Supplementary Materials

Synthesis of Hierarchical Porous Carbon from Metal Carbonates Towards High-Performance Lithium Storage

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1. Experimental section

Materials synthesis

The HPC was synthesized by calcining the mixture of LiH (97%, Aladdin) and metal carbonates such as Li$_2$CO$_3$ (>99%, Aladdin), Na$_2$CO$_3$ (99.5%, Aladdin), MgCO$_3$ (40–47% MgO, Macklin) and CaCO$_3$ (99%, Aladdin) in a homemade reactor with online gaseous pressure and sample temperature detectors (schematic diagram). The LiH was mixed with metal carbonates in a molar ratio of 4:1 via ball milling for 1 h. In a typical ball milling, 0.06 mol LiH and 0.015 mol metal carbonates were weighted and loaded into each milling jar (100 mL). The mixtures of LiH and metal carbonates were prepared on a planetary ball mill (QM–3SP4, Nanjing) rotating at 200 rpm. The weight ratio of balls to samples is about 20:1. For the each experiment, the mixture (0.06 mol LiH and 0.015 mol metal carbonate) was loaded into a stainless reactor (35 mL) and heated at a rate of 0.5 °C min$^{-1}$ from room temperature (RT) to a preset temperature in an initial vacuum. After cooling, the solid products were collected and washed by hydrochloric acid (6 M), deionized water and absolute ethanol to remove impurity. Finally, the HPC was obtained by drying the post–washed solid products at 100 °C for 12 h in a vacuum oven.
Schematic diagram: the homemade reactor with online gaseous pressure and sample temperature detectors.

Characterization

X–ray diffraction (XRD, X'Pert Pro diffractometer, Cu Ka, λ=1.5418 Å) technique was used to analyse the phase structure. XRD patterns were recorded in a 2θ range of 10–80° with a step length of 0.02°. The thermal behaviour of the reaction between LiH and metal carbonates was investigated on a differential scanning calorimetry (DSC, Mettler Toledo DSC–1). DSC curves were measured at a heating rate of 5 °C min⁻¹ under Argon atmosphere. Transmission electron microscopy (TEM, FEI, Tecnai G² F30) and scanning electron microscopy (SEM, Hitachi S–4700) equipped with an energy–dispersive spectroscopy (EDS) detector were employed to characterize the microstructure, morphology and chemical composition of as–synthesized HPC. Mass spectrometer (QIC–20, Hiden) was used to analyse the composition of gases desorbed from the synthesis reaction of HPC. The graphitization degree of HPC was evaluated by Raman spectrum measured on a micro–Raman spectrometer.
Nitrogen adsorption and desorption isotherms were measured at 77 K by using an automated adsorption apparatus (Micromeritics ASAP 2020). The specific surface area and pore size distribution were calculated by using the Brunauer–Emmett–Teller (BET) model. Mercury porosimeter (AutoPore IV 9500) was employed to determine the macro–pore size distribution of HPC.

Fourier transform infrared (FT–IR) spectrum was measured on an infrared spectrophotometer (Nicolet 6700).

**Electrochemical measurements**

The electrochemical lithium storage performance of carbon materials was evaluated by using 2032 coin–type cells with lithium foil as the counter and reference electrode. For the fabrication of working electrodes, the N–methyl–2–pyrrolidinone (NMP) slurry of 85 wt% carbon materials and 15 wt% polyvinylidene fluoride binder was first coated onto a copper foil, followed by removing liquid NMP at a temperature of 100 °C for 12 h in a vacuum oven. After surface rolling, the working electrode was used to assemble lithium–ion cell in a MBRAUN glovebox under argon atmosphere. The celgard 2500 membrane and 1 M LiPF₆ solution of diethyl carbonate and ethylene carbonate in a volume ratio of 1:1 were selected as the separator and electrolyte, respectively. Galvanostatic charge/discharge tests of lithium–ion cells were carried out on a battery test system (CT–3008W, Neware) in a voltage window of 0.01–3.0 V at various current densities. Cyclic voltammograms (CV) were performed by using an electrochemical workstation (CHI660E, Chenhua) at a scan
rate of 0.1 mV s\(^{-1}\).

2. Results and discussion

The kinetics of Li\(^+\) intercalated into the sponge–like HPC electrode was satisfied the power–law relationship between the current \(i\) and scan rate \(v\):\(^{1-3}\)

\[
i = av^b
\]

where \(a\) and \(b\) are adjustable values. The \(b=0.5\) and \(1\) indicate a diffusion controlled and a surface controlled lithium storage behaviors, respectively.

The ratios of capacitive contribution can be quantitatively determined by calculating the current \(i\) at a certain scan rate \(v\). The current response with \(v^{1/2}\) can be confirmed the diffusion controlled processes, the current response with \(v\) can be ensured the capacitive effects. Therefore, the Equation (1) can be described as follow:

\[
i (V) = k_1v^{1/2} + k_2v
\]

\[
i (V)/v^{1/2} = k_1 + k_2v^{1/2}
\]

where \(k_1\) and \(k_2\) are constant values. Their values of \(k_1\) (the y–axis intercept point) and \(k_2\) (the slope) can be obtained by plotting \(i(V)/v^{1/2}\) vs \(v^{1/2}\) at different potentials with a straight line. The capacitive contribution of the sponge–like HPC electrode can be obtained by calculating and separating the total measured current of the values( \(i(V)=k_2v\) ) (Fig.6c).\(^{4-6}\)
3. Figures

**Fig. S1.** Temperature derivative of the gaseous pressures in the reactor (dP/dT) for the reaction between Li$_2$CO$_3$ and LiH.

**Fig. S2.** Hydrogen signal of the gaseous products desorbed from the reaction between Li$_2$CO$_3$ and LiH.
**Fig. S3.** Photographs of LiH, Li$_2$CO$_3$ and solid products of LiH reacting with Li$_2$CO$_3$.

**Fig. S4.** EDS spectrum of as–synthesized sponge–like HPC.
**Fig. S5.** Differential scanning calorimetry (DSC) curve of the Li$_2$CO$_3$–4LiH mixture heated at a rate of 5 °C min$^{-1}$.

**Fig. S6.** The synthesis and characterization of HPCs derived from metal carbonates. Time dependence of temperatures and gaseous pressures in the reactor of the mixtures of (a) 4LiH–Na$_2$CO$_3$, (b) 4LiH–MgCO$_3$, (c) 4LiH–CaCO$_3$. (d–f) SEM images and EDS spectra, and (g–i) TEM images of the HPCs derived from Na$_2$CO$_3$, MgCO$_3$, and CaCO$_3$, respectively.
Fig. S7. XRD pattern of sponge–like HPC.

Fig. S8 FTIR spectrum of sponge–like HPC.
**Fig. S9.** Charge and discharge curves of sponge–like HPC at 0.2 A g\(^{-1}\).

**Fig. S10.** Charge and discharge curves of graphite at 0.2 A g\(^{-1}\).
Fig. S11. Cyclic voltammograms of graphite at a scan rate of 0.1 mV s$^{-1}$.

Fig. S12. Charge and discharge curves of the sponge–like HPC at 0.2, 0.5, 1, 2 and 4 A g$^{-1}$. 
Fig. S13. Comparison of the rate capabilities of sponge-like HPC and various nanocarbons.
4. Tables

Table S1. The melting points and decomposition temperatures of LiH and \( \text{Li}_2\text{CO}_3 \)

<table>
<thead>
<tr>
<th>Related compounds</th>
<th>Melting point</th>
<th>Decomposition temperature</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Li}_2\text{CO}_3 ) (s)</td>
<td>723 °C</td>
<td>1310 °C</td>
<td>[1]</td>
</tr>
<tr>
<td>LiH (s)</td>
<td>680 °C</td>
<td>900‒1000 °C</td>
<td>[1,2]</td>
</tr>
</tbody>
</table>


Table S2. The values of standard enthalpy of formation for related compounds from the elements

<table>
<thead>
<tr>
<th>Related compounds</th>
<th>LiH (s)</th>
<th>( \text{Li}_2\text{O} ) (s)</th>
<th>( \text{Li}_2\text{CO}_3 ) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard enthalpy of formation (kJ/mol)</td>
<td>–90.5</td>
<td>–597.9</td>
<td>–1215.9</td>
</tr>
</tbody>
</table>

\[ 4\text{LiH} + \text{Li}_2\text{CO}_3 \rightarrow \text{C} + 3\text{Li}_2\text{O} + 2\text{H}_2 \] \hspace{1cm} (4)

According to the standard enthalpies of the reactants and products (Table S1), the reaction between LiH and \( \text{Li}_2\text{CO}_3 \) from equation (1) was calculated to be \(-215.8\) kJ mol\(^{-1}\). These results imply that the above reaction is an exothermic nature, which is consistent with the DSC result (Fig. S5).
Table S3. Comparison of the electrochemical properties of various nanocarbons used as anode materials for lithium ion batteries.

<table>
<thead>
<tr>
<th>Various Nanocarbons</th>
<th>Current (mA g⁻¹)</th>
<th>Capacity (mAh g⁻¹) @ cycles number</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hierarchical Porous Carbon Monoliths</td>
<td>74.4</td>
<td>500@40</td>
<td>7</td>
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<tr>
<td>Carbon fibers (Hierarchical porous)</td>
<td>137.6</td>
<td>360@800</td>
<td>8</td>
</tr>
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<td>Mesoporous Carbon–Carbon Nanotube (Hierarchical porous)</td>
<td>37.2</td>
<td>786@20</td>
<td>9</td>
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<tr>
<td>Hierarchical porous carbon monoliths</td>
<td>100</td>
<td>669@50</td>
<td>10</td>
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<tr>
<td>Hierarchical porous carbon microrods</td>
<td>1000</td>
<td>833@700</td>
<td>11</td>
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<tr>
<td>Hierarchical porous carbon</td>
<td>1000</td>
<td>825@1000</td>
<td>12</td>
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<tr>
<td>Micro–sized porous carbon spheres</td>
<td>100</td>
<td>507@100</td>
<td>13</td>
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<tr>
<td>Carbon Nanofiber Films</td>
<td>500</td>
<td>333@500</td>
<td>14</td>
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<tr>
<td>Multiwall Carbon Nanotubes</td>
<td>372</td>
<td>460@1200</td>
<td>15</td>
</tr>
<tr>
<td>Highly porous carbon nanofibers</td>
<td>50</td>
<td>1780@40</td>
<td>16</td>
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<tr>
<td>Hybrid carbon nanotube and graphene nanostructures</td>
<td>600</td>
<td>588@250</td>
<td>17</td>
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<tr>
<td>Hollow carbon nanospheres</td>
<td>37.2</td>
<td>630@50</td>
<td>18</td>
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<td>Two–dimensional hierarchical carbon architecture</td>
<td>2000</td>
<td>748@400</td>
<td>19</td>
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<td>Highly defect carbon nanofibers</td>
<td>500</td>
<td>340@200</td>
<td>20</td>
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<td>Phosphorus film coating on interconnected carbon nanotubes</td>
<td>50</td>
<td>1396.6@50</td>
<td>21</td>
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<tr>
<td>Sponge–like HPC</td>
<td>200</td>
<td>1750@610</td>
<td>Our work</td>
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<tr>
<td></td>
<td>1000</td>
<td>1030@600</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4000</td>
<td>505@2000</td>
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</table>
5. References


