Supplementary Information for the article

Anion-exchange phase control of manganese sulfide for oxygen evolution reactions

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Table S1: PF calculations for rhomboedral MnCO$_3$ and all polymorphs of manganese sulfide prepared in the present study.

<table>
<thead>
<tr>
<th>Sr. no.</th>
<th>Material</th>
<th>Crystal structure</th>
<th>Lattice constant (Å)</th>
<th>Volume of unit cell (Å$^3$)</th>
<th>Ionic radii</th>
<th>Number of ions per unit cell</th>
<th>Total volume occupied by ions in unit cell (Å$^3$)</th>
<th>PF</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>MnCO$_3$</td>
<td>Rhomboedral</td>
<td>a = b = c = 5.84</td>
<td>99.99</td>
<td>Mn$^{2+}$ = 0.81, C$^{4+}$ = 0.3, O$^{2-}$ = 1.26</td>
<td>Mn$^{2+}$ = 2, C$^{4+}$ = 2, O$^{2-}$ = 6</td>
<td>54.92</td>
<td>0.55</td>
</tr>
<tr>
<td>2.</td>
<td>MnS$_2$</td>
<td>Cubic</td>
<td>a = b = c = 6.11</td>
<td>227.98</td>
<td>Mn$^{2+}$ = 0.67, S$^{2-}$ = 1.7</td>
<td>Mn$^{2+}$ = 4, S$^{2-}$ = 8</td>
<td>169.58</td>
<td>0.74</td>
</tr>
<tr>
<td>3.</td>
<td>γ-MnS</td>
<td>Wurtzite</td>
<td>a = b = c = 3.97</td>
<td>88.05</td>
<td>Mn$^{2+}$ = 0.81, S$^{2-}$ = 1.7</td>
<td>Mn$^{2+}$ = 3, S$^{2-}$ = 3</td>
<td>68.38</td>
<td>0.77</td>
</tr>
<tr>
<td>4.</td>
<td>α-MnS</td>
<td>Rock salt</td>
<td>a = b = c = 5.24</td>
<td>143.87</td>
<td>Mn$^{2+}$ = 0.81, S$^{2-}$ = 1.7</td>
<td>Mn$^{2+}$ = 4, S$^{2-}$ = 4</td>
<td>91.17</td>
<td>0.63</td>
</tr>
</tbody>
</table>
**Figure S1:** XRD patterns of manganese sulfide thin films prepared at different temperatures via anion exchange of MnCO$_3$ with the same mass ratio (1:1) of MnCO$_3$ to Na$_2$S.
**Figure S2:** XRD patterns of manganese sulfide samples prepared via the anion-exchange chemical reaction between MnCO$_3$ and Na$_2$S precursors with different mass ratios at a hydrothermal temperature of 363 K.
**Figure S3:** XRD patterns of manganese sulfide prepared at 303 and 453 K via the anion-exchange reaction with MnCO$_3$:Na$_2$S mass ratio of 1:5.
Figure S4: Comparative XPS survey profiles of the MnS$_2$, $\gamma$-MnS, and $\alpha$-MnS phases of manganese sulfide.
**Figure S5:** FE-SEM images of manganese sulfide thin films prepared via the anion-exchange reaction with MnCO$_3$:Na$_2$S mass ratio of 1:1 at different temperatures: (a, b) 333 K, (c, d) 393 K, and (e, f) 423 K.
**Figure S6:** FE-SEM images of manganese sulfide thin films prepared via the anion-exchange reaction with MnCO$_3$:Na$_2$S mass ratio of 1:5 at different temperatures: (a, b) 303 K (c, d) 363 K, and (e, f) 453 K.
Figure S7: Crystal structure models of MnCO$_3$ and different phases of manganese sulfide.
Figure S8: Cyclic voltammetry curves of (a) MnCO₃ (b) MnS₂ (c) γ-MnS, and (d) α-MnS catalysts obtained within non-faradaic region of 1.00 to 1.20 V/RHE in 1 M KOH.
**Figure S9:** Current density versus scan rate plots of different electrodes for measurement of electrochemical active surface area.