<td>Chlorine-doped ordered mesoporous carbon</td>
<td>6 M KOH</td>
<td>0.5 A·g(^{-1})</td>
<td>220</td>
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</table>
**Fig. S5** Electrochemical performance characteristics of ‘HPGC-3’ measured in a two-electrode system using EMIMBF$_4$ electrolyte operating at 25 °C, 50 °C, 100 °C and 150 °C, respectively. CV curves at a scan rate of (a) 100 mV s$^{-1}$; (b) 500 mV s$^{-1}$. Charge–discharge curves at a current density of (c) 1 A g$^{-1}$; (d) 10 A g$^{-1}$.

**Fig. S6** (c) Cycling stabilities measured at 2 A g$^{-1}$ operating at 150 °C, with the magnified galvanostatic charge-discharge curves before and after 1500 cycles in the inset. (b) Long-term stability of HPGC-3’-based supercapacitors under dynamic thermal stresses, with the magnified galvanostatic charge-discharge curves before and after 500 cycles in the inset. (c) Ragone plot of ‘HPGC-3’.
Fig. S7 Electrochemical performance of ‘HPGC-3G’, ‘HPGC-3P’ and ‘HPGC-3H’ using glycine (G), polyvinylpyrrolidone (P) and hexamethylenetetramine (H) to replace urea during the HPGC synthesis, measured in a three-electrode system in the 6 mol L$^{-1}$ KOH electrolyte. Charge–discharge curves of (a) ‘HPGC-3G’; (c) ‘HPGC-3P’; (e) ‘HPGC-3H’ at different current densities. CV curves of (b) ‘HPGC-3G’; (d) ‘HPGC-3P’; (f) ‘HPGC-3H’ at different scan rates.
References


