Electronic Supporting Information

Enhanced catalytic performance of pillared $\delta$-MnO$_2$ with enlarged layer spaces for lithium- and sodium-oxygen batteries: A theoretical investigation

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Table S1 and Figure S1 include the information for C-C bond lengths of various molecules. Figure S2 records the density of states of bare-MnO$_2$. Figure S3 is the information for the d-electron states of three pillared structures. Figure S4 is the AIMD simulation configurations of three pillared structures. The configurations of deep reduction product Li$_3$O$_2$ and Li$_4$O$_2$ adsorbed H-MnO$_2$ are shown in Figure S5 (a) and (b). The configurations of deep reduction product Li$_3$O$_2$, Li$_4$O$_2$, Na$_3$O$_2$ and Na$_4$O$_2$ adsorbed Cl-MnO$_2$ are shown in Figure S5 (c) and (f).

The complete battery reaction including the deep reduction of lithium and sodium is

\[ \text{X + Sub} \rightarrow \text{X@Sub} \rightarrow \text{XO}_3\text{@Sub} \rightarrow \text{X}_2\text{O}_5\text{@Sub} \rightarrow \text{X}_4\text{O}_7\text{@Sub} \rightarrow \text{X}_4\text{O}_7\text{@Sub} \rightarrow \text{X}_4\text{O}_9\text{@Sub} \quad (\text{X = Li or Na}) \quad (S1) \]

The d-band center ($E_d$) of substrates can be computed by:

\[
E_d = \frac{\int \varepsilon \cdot P(\varepsilon) \, d\varepsilon}{\int P(\varepsilon) \, d\varepsilon} \quad (S2)
\]

where $\varepsilon$ denotes the energy-level of electrons and $P(\varepsilon)$ is the number of electrons occupied in energy level $\varepsilon$. The upper and lower limits of the integral are selected as electrons below the Fermi level.

**Table S1** The various C-C bond lengths of bare molecules and molecules in pillared systems.

<table>
<thead>
<tr>
<th>system</th>
<th>C-C bond length (Å)</th>
</tr>
</thead>
</table>

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S2
Fig. S1 The C-C bond lengths of bare anions of (a) 1,4-benzenedisulfonic acid, (b) 2-chloro-1,4-benzenedisulfonic acid, and (c) 2-fluoro-1,4-benzenedisulfonic acid.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond Lengths (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_6\text{H}_4\text{O}_6\text{S}_2$</td>
<td>1.397 1.398 1.395 1.398 1.397 1.395</td>
</tr>
<tr>
<td>$\text{H-MnO}_2$</td>
<td>1.397 1.392 1.380 1.397 1.393 1.383</td>
</tr>
<tr>
<td>$\text{C}_6\text{H}_4\text{O}_6\text{S}_2\text{Cl}$</td>
<td>1.406 1.401 1.395 1.397 1.396 1.397</td>
</tr>
<tr>
<td>$\text{Cl-MnO}_2$</td>
<td>1.414 1.406 1.391 1.397 1.389 1.402</td>
</tr>
<tr>
<td>$\text{C}_6\text{H}_4\text{O}_6\text{S}_2\text{F}$</td>
<td>1.399 1.398 1.396 1.396 1.397 1.389</td>
</tr>
<tr>
<td>$\text{F-MnO}_2$</td>
<td>1.405 1.402 1.391 1.398 1.392 1.391</td>
</tr>
</tbody>
</table>

Fig. S2 (a) The partial density of states of bare-$\text{MnO}_2$ and (b) d-orbital density of states. Both spin-up and spin-down electrons are plotted and their d-band centers are calculated.
Fig. S3 The d-orbital density of states and corresponding d-band centers of (a) H-MnO₂, (b) Cl-MnO₂, and (c) F-MnO₂ pillared structures. States of both spin-up and spin-down electrons are plotted and their d-band centers are calculated separately.

Fig. S4 The configurations of (a) H-MnO₂, (b) Cl-MnO₂, and (c) F-MnO₂, in the AIMD
Fig. S5 The configurations of deep reduction product (a) Li$_3$O$_2$ and (b) Li$_4$O$_2$ adsorbed H-MnO$_2$.

The configurations of deep reduction product (c) Li$_3$O$_2$, (d) Li$_4$O$_2$, (e) Na$_3$O$_2$ and (f) Na$_4$O$_2$
adsorbed Cl-MnO₂. In each group, the configuration on the left is more stable than the configuration on the right.