Supporting information

Triple-Layered Carbon-SiO₂ Composite Membrane for High Energy Density and Long Cycling Li-S Batteries

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Table S1. The structure parameters of the C, C/SiO$_2$, and S filled electrode membrane materials

<table>
<thead>
<tr>
<th>Structure parameters</th>
<th>C membrane</th>
<th>PAN/SiO$_2$</th>
<th>C/SiO$_2$</th>
<th>C/SiO$_2$+S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparent density (mg/mm$^3$)</td>
<td>1.80</td>
<td>1.38</td>
<td>1.88</td>
<td></td>
</tr>
<tr>
<td>Porosity / %</td>
<td>82.0</td>
<td>91.1</td>
<td>87.9</td>
<td></td>
</tr>
<tr>
<td>BET surface (m$^2$/g)</td>
<td>5.1</td>
<td>18.8</td>
<td>12.7</td>
<td></td>
</tr>
</tbody>
</table>

Table S2. Summary of the amount of sulfur loading and electrolyte/sulfur ratio reported by previous works

<table>
<thead>
<tr>
<th>Material</th>
<th>Areal sulfur loading (mg cm$^{-2}$)</th>
<th>E/S ratio (µl mg$^{-1}$)</th>
<th>Areal capacity (mAh cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S/Graphene/porous Carbon$^1$</td>
<td>0.7</td>
<td>—</td>
<td>0.7</td>
</tr>
<tr>
<td>S/Graphene $^2$</td>
<td>0.8</td>
<td>19</td>
<td>0.9</td>
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<tr>
<td>Ti$_6$O$_7$/S$^3$</td>
<td>1.8</td>
<td>28</td>
<td>1.9</td>
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<tr>
<td>RGO-interlayer$^4$</td>
<td>1.8</td>
<td>60</td>
<td>1.5</td>
</tr>
<tr>
<td>S/CF/RGO$^5$</td>
<td>3.6</td>
<td>20</td>
<td>4.7</td>
</tr>
<tr>
<td>S/CNT$^6$</td>
<td>3.7</td>
<td>10</td>
<td>4.1</td>
</tr>
</tbody>
</table>
Figure S1. (a) sulfur loading in the hierarchical macropores, alleviating volume expansion of sulfur species and facilitating ion/electrolyte transport for fast kinetics, sponge-like pores in top layer of the composite membranes enable further S loading, (b) comparisons to thick S slurry on the top layer of the membranes and conventional Al foil electrodes, (c) self-supporting C/SiO$_2$ membranes with simultaneous high S loading in the macropores and thin S slurry on the top layer are ideal Al-free electrode for high energy density Li-S battery.
Figure S2. (a, b) the cross-sectional SEM images of PAN/SiO$_2$ and PAN membranes prepared by a facile phase inversion method, (c) the top surface with sponge-like pore of the PAN/SiO$_2$ membranes, the red arrows show the SiO$_2$ nanoparticles are well encapsulated into the polymer skeleton, (d) pure carbon membranes from (b). (e, f) the cross-sectional SEM image of preoxidized PAN/SiO$_2$ membrane, (g) the bottom surface and (h) top surface of the preoxidized PAN/SiO$_2$ membrane.
Figure S3. (a) and (b) the dense layer and smooth back surface of the C/SiO$_2$ membranes, which can work as Al foil for current collection; (c) the hierarchical macropores in the C/SiO$_2$ membranes from the broken surface (red cycle in Figure 1e); (d, e) top surface of the C/SiO$_2$ membranes with sponge-like pores; (f) thermal gravimetric analysis proves content of SiO$_2$ is 21.3wt% in the composite membranes; (g-l) EDX elemental mapping confirms the presence of C, N, O and uniform distribution of SiO$_2$ nanoparticles in the porous C/SiO$_2$ membranes.
Figure S4. Cross-section SEM images of C/SiO$_2$ membranes with different SiO$_2$ contents, (a) 5.3%, (b) 10.2%, (c) 28.6%, (d) 37.5%.
Figure S5. S loaded C/SiO$_2$ membranes and the uniform distributions of O, N throughout the membranes
Figure S6. (a) Thermal weight analysis proves that the C/SiO$_2$ composite membranes shows a high sulfur loading (76.8%) and sulfur thermal stability (> 300°C) compared to the conventional Al cathode (64.6%, ~250°C), (b) Raman spectra of the C and C/SiO$_2$ composite membranes, (c) FTIR spectra show the well dispersion of SiO$_2$ nanoparticles in the C/SiO$_2$ composite membranes, (d) XPS spectrum of C1s of the C/SiO$_2$ composite membranes.
Figure S7. (a-c) the typical charge-discharge curves of Al, C membranes and C/SiO$_2$ membrane electrodes at 0.1-2 C; (d-e) the cycling performance of different cathodes at 0.5 C and 1.0 C respectively
Figure S8. (a, b) cycling stability and rate performance of the C/SiO$_2$ membrane electrode with thick S slurry of 1.5 mg cm$^{-2}$, (c) coating thick S slurry on the C/SiO$_2$ membranes may induce serious “shuttle effect” of LiPSs and slow diffusion of ions/electrolyte in the thick S slurry layer.
Figure S9. Nyquist plots of Li–S cells with C/SiO$_2$ membrane and Al foil as cathodes respectively before cycling.

References