Supporting Information

Amorphous S-rich $S_{1-x}Se_x/C$ (x≤0.1) Composites Promise Better Lithium Sulfur Batteries in Carbonate-based Electrolyte

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Figure S1. (a) TEM image, (b) nitrogen sorption isotherms, and (c) pore size distributions of the as-prepared porous carbon.

Figure S2. (a,b) TEM images of the mixture of Se, S and porous carbon after the ball-milled process.
Figure S3. Thermogravimetric analysis of the as-prepared $S_{1-x}Se_x/C$ composites. All the tests were conducted with a temperature ramp of 10 °C min$^{-1}$ in N$_2$.

Table S1. The Se, S and C content in the $S_{1-x}Se_x/C$ samples ($x=0.05, 0.06, 0.08, 0.1$) based on thermogravimetric analysis and elemental analysis.

<table>
<thead>
<tr>
<th>Statement</th>
<th>Se (wt%)</th>
<th>S (wt%)</th>
<th>C (wt%)</th>
<th>$x$ in $S_{1-x}Se_x/C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{0.9}Se_{0.1}/C$</td>
<td>10.9</td>
<td>38.9</td>
<td>50.2</td>
<td>0.102</td>
</tr>
<tr>
<td>$S_{0.92}Se_{0.08}/C$</td>
<td>8.65</td>
<td>41.05</td>
<td>50.3</td>
<td>0.079</td>
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<tr>
<td>$S_{0.94}Se_{0.06}/C$</td>
<td>7.4</td>
<td>42.9</td>
<td>49.7</td>
<td>0.065</td>
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<tr>
<td>$S_{0.95}Se_{0.05}/C$</td>
<td>6.4</td>
<td>45.3</td>
<td>48.3</td>
<td>0.054</td>
</tr>
</tbody>
</table>

Figure S4. EDS spectrum of the $S_{0.94}Se_{0.06}/C$ sample.
Figure S5. (a) Raman spectra of $\text{S}_{1-x}\text{Se}_x$/C samples recorded at room temperature, (b) Raman spectra of $\text{S}_{1-x}\text{Se}_x$/C samples ($x=0.05, 0.08, 0.1$) recorded at -110 °C. (c) Raman spectra of $\text{S}_{1-x}\text{Se}_x$/C samples in CS$_2$ solution, (d) Raman spectrum of CS$_2$ solution.
Figure S6. The phase diagram of sulphur-selenium binary system.

Figure S7. XPS spectra of S 2p and Se 3p in the S_{0.94}Se_{0.06} sample without carbon after heat treatment.
Figure S8. XRD patterns of $S_{0.9}Se_{0.1}$, $S_{0.92}Se_{0.08}$ and $S_{0.95}Se_{0.05}$ samples without carbon after heat treatment.

Figure S9. Raman spectra of $S_{1-x}Se_x$ ($x = 0.05, 0.06, 0.08, 0.1$) samples recorded at room temperature.
Figure R10. Typical galvanostatic discharge-charge curves of the cell with $S_{0.94}Se_{0.06}$ in the potential region of 0.8–3 V versus Li/Li$^+$ at 0.02 A g$^{-1}$.

Figure S11. Discharge/charge profiles of $S_{0.94}Se_{0.06}$/C samples obtained at 110 and 200 °C, respectively, with current density of 0.2 A g$^{-1}$. 
Figure S12. Cycling performance of S$_{1-x}$Se$_x$/C samples (x=0.05, 0.08, 0.1) at 1 A g$^{-1}$.

Figure S13. Cycling performance of S/C composites at 0.2 A g$^{-1}$. 
Figure S14. Raman spectra of $S_{1-x}Se_x/C$ electrodes at charge state recorded in CS$_2$ solution.
Figure R15. (a) Cycling performance of $S_{0.94}Se_{0.06}/C$ electrode with higher loading about 2-3 mg cm$^{-2}$ at current density of 0.5, 1 and 2 A g$^{-1}$. (b) Cycle performance of $S_{0.94}Se_{0.06}/C$ electrode with higher loading about 2-3 mg cm$^{-2}$ at various current rates: 0.1, 0.2, 0.5, 1, 2, 5, 10, and 20 A g$^{-1}$ and then back to 0.5 A g$^{-1}$. (c) Cycling performance of $S_{0.94}Se_{0.06}/C$-20 and $S_{0.94}Se_{0.06}/C$-40 electrodes at current density of 0.5 A g$^{-1}$. (d) Cycle performance of $S_{0.94}Se_{0.06}/C$-20 and $S_{0.94}Se_{0.06}/C$-40 electrodes at various current rates: 0.1, 0.2, 0.5, 1, 2, 5, 10, and 20 A g$^{-1}$ and then back to 0.5 A g$^{-1}$. 
Figure S16. (a) The electrochemical impedance spectra of the different $S_{1-x}Se_x/C$ samples ($x=0.05$, 0.06, 0.08, 0.1) and S/C composite cathodes (the scattered data points and continuous lines represent experimental data and corresponding fitting results, respectively). (b) The corresponding equivalent circuits. The impedance of different $S_{1-x}Se_x/C$ ($x=0.05$, 0.06, 0.08, 0.1) electrodes are measured by alternating current (AC) impedance spectroscopy in their full charge state after 1 cycle (Figure S13a). All of the impedance diagrams consist of a large-radius semicircle in the high-frequency region and inclined line in the low-frequency region. Although complex impedance plot looks to give single semicircle, it has two relaxation processes in the high-frequency region. The complex modulus plots (Figure S13c) make these clear, giving two distinct semicircles in high-frequency region. Due to the cell is combined with solid electrode and electrolyte, one is attributed to the surface SEI layers ($R_{SEI}$) and the other to the charge transfer in electrode material ($R_{CT}$). Thus, all EIS plots are fitted with equivalent circuits by series of R (electrolyte resistance, $R_s$) and two parallel RC circuits (Figure S13b). The obtained results are shown in Table S2 in the Supporting Information. As shown in Table S2, the $S_{0.95}Se_{0.05}/C$ composite cathode demonstrated the highest $R_{CT}$ which means the highest resistance compared with other three electrodes. Moreover, the electrical conductivity of the $S_{1-x}Se_x/C$ composite cathodes increases significantly along with the increase of the content of Se.

Table S2. Equivalent-circuit parameters obtained from fitting the experimental impedance spectra.

<table>
<thead>
<tr>
<th>Statement</th>
<th>$R_s$(Ω)</th>
<th>$R_{SEI}$(Ω)</th>
<th>$R_{CT}$(Ω)</th>
<th>CPE$_{SEI}$(F) $^a$</th>
<th>CPE$_{CT}$(F) $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S/C</td>
<td>2.39</td>
<td>3.00</td>
<td>172.8</td>
<td>3.28E-6</td>
<td>1.15E-5</td>
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<tr>
<td>$S_{0.95}Se_{0.05}/C$</td>
<td>2.44</td>
<td>1.02</td>
<td>67.54</td>
<td>1.16 E-7</td>
<td>6.27 E-5</td>
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<tr>
<td>$S_{0.94}Se_{0.06}/C$</td>
<td>2.43</td>
<td>2.52</td>
<td>60.1</td>
<td>7.93E-7</td>
<td>1.50E-5</td>
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<tr>
<td>$S_{0.92}Se_{0.08}/C$</td>
<td>2.03</td>
<td>3.49</td>
<td>27.06</td>
<td>4.52 E-6</td>
<td>1.22 E-5</td>
</tr>
<tr>
<td>$S_{0.90}Se_{0.1}/C$</td>
<td>2.04</td>
<td>2.72</td>
<td>21.96</td>
<td>4.03 E-6</td>
<td>1.35 E-5</td>
</tr>
</tbody>
</table>

$^a$ CPE$_1$ and CPE$_2$: represent the two resistors with constant phase elements.
Figure S17. CV curves for $S_{0.94}Se_{0.06}/C$ electrode at a scan rate of 0.1 mV $s^{-1}$ in the voltage range of 3.0–0.8 V vs Li$^+$/Li after 300 cycles test.

Figure S18. (a) SEM and (b) TEM images of the $S_{0.94}Se_{0.06}/C$ electrode after 500 cycles.