Supplemental Information

Lightweight Metallic MgB$_2$ Mediates Polysulfide Redox and Promises High-Energy-Density Lithium-Sulfur Batteries

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Figure S1. SEM image of the boron nanopowder used for the synthesis of MgB$_2$ and the TEM image of the MgB$_2$ synthesized without carbon nanopowder.

Figure S2. The most stable geometry of Li$_2$S, Li$_2$S$_2$ and Li$_2$S$_4$ molecules, simulated by first-principles calculations.
**Figure S3.** First-principles calculations for interactions of carbon, MgB$_2$, and MgO with lithium polysulfides. The optimized coordination of (a) Li$_2$S$_2$ adsorbed on the graphitic carbon; Li$_2$S$_4$ on (b) B-terminated and (c) Mg-terminated MgB$_2$ (0001) surfaces; (d) Li$_2$S and (e) Li$_2$S$_4$ on the MgO (110) surface.

**Figure S4.** The Li$_2$S$_4$ adsorptivity of MgB$_2$ measured by electrochemical titration, compared to meso-TiO$_2$, nanostructured Ti$_4$O$_7$, Vulcan® carbon and Super P® carbon.
Figure S5. High-resolution XPS spectra of the (a) S 2p and (b) B 1s, (c) Li 1s and Mg 2p$_{3/2}$ regions for pristine Li$_2$S$_4$, pristine MgB$_2$, and MgB$_2$-Li$_2$S$_4$. Note that the Li 1s spectrum of Li$_2$S$_4$ and the Mg 2p$_{3/2}$ spectrum of MgB$_2$ are jointly plotted as one panel in (c) top panel, for ease of comparison with the MgB$_2$-Li$_2$S$_4$ (note that the Li 1s and Mg 2p$_{3/2}$ regions are very close and the data was collected in a single scan). Black circles and solid lines represent the experimental and overall fitted spectra, respectively. Panel (a) shows that upon interaction with MgB$_2$, the terminal sulfur (S$_T$) in the Li$_2$S$_4$ molecule undergoes a positive shift and a new component at ~165 eV appears, indicating electron density loss for the sulfur as a consequence of S-B and S-Mg bonding. Correspondingly, in the B 1s spectra (b), the B in MgB$_2$ undergoes a negative shift, indicating electron density transfer from the S$_T$ to B. The Li 1s component in (c) remains almost constant after interaction with MgB$_2$, indicating that Li is not involved in strong bonding with B or Mg.
Figure S6. Galvanostatic intermittent titration (GITT) voltage profiles of sulfur cathodes during (a) discharge and (b) charge for the MgB$_2$-S60 and MgO-S60 cathodes. A protocol of a current pulse at C/20 for 15 min with 30 min of rest was used. The GITT experiment confirms a purely kinetic effect rather than one based on thermodynamics (Figure S3). The equilibrium voltage remains the same at all states of (dis)charge for MgB$_2$/S and MgO/S electrodes; however, upon applying the current pulse, the voltage penalty for initiating polysulfide reduction/oxidation is higher for the MgO than the MgB$_2$ electrode.

Figure S7. SEM images of (a) G-MgB$_2$ and the G-MgB$_2$/S75 composite (showing the absence of sulfur aggregates).
**Figure S8.** Capacity retention of G-MgB\(_2\), pure graphene and MgB\(_2\) based sulfur composites (75 wt% sulfur) with an areal loading of 2.0 mg cm\(^{-2}\) at C/2; the first cycle is at C/20.

**Figure S9.** The cell separators after ten cycles at a fully discharged state for the cells using (a) G/S75 and (b) G-MgB\(_2\)/S75 electrodes. The distinct yellow color in the G/S75 cell indicates extensive polysulfide shuttling in the electrolyte which is absent in the G-MgB\(_2\)/S75 cell.
Figure S10. XRD pattern of the discharged G/S75 electrode, indicating the presence of crystalline Li$_2$S.

Table S1. A list of recently reported transition metal compound based sulfur composites and their electrochemical measurement and performance parameters.

<table>
<thead>
<tr>
<th>Sulfur host [Reference]</th>
<th>Sulfur fraction in composite</th>
<th>Sulfur loading (mg cm$^{-2}$)</th>
<th>Electrolyte/sulfur ratio (µL mg$^{-1}$)</th>
<th>Initial capacity mAh/g</th>
<th>capacity retention (cycle number)</th>
<th>Binding energy with polysulfide computed ab initio</th>
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<tbody>
<tr>
<td>CoS$_2$+GO [1]</td>
<td>75%</td>
<td>2.9</td>
<td>N/A</td>
<td>1003 (2C)</td>
<td>32% (1000)</td>
<td>1.97 eV CoS$_2$ (111)-Li$_2$S$_4$</td>
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<td>Co$_3$S$_4$ [2]</td>
<td>74.2%</td>
<td>2.0</td>
<td>20</td>
<td>1050 (2C)</td>
<td>78% (200)</td>
<td>2.26 eV Co$_3$S$_4$ (111)-Li$_2$S$_4$</td>
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<tr>
<td>CNT-Co$_3$S$_4$ [3]</td>
<td>70%</td>
<td>3.5</td>
<td>15</td>
<td>1535 (0.2C)</td>
<td>82% (100)</td>
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</tr>
<tr>
<td>MoS$_2$ [4]</td>
<td>65%</td>
<td>1.5</td>
<td>N/A</td>
<td>1089 (1C)</td>
<td>55% (1000)</td>
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<tr>
<td>Co$_4$N [6]</td>
<td>73%</td>
<td>2.4-2.8</td>
<td>40</td>
<td>1428 (2C)</td>
<td>48% (800)</td>
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<td>VN+GO [7]</td>
<td>60%</td>
<td>3.0</td>
<td>31</td>
<td>1241 (0.5C)</td>
<td>81% (200)</td>
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<tr>
<td>Ti$_3$C$_2$Tx+C [8]</td>
<td>72.8%</td>
<td>2.0</td>
<td>20</td>
<td>1226 (0.5C)</td>
<td>56% (300)</td>
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References


