Supporting Information

Introduction of Mn(III) to regulate the electronic structure of F-doped nickel hydroxide for efficient water oxidation

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Computational details

Our density functional theory (DFT) calculations were performed by applying the QuantumATK software package [1]. The local density approximation (LDA) with the Perdew-Zunger parametrization [2] of the correlation energy was adopted as the exchange correlation potential. The interaction between cores and valence electrons
for all atoms is modeled with Troullier-Martins nonlocal pseudopotential, and double-zeta plus polarized (DZP) basis sets are employed.

The OER reaction process can be represented as follows in an alkaline electrolyte solution:

\[ \text{OH}^- + \ast \rightarrow \text{OH}^* + e^- \quad (1) \]
\[ \text{OH}^* + \text{OH}^- \rightarrow \text{O}^* + \text{H}_2\text{O} + e^- \quad (2) \]
\[ \text{O}^* + \text{OH}^- \rightarrow \text{OOH}^* + e^- \quad (3) \]
\[ \text{OOH}^* + \text{OH}^- \rightarrow \text{O}_2 + \text{H}_2\text{O} + e^- \quad (4) \]

where \* presents the adsorption site on the surface of catalysts, \text{OH}^*, \text{O}^*, and \text{OOH}^* represents the intermediate of the reaction.

In order to simplify the calculation process, the basic steps (1)-(4) are converted to the form of acidic conditions as follows

\[ 2\text{H}_2\text{O} + \ast \rightarrow \text{OH}^* + \text{H}_2\text{O} + e^- + \text{H}^+ \quad (5) \]
\[ \text{OH}^* + \text{H}_2\text{O} \rightarrow \text{O}^* + \text{H}_2\text{O} + e^- + \text{H}^+ \quad (6) \]
\[ \text{O}^* + \text{H}_2\text{O} \rightarrow \text{OOH}^* + e^- + \text{H}^+ \quad (7) \]
\[ \text{OOH}^* \rightarrow \text{O}_2 + e^- + \text{H}^+ \quad (8) \]

The steps (1)-(4) are equivalent to (5)-(8).

At standard conditions, the Gibbs free energy changes for reaction (5)-(8) are calculated as:

\[ \Delta G_1 = \Delta G_{\text{OH}^*} - eU + kT \ln 10\text{pH} \quad (9) \]
\[ \Delta G_2 = \Delta G_{\text{O}^*} - \Delta G_{\text{OH}^*} - eU + kT \ln 10\text{pH} \quad (10) \]
\[ \Delta G_3 = \Delta G_{\text{OOH}^*} - \Delta G_{\text{O}^*} - eU + kT \ln 10\text{pH} \quad (11) \]
\[ \Delta G_4 = 4.92 \text{ eV} - \Delta G_{\text{OOH}^*} - eU + kT \ln 10\text{pH} \quad (12) \]

The theoretical overpotential is defined as:

\[ \eta_{\text{theory}} = \max[\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4]/e - 1.23 \text{ V.} \]

G represents the Gibbs free energy, and U represents external bias against normal hydrogen electrode (NHE) at standard conditions (T = 298.15 K, P = 1 bar, pH = 0). So, eU and pH are 0. According to the calculation of Gibbs free-energy, the
theoretical overpotential of NiOOH, F/NiOOH and Mn-F/NiOOH is 1.90, 0.47, and 0.35 eV, respectively.

**Table. S1.** Calculated Gibbs free energies (eV) of OER elementary steps and overpotential under reaction condition (pH = 14) on NiOOH, F/NiOOH and Mn-F/NiOOH.

<table>
<thead>
<tr>
<th>Materials</th>
<th>( \Delta G_1 )</th>
<th>( \Delta G_2 )</th>
<th>( \Delta G_3 )</th>
<th>( \Delta G_4 )</th>
<th>Overpotential(eV)</th>
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<tbody>
<tr>
<td>NiOOH</td>
<td>1.28</td>
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<td>1.58</td>
<td>0.76</td>
<td>1.45</td>
<td>0.35</td>
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</tbody>
</table>

References

[1] QuantumATK version 2018.06, Synopsys QuantumATK.