Active-Site Revealed for Water Oxidation on Electrochemically Induced δ-MnO₂: Role of Spinel-to-layer Phase Transition

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1. Details for SSW Reaction Pathway Sampling

First, we determine the relevant ions/molecules that may trigger the spinel-to-layer phase transition. These ions/molecules should satisfy at least two criteria in thermodynamics: (i) The addition of them should stabilize spinel phase compared to the pristine Mn₃O₄ spinel in OER condition (voltage > 1.23V), and (ii) the spinel-to-layer phase transition is thermodynamically favored (ΔG<0). The possibility of water molecules insertion into spinel frameworks of MnO₂ is first examined, which is found to be thermodynamically unfavorable (>1eV per water) due to the strong repulsion between H₂O and lattice O (too small cage with radius of ~2.0Å in the spinel lattice). This indicates the insertion of water into spinel bulk cannot occur before the phase transition. Furthermore, by examining the spinel and layer structures for a set of crystal phases, including Mn₃O₄, Mn₅O₈, MnO₂, H₀.₅MnO₂, Li₀.₅MnO₂ and Mg₀.₅MnO₂, as listed in Table 1, we found that only for H₀.₅MnO₂ and MnO₂ phases, the layer structure is more stable than their spinel counterpart. For Mn₃O₄, Mn₅O₈, Li₀.₅MnO₂, and Mg₀.₅MnO₂, the spinel phase is at least 0.13 eV/f.u. more stable than the layer phase. These preliminary energetics screening suggests that the hydrogenated-MnO₂ and MnO₂ are the most likely precursor phase for the spinel-to-layer transition.

Table 1. Reaction energy ΔE for the spinel-to-layer transition for different MnOₓ-based phases.

<table>
<thead>
<tr>
<th>Component</th>
<th>ΔE*</th>
<th>Component</th>
<th>ΔE</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₀.₅MnO₂</td>
<td>-0.03</td>
<td>Mn₅O₈</td>
<td>+0.13</td>
</tr>
<tr>
<td>MnO₂</td>
<td>-0.06</td>
<td>Li₀.₅MnO₂</td>
<td>+0.17</td>
</tr>
<tr>
<td>Mn₃O₄</td>
<td>+0.49</td>
<td>Mg₀.₅MnO₂</td>
<td>+0.35</td>
</tr>
</tbody>
</table>

*ΔE = E_{layer} − E_{spinel} (eV per Mn f.u.).

Second, we choose MnO₂, H₀.₅MnO₂ and Li₀.₅MnO₂ as the initial state (IS) for SSW pathway sampling to identify the spinel-to-layer pathways. Our test SSW-RS calculations show that Li₀.₅MnO₂ as the IS can visit frequently the spinel-to-layer phase transition pathways, while the proton shifting reactions due to their low barriers are much preferable in the pathway sampling of H₀.₅MnO₂ and no spinel-to-layer pathway was found in the pathway sampling of MnO₂ This agrees with the fact that Mn⁴⁺ is difficult to migrate within MnO₂ framework as observed in experiment. Therefore, starting from Li₀.₅MnO₂, 20 SSW-RS jobs for each phase were run massively parallel. With 2000 SSW sampling steps, 320 pathways were collected, from which 10 low energy pathways with barrier lower than 0.7 eV/f.u. were identified.
Third, we replace Li with proton in the located four lowest energy pathways and by considering all the likely proton positions (proton adsorbs at the lattice O), we refine all the reaction pathways using the VC-DESW method. All located TSs have been confirmed by extrapolating the TS towards the IS and FS and also the numerical vibrational frequency analysis.

2. Calculation Details for Theoretical Overpotential

To calculate the OER overpotential, we use the Standard Hydrogen Electrode (SHE: H\(^+\) + e\(^-\) → H\(_2\)) as reference, where we get

\[ \Delta G^0_{\text{SHE}} = \frac{1}{2} G^0[H_2] - G^0[H^+] - G^0[e^-] = 0 \]  
\[ G^0[H^+] = \frac{1}{2} G^0[H_2] - G^0[e^-] = \frac{1}{2} G^0[H_2] + \Phi_w \]  

where \( G^0[H_2], G^0[H^+] \) are the Gibbs free energy changes of H\(_2\) and H\(^+\) in standard condition, while \( \Phi_w \) is the work function of Pt electrode in SHE. For other pH, the free energy \( G[H^+] \) can be calculated as

\[ G[H^+] = G^0[H^+] - 0.059pH \]  

Using Eq. 2-3, we can derive the \( \Delta G \) of an electrochemical half-reaction as described by formula 4.

\[ \text{HA} → A + nH^+ + ne^- \]  

The \( \Delta G \) is written as

\[ \Delta G = G[A] + nG[H^+] + nG[e^-] - G[H_nA] \]  

Substituting Eq. 3 into Eq. 4, we get

\[ \Delta G = G[A] + n(\frac{1}{2}G^0[H_2] - G[e^-]_{\text{SHE}} - 0.059pH + nG[e^-] - G[H_nA]) \]  
\[ = G[A] + \frac{n}{2}G^0[H_2] - n\times0.059pH + nG[e^-] + \Phi_w - G[H_nA] \]  
\[ = G[A] + \frac{n}{2}G^0[H_2] - G[H_nA] + n|e|U - n\times0.059pH \]  

Setting \( \Delta G = 0 \), the parameter U then is the electrochemical potential for half-reaction of \( \text{H}_n\text{A} → A + nH^+ + ne^- \). The calculated overpotential (\( \eta \)) then be calculated by Eq. 6.

\[ \eta = U - 1.23 \]

3. Calculation Details for Phase Diagram of Mn\(_3\)O\(_4\), \( \text{H}_0\text{.MnO}_2 \) and \( \text{MnO}_2 \)

The phase diagram of Mn\(_3\)O\(_4\), \( \text{H}_0\text{.MnO}_2 \) and \( \text{MnO}_2 \) involves three consecutive reactions from spinel Mn\(_3\)O\(_4\) to \( \text{H}_0\text{.MnO}_2 \) and to \( \text{MnO}_2 \) following the chemical formula below.

\[ 2\text{Mn}_3\text{O}_4 + 4\text{H}_2\text{O} → 6\text{H}_0\text{.MnO}_2 + 5\text{H}^+ + 5\text{e}^- \]  
\[ 4\text{H}_0\text{.MnO}_2 → 4\text{H}_0\text{.25MnO}_2 + 5\text{H}^+ + 5\text{e}^- \]  
\[ 4\text{H}_0\text{.25MnO}_2 → 4\text{MnO}_2 + 4\text{H}^+ + 4\text{e}^- \]  

Using Mn\(_3\)O\(_4\) phase as energy zero point, we rewrite the Eq. 7-9 as

\[ \text{Mn}_3\text{O}_4 + 2\text{H}_2\text{O} → 3\text{H}_0\text{.5MnO}_2 + \frac{5}{2}\text{H}^+ + \frac{5}{2}\text{e}^- \]  
\[ \text{Mn}_3\text{O}_4 + 2\text{H}_2\text{O} → 3\text{H}_0\text{.25MnO}_2 + \frac{13}{3}\text{H}^+ + \frac{13}{3}\text{e}^- \]  
\[ \text{Mn}_3\text{O}_4 + 2\text{H}_2\text{O} → 3\text{MnO}_2 + 4\text{H}^+ + 4\text{e}^- \]  

Using SHE as reference (see Section 2 of SI), free energy change in reactions 10-12 can be calculated by following formula.

\[ \Delta G[\text{H}_0\text{.5MnO}_2] = 3G[\text{H}_0\text{.5MnO}_2] + \frac{5}{4}G[H_2] - G[\text{Mn}_3\text{O}_4] - 2G[\text{H}_2\text{O}] - \frac{5}{2}|e|U \]  
\[ \Delta G[\text{H}_0\text{.25MnO}_2] = 3G[\text{H}_0\text{.25MnO}_2] + \frac{13}{6}G[H_2] - G[\text{Mn}_3\text{O}_4] - 2G[\text{H}_2\text{O}] - \frac{13}{3}|e|U \]

(15)

The relative stabilities of \( H_nMnO_2 \) and \( MnO_2 \) compared with \( Mn_3O_4 \) can thus be estimated by Eq. 13-15. By plotting \( \Delta G \) vs. \( U \), we finally get the phase diagram of \( Mn_3O_4 \), \( H_nMnO_2 \) and \( MnO_2 \). It should be mentioned that the line for \( Mn_3O_4 \) is horizontal, since \( Mn_3O_4 \) is the reference state where the free energy change is zero for this component.

**Figure S1.** Phase diagram for (a) \( \delta \)-MnO\(_2\) and (b) pristine spinel Mn\(_3\)O\(_4\) in aqueous electrolyte.
**Figure S2.** (a) Complete energetic profiles for solid-to-solid phase transition of H$_{0.5}$MnO$_2$ and MnO$_2$. (b) Side view of key intermediate states of H$_{0.5}$MnO$_2$ during phase transition. The dashed boxes are unit cell. The directions are relative to the hexagonal unit cell of δ-MnO$_2$. It should be mentioned that the Mn atom chains along A site and B site of MnO$_2$ layers are different. Colors in (c): red ball: O; white ball: H; violet ball: Mn; yellow ball: Mn$^{\text{ic}}$.

**Figure S3.** The interfacial strain build in layer-to-spinel transition. (a) spinel (b) layered H$_{0.5}$MnO$_2$. The dotted lines indicate the [2110] direction, and the green number is the Mn-Mn distance along this direction.
**Figure S4.** 3D isosurface contour plot for addatom and dislocation structures. The isosurface value is set as $0.0025 \text{ (e/Å}^3\text{)}^2$.

**Figure S5.** Alignment of energy levels between OH and $\delta$-MnO$_2$. (a) OH adsorbs on pristine edge and (b) OH adsorbs on edge-NV.
Figure S6. 3D isosurface contour plot of charge density difference for OH adsorption on (a) pristine edge and (b) edge-NV before and after the OH adsorption. The isosurface value is set as 0.0025 (e/Å³)². Yellow and Blue density indicate where the charge accumulation and depletion occur, respectively.

References