Supporting Information

Theoretical prediction of 2D biphenylene as a potential anchoring material for lithium-sulfur batteries

Han Wang, Fan Kong, Zonggang Qiu, Jiyuan Guo*, Huabing Shu, Qin Wei
School of Science, Jiangsu University of Science and Technology, Zhenjiang, 212100, China

Fig. S1 The schematic diagram of the unit cell of 2D biphenylene (BIP).

Table S1 The calculated adsorption energies ($E_{\text{ads}}$), the average adsorption heights ($H_{\text{ave}}$), Li-S bond lengths ($D_{\text{Li-S}}$) and S-S bond lengths ($D_{\text{S-S}}$) of LiPSs adsorbed on the BIP.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>S_8</th>
<th>Li_2S_8</th>
<th>Li_2S_6</th>
<th>Li_2S_4</th>
<th>Li_2S_2</th>
<th>Li_2S</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_{\text{ave}}$(Å)</td>
<td>3.08</td>
<td>1.99</td>
<td>1.98</td>
<td>2.20</td>
<td>1.80</td>
<td>1.50</td>
</tr>
<tr>
<td>$E_{\text{ads}}$(eV)</td>
<td>1.05</td>
<td>1.59</td>
<td>1.37</td>
<td>1.25</td>
<td>2.16</td>
<td>2.55</td>
</tr>
<tr>
<td>$D_{\text{Li-S}}$(Å)</td>
<td>/</td>
<td>2.39</td>
<td>2.41</td>
<td>2.37</td>
<td>2.23</td>
<td>2.06</td>
</tr>
<tr>
<td>$D_{\text{S-S}}$(Å)</td>
<td>2.08</td>
<td>2.01</td>
<td>2.05</td>
<td>2.11</td>
<td>2.22</td>
<td>/</td>
</tr>
</tbody>
</table>

*Corresponding author
E-mail address: jyguo@just.edu.cn
Fig. S2 Optimized structures and adsorption energies between Li$_2$S$_n$ (n = 4, 6, 8) and DME/DOL.

Table S2 The calculated adsorption energies of Li$_2$S$_n$ (n = 8, 6, 4) with the electrolyte solvents DOL and DME.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Li$_2$S$_8$</th>
<th>Li$_2$S$_6$</th>
<th>Li$_2$S$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>E$_{ads}$-DOL (eV)</td>
<td>1.23</td>
<td>1.22</td>
<td>1.18</td>
</tr>
<tr>
<td>E$_{ads}$-DME (eV)</td>
<td>1.05</td>
<td>1.10</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Fig. S3 Adsorption energy of Li$_2$S$_n$ (n = 8, 6, 4) on BIP and interaction energy of LiPSs with DME and DOL.
**Table S3** The formation energies of the M (M = B, N, O, F, Br) atoms doped BIP

<table>
<thead>
<tr>
<th>Element</th>
<th>B</th>
<th>N</th>
<th>O</th>
<th>F</th>
<th>Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_f$ $T_1$ (eV)</td>
<td>-0.77</td>
<td>-1.28</td>
<td>9.69</td>
<td>0.91</td>
<td>3.80</td>
</tr>
<tr>
<td>$E_f$ $T_2$ (eV)</td>
<td>-0.55</td>
<td>-0.75</td>
<td>11.44</td>
<td>2.31</td>
<td>4.07</td>
</tr>
</tbody>
</table>

**Fig. S4** Optimized structures of doped M atoms (M = B, N, O, F, Br), a-l corresponding the optimized structures of B, N, O, F, Br atom replacing C atom at $T_1/T_2$ site, respectively.
**Fig. S5** Top views of the optimized B doped BIP structures and AIMD simulations results at 350 K lasting for 10 ps of the B doped BIP monolayer.

**Fig. S6** Top views of the optimized N doped BIP structures and AIMD simulations results at 350 K lasting for 10 ps of the N doped BIP monolayer.
Fig. S7 Top and side views of the most stable adsorption configurations for (a) $S_8@BIP$ and (b)-(f) $Li_2S_n$ ($n = 8, 6, 4, 2, 1$)@B doped BIP.

Fig. S8 Top and side views of the most stable adsorption configurations for (a) $S_8@BIP$ and (b)-(f) $Li_2S_n$ ($n = 8, 6, 4, 2, 1$)@N doped BIP.
Table S4 The calculated adsorption energies ($E_{\text{ads}}$), the average adsorption heights ($H_{\text{ave}}$), Li-S bond lengths ($D_{\text{Li-S}}$) and S-S bond lengths ($D_{\text{S-S}}$) of LiPSs adsorbed on the B doped BIP.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>$S_8$</th>
<th>$\text{Li}_2S_8$</th>
<th>$\text{Li}_2S_6$</th>
<th>$\text{Li}_2S_4$</th>
<th>$\text{Li}_2S_2$</th>
<th>$\text{Li}_2S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_{\text{ave}}$(Å)</td>
<td>3.12</td>
<td>1.98</td>
<td>1.97</td>
<td>2.17</td>
<td>1.26</td>
<td>1.09</td>
</tr>
<tr>
<td>$E_{\text{ads}}$(eV)</td>
<td>1.06</td>
<td>1.67</td>
<td>1.46</td>
<td>1.38</td>
<td>2.38</td>
<td>2.86</td>
</tr>
<tr>
<td>$D_{\text{Li-S}}$(Å)</td>
<td>/</td>
<td>2.49</td>
<td>2.46</td>
<td>2.47</td>
<td>2.43</td>
<td>2.27</td>
</tr>
<tr>
<td>$D_{\text{S-S}}$(Å)</td>
<td>2.09</td>
<td>2.10</td>
<td>2.11</td>
<td>2.10</td>
<td>2.13</td>
<td>/</td>
</tr>
</tbody>
</table>

Table S5 The calculated adsorption energies ($E_{\text{ads}}$), the average adsorption heights ($H_{\text{ave}}$), Li-S bond lengths ($D_{\text{Li-S}}$) and S-S bond lengths ($D_{\text{S-S}}$) of LiPSs adsorbed on the N doped BIP.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>$S_8$</th>
<th>$\text{Li}_2S_8$</th>
<th>$\text{Li}_2S_6$</th>
<th>$\text{Li}_2S_4$</th>
<th>$\text{Li}_2S_2$</th>
<th>$\text{Li}_2S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_{\text{ave}}$(Å)</td>
<td>3.12</td>
<td>2.13</td>
<td>2.04</td>
<td>2.37</td>
<td>1.36</td>
<td>1.13</td>
</tr>
<tr>
<td>$E_{\text{ads}}$(eV)</td>
<td>1.03</td>
<td>1.38</td>
<td>1.22</td>
<td>1.05</td>
<td>2.14</td>
<td>2.75</td>
</tr>
<tr>
<td>$D_{\text{Li-S}}$(Å)</td>
<td>/</td>
<td>2.46</td>
<td>2.43</td>
<td>2.41</td>
<td>2.39</td>
<td>2.25</td>
</tr>
<tr>
<td>$D_{\text{S-S}}$(Å)</td>
<td>2.09</td>
<td>2.11</td>
<td>2.11</td>
<td>2.10</td>
<td>2.14</td>
<td>/</td>
</tr>
</tbody>
</table>

Fig. S9 (a) Proportion of vdW interactions between the intrinsic and B doped BIP at different stages of lithiation.

Gibbs free energy calculation of sulfur reduction reaction (SRR) in vacuum and BIP Surface

Overall, the SRR during the discharge of Li-S batteries is a 16 electrons process with the formation of eight $\text{Li}_2S$ molecules
S₈ + 16 Li⁺ + 16 e⁻ = 8Li₂S \hspace{1cm} (S1)

The rudimentary step involved in the generation of one Li₂S molecules is as follows;

* S₈ + 2 Li⁺ + 2e⁻ = * Li₂S₈ \hspace{1cm} (S2)
* Li₂S₈ = * Li₂S₆ + 1/4 S₈ \hspace{1cm} (S3)
* Li₂S₆ = * Li₂S₄ + 1/4 S₈ \hspace{1cm} (S4)
* Li₂S₄ = * Li₂S₂ + 1/4 S₈ \hspace{1cm} (S5)
* Li₂S₂ = * Li₂S + 1/8 S₈ \hspace{1cm} (S6)

Wherein * represents an active site on the catalytic substrate.

The Gibbs free energy (ΔG) for each SRR during the Li-S discharge process is calculated as

\[ \Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S \] \hspace{1cm} (S7)

Where ΔE represents the adsorption energy and ΔE_{ZPE} and TΔS denotes the zero point energy difference and entropy difference between the gas phase and adsorbed phase calculated from the frequency calculations at 298.15 K.

The change in Gibbs free energy for each SRR electrochemical steps is attained from the given relations;

\[ \Delta G₁ = (E_{*Li₂S₈} + E_{ZPE(*Li₂S₈)} - TS_{*Li₂S₈}) - (E_{*S₈} + E_{ZPE(*S₈)} - TS_{*S₈}) \]
\[ -2(E_{Li} + E_{ZPE(Li)} - TS_{Li}) \] \hspace{1cm} (S8)

\[ \Delta G₂ = (E_{*Li₂S₆} + E_{ZPE(*Li₂S₆)} - TS_{*Li₂S₆}) + \frac{1}{4}(E_{*S₈} + E_{ZPE(*S₈)} - TS_{*S₈}) \]
\[ -2(E_{*Li₂S₄} + E_{ZPE(*Li₂S₄)} - TS_{*Li₂S₄}) \] \hspace{1cm} (S9)

\[ \Delta G₃ = (E_{*Li₂S₄} + E_{ZPE(*Li₂S₄)} - TS_{*Li₂S₄}) + \frac{1}{4}(E_{*S₈} + E_{ZPE(*S₈)} - TS_{*S₈}) \]
\[ -2(E_{*Li₂S₂} + E_{ZPE(*Li₂S₂)} - TS_{*Li₂S₂}) \] \hspace{1cm} (S10)

\[ \Delta G₄ = (E_{*Li₂S₂} + E_{ZPE(*Li₂S₂)} - TS_{*Li₂S₂}) + \frac{1}{4}(E_{*S₈} + E_{ZPE(*S₈)} - TS_{*S₈}) \]
\[ -2(E_{*Li₂S} + E_{ZPE(*Li₂S)} - TS_{*Li₂S}) \] \hspace{1cm} (S11)

\[ \Delta G₅ = (E_{*Li₂S} + E_{ZPE(*Li₂S)} - TS_{*Li₂S}) + \frac{1}{8}(E_{*S₈} + E_{ZPE(*S₈)} - TS_{*S₈}) \]
\[ -2(E_{*Li₂S} + E_{ZPE(*Li₂S)} - TS_{*Li₂S}) \] \hspace{1cm} (S12)

Pathway a:

*Li₂S₂ + * → 2LiS \hspace{1cm} (S13)

2*LiS + 2Li⁺ + 2e⁻ → 2*Li₂S \hspace{1cm} (S14)

Pathway b:

( *Li₂S₂ + Li⁺ + e⁻ → *Li₃S₂ ) \hspace{1cm} (S15)

*Li₃S₂ + * → *LiS + *Li₂S \hspace{1cm} (S16)

*LiS + Li⁺ + e⁻ → *Li₂S \hspace{1cm} (S17)
Pathway c:

\[ \ast \text{Li}_2\text{S}_2 + \ast \rightarrow \text{S} + \text{Li}_2\text{S} \]  \hspace{1cm} (S18)

\[ \ast\text{S} + 2\text{Li}^+ + 2e^- \rightarrow \ast\text{Li}_2\text{S} \]  \hspace{1cm} (S19)

Wherein \ast represents an active site on the catalytic substrate.

Fig. S10 The Gibbs energy differences for the first step (\(\Delta G_1\)) and the second step (\(\Delta G_2\)) of three possible reaction pathways in the conversion from \(\text{Li}_2\text{S}_2\) to \(\text{Li}_2\text{S}\).

Fig. S11 The Gibbs energy differences for two elementary steps in every possible pathway. The pentagram symbols indicate the optimal reaction pathway on intrinsic and B doped BIP. Yellow with gridding, and red without gridding represent the Gibbs energy differences for the first step (\(\Delta G_1\)) and the second step (\(\Delta G_2\)), respectively.
Fig. S12 Paths of Li$_2$S decomposition and the corresponding energy barriers on the BIP