Electronic Supporting Information

Discovery of a high-pressure phase of rutile-like CoO$_2$ and its potential as a cathode material

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The formulae to calculate bulk moduli (B), shear moduli (G), Young’s modulus (E) and Possion’s ratio ($\nu$) in orthorhombic phase are taken from Ref$^1$. In the following, subscript V denotes the Voigt bound, R denotes the Reuss bound, and H denotes the Hill average which is the arithmetic average of Voigt and Reuss bounds. It is known that the Voigt bound is obtained by the average polycrystalline moduli based on an assumption of uniform strain throughout a poly-crystal, which is the upper limit of the actual effective moduli. However, the Reuss bound is obtained by assuming a uniform stress and is the lower limit of the actual effective moduli$^2$.

\[
B_v = \frac{1}{9} \left( C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23}) \right)
\]

\[
G_v = \frac{1}{15} \left( C_{11} + C_{22} + C_{33} + 3(C_{44} + C_{55} + C_{66}) - (C_{12} + C_{13} + C_{23}) \right)
\]

\[
B_r = \Delta \left( C_{11} (C_{22} + C_{33} - 2C_{23}) + C_{22} (C_{33} - 2C_{13}) - 2C_{33}C_{12} + C_{12} (2C_{23} - C_{13}) + C_{13} (2C_{12} - C_{23}) + C_{23} (2C_{13} - C_{23}) \right)^{-1}
\]

\[
G_r = 15 \left( 4C_{11} (C_{22} + C_{33} + C_{23}) + C_{22} (C_{33} + C_{13}) + C_{33} (C_{12} + C_{13}) + C_{12} (C_{23} + C_{13}) - 3C_{23} (C_{13} + C_{23}) \right) / \Delta + 3 \left( 1/C_{44} + 1/C_{55} + 1/C_{66} \right)^{-1}
\]

Young’s modulus $E$ and Possion’s ratio $\nu$ are obtained by using following formulae

\[
E = \frac{9BG}{3B+G}
\]

\[
\nu = \frac{(3B-2G)}{(6B+2G)}
\]

The results are shown in Table 1 in the text.
Table S1. Lattice parameters of rutile-like CoO$_2$ after removing pressure.

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>α=β=γ(°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pnnm</td>
<td>4.41</td>
<td>4.10</td>
<td>2.85</td>
<td>90</td>
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</table>

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>site</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>0.00</td>
<td>0.00</td>
<td>1.00</td>
<td>2a</td>
</tr>
<tr>
<td>O</td>
<td>0.84</td>
<td>0.77</td>
<td>0.50</td>
<td>4g</td>
</tr>
</tbody>
</table>

Table S2. Elastic stiff constants (GPa) $C_{ij}$ of rutile-like CoO$_2$ after removing pressure.

<table>
<thead>
<tr>
<th>System</th>
<th>$C_{11}$</th>
<th>$C_{22}$</th>
<th>$C_{33}$</th>
<th>$C_{44}$</th>
<th>$C_{55}$</th>
<th>$C_{66}$</th>
<th>$C_{12}$</th>
<th>$C_{13}$</th>
<th>$C_{23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoO$_2$</td>
<td>368.9</td>
<td>184.7</td>
<td>402.4</td>
<td>120.2</td>
<td>138.3</td>
<td>206.9</td>
<td>191.9</td>
<td>153.4</td>
<td>52.1</td>
</tr>
</tbody>
</table>

Figure S1. (a) Phonon spectra of standard-rutile CoO$_2$ at vacuum and 50GPa. (b) Pressure dependence of the lattice distortion for rutile-like CoO$_2$. 

Pressure dependence of the lattice distortion for rutile-like CoO$_2$. 

Figure S2. Pressure dependence of enthalpy of the predicted structure compared with the layered structure.

![Graph showing pressure dependence of enthalpy](image)

Figure S3. DFT optimized structural changes of oxygen dimer in (a) rutile-like, (b) layered CoO$_2$.

The arrow marks the direction of atomic displacement. Red and blue represent O and Co, respectively.

![Diagram showing structural changes](image)
Figure S4. The initial and final structural diagrams of (a) rutile-like, (b) layered CoO$_2$ obtained by MD simulation at 1500K.

Figure S5. MSD$_{Li}$ as a function of simulation time at different temperatures in 3×3×4 supercell of layered-structure LiCoO$_2$ used in the molecular dynamics (MD) simulation.
Figure S6. MSD of Li, O, Co as a function of simulation time at (a) 1000K and (b) 1500K in 2×2×4 supercell of rutile-like Li$_{0.5}$CoO$_2$ used in the molecular dynamics (MD) simulation.

Figure S7. Configurations of lithiated/delithiated and three stable intermediate phases for rutile-like Li$_{1-x}$CoO$_2$.