Supporting Information

Prussian blue analogue-derived Ni and Co bimetallic oxide nanoplate arrays block-built from porous and hollow nanocubes for the efficient oxygen evolution reaction

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Computational details:

Density functional theory (DFT) calculations are done using the projector-augmented wave method and a plane-wave basis set as implemented in the Vienna Ab initio Simulation Package (VASP).\cite{1,2} The valence configurations are treated as 1s\(^1\) for H, 2s\(^2\)2p\(^4\) for O, 3d\(^8\)4s\(^1\) for Co, 3d\(^9\)4s\(^1\) for Ni, and 4d\(^7\)5s\(^1\) for Ru. The Bayesian Error Estimation Functional with van der Waals correlation (BEEF–vdW) is employed.\cite{3} The cutoff energy for plane-wave basis functions is 550 eV. By substituting half Co atoms with Ni atoms within the inverse spinel structure of NiCo\(_2\)O\(_4\) (JCPDS No. 20-0781), the bulk structure of Ni\(_2\)CoO\(_4\) is generated via the Special Quasirandom Structures (SQS) method, which has been widely used to determine the atomic distributions in solid solutions.\cite{4} The bulk lattice parameters of NiO and RuO\(_2\) are fully optimized based on experimental data (NiO JCPDS No. 47-1049, RuO\(_2\) JCPDS No. 40-1290). Based on the optimized structural parameters, we construct periodic surface slabs with six to eight Co/Ni or Ru layers separated by at least 16 Å of vacuum for Ni\(_2\)CoO\(_4\) (001), NiO (100) and RuO\(_2\) (110). Atomic positions within the top three layers of the slabs are allowed to relax in OH*, O* and OOH* binding energy calculations. All calculations are done in \(\Gamma\)-centered Monkhorst–Pack \(k\)-point meshes with a reciprocal-space resolution of 0.15 Å\(^{-1}\). The energy convergence is 10\(^{-5}\) eV and the force convergence 0.01 eV/Å.

As is known, catalytic activity of the material is determined by the binding energies of the reaction intermediates to the active sites of the catalyst. In the oxygen evolution reaction, OH*, O* and OOH* intermediates are involved. To estimate the adsorption free energies \(\Delta G\) of different intermediate at zero potential and pH = 0, we calculate the binding energies \(\Delta E\) of each individual intermediate and corrected them with zero point energy (ZPE) and entropy (TS) using \(\Delta G = \Delta E + \Delta ZPE - T \Delta S\).\cite{5} Here, we use the computational hydrogen electrode (CHE) model, which exploits that the chemical potential of a proton-electron pair is equal to gas-phase H\(_2\) at standard conditions. As the ground state of the O\(_2\) is poorly described in DFT calculations we use gas phase...
H₂O and H₂ as reference states as they are readily treated in the DFT calculations. The entropy for H₂O is calculated at 0.035 bar which is the equilibrium pressure of H₂O at 300 K. The free energy of this state is therefore equal to that of liquid water. [5]

The theoretical overpotential η is defined as the difference between the limiting potential and equilibrium potential. In the oxygen evolution reaction, the limiting potential is related to the highest free energy step ΔG^{OER} = Max[(ΔG_{O}−ΔG_{OH}⁺), (ΔG_{OOH}−ΔG_{O}⁺)], and the equilibrium potential is 1.23 V. Thus, we get η = (ΔG^{OER}/e) −1.23 V. [6]
Fig. S1 XRD patterns of (a) Ni$_x$Co$_{3-x}$O$_4$/NF and (b) NiO/NF (peaks at 44°, 52° and 76° ascribed to Ni substrate).
Fig. S2 TEM image of Ni₃₋ₓCoₓ₋₃₋ₓO₄/NF.
Fig. S3 (a) and (b) FESEM images of NiO/NF.
Fig. S4 (a) TEM and (b) HRTEM images of NiO/NF.
Fig. S5 SEM-EDX (a) elemental mapping and (b) spectrum of Ni$_x$Co$_{3-x}$O$_4$. (Trace amount of K element was from the residual potassium cations embedded at the interstitial sites of the frameworks.)
Fig. S6 Nitrogen adsorption-desorption isotherms of Ni$_x$Co$_{3-x}$O$_4$/NF (inset corresponding to pore size distribution).
Fig. S7 Low-magnified FESEM images of (a) bare NF and (b) Ni$_x$Co$_{3-x}$O$_4$/NF.
Fig. S8 (a) Full XPS spectrum of NiO and high-resolution spectra of (b) Ni 2p and (c) O 1s.
Fig. S9 CV curves of the (a) Ni₃Co₃-xO₄/NF, (b) NiO/NF, (c) Ni-Co PBA/NF, (d) Ni(OH)₂/NF, (e) RuO₂, (f) NF and (g) Ni₃Co₃-xO₄ P measured in 1.0 M KOH solution at scan rates from 20 to 80 mV s⁻¹.
Fig. S10 FESEM images of (a) Ni-Co PBA P and (b) Ni$_x$Co$_{3-x}$O$_4$ P.
Fig. S11 (a-c) FESEM images and (d) TEM image of Ni$_x$Co$_{3-x}$O$_4$/NF after 24 h electrocatalysis.
Fig. S12 High-resolution spectra of (a) Co 2p, (b) O 1s and (c) Ni 2p for Ni$_x$Co$_{3-x}$O$_y$/NF before and after 24 h electrocatalysis.
Table S1. OER activity\(^{a}\) of some reported electrocatalysts based on PBAs.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Precursor</th>
<th>Structure</th>
<th>(\eta ) (^{b}) at 10 mA cm(^{-2}) (mV)</th>
<th>Tafel Slope (mV dec(^{-1}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(<em>{x})Co(</em>{3-x})O(_4) /NF</td>
<td>Ni-Co PBA arrays on nickel foam (NF)</td>
<td>Hierarchical nanoplate arrays composed of porous and hollow nanocubes on NF</td>
<td>287</td>
<td>88</td>
<td>This work</td>
</tr>
<tr>
<td>Ni-Co-Fe PBA</td>
<td>--</td>
<td>Hierarchical hollow nanocuboids</td>
<td>320</td>
<td>49</td>
<td>[7]</td>
</tr>
<tr>
<td>NiO/NiCo(_2)O(_4)</td>
<td>Ni-Co PBA nanocubes</td>
<td>Nanocages consisting of pyramidal walls</td>
<td>380</td>
<td>50</td>
<td>[8]</td>
</tr>
<tr>
<td>CoS(<em>{4.6})O(</em>{0.6})</td>
<td>Co-Fe PBA nanocubes</td>
<td>Amorphous porous nanocubes</td>
<td>290</td>
<td>67</td>
<td>[9]</td>
</tr>
<tr>
<td>Ni(_5)P(_4)/Ni(_2)P</td>
<td>Ni-Ni PBA nanoplates</td>
<td>Porous carbon coated nanoplates</td>
<td>300</td>
<td>64</td>
<td>[10]</td>
</tr>
<tr>
<td>Co(_3)S(_4)/MoS(_2)</td>
<td>Co-Fe PBA nanocubes</td>
<td>Hollow core-shell cubic heterostructure</td>
<td>280</td>
<td>43</td>
<td>[12]</td>
</tr>
<tr>
<td>NiFeSe@NiSe</td>
<td>O/CC</td>
<td>Ni-Fe PBA@ Ni(_2)CO(_3)(OH)(_2) nanosheet arrays on carbon cloth (CC)</td>
<td>Porous and interconnected heterostructures elaborated with defects on CC</td>
<td>270</td>
<td>63.2</td>
</tr>
</tbody>
</table>

(a) The electrolyte is 1.0 M KOH except for Ref. [7] (0.1 M KOH).
(b) \(\eta\) is overpotential.
Table S2. Free energies of adsorption for OH*, O* and OOH*, $\Delta G^{\text{OER}}$ and $\eta$ for oxygen evolution reaction over $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ (001), RuO$_2$ (110) and NiO (100).

<table>
<thead>
<tr>
<th>Electro catalyst</th>
<th>$\Delta G_{\text{OH}}$ (eV)</th>
<th>$\Delta G_{\text{O}}$ (eV)</th>
<th>$\Delta G_{\text{OOH}}$ (eV)</th>
<th>$\Delta G^{\text{OER}}$ (eV)</th>
<th>$\eta$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ni}<em>x\text{Co}</em>{3-x}\text{O}_4$ (001)</td>
<td>1.05</td>
<td>2.84</td>
<td>3.87</td>
<td>1.79</td>
<td>0.56</td>
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<tr>
<td>RuO$_2$ (110)</td>
<td>0.49</td>
<td>1.45</td>
<td>3.33</td>
<td>1.88</td>
<td>0.65</td>
</tr>
<tr>
<td>NiO (100)</td>
<td>0.22</td>
<td>1.52</td>
<td>3.42</td>
<td>1.90</td>
<td>0.67</td>
</tr>
</tbody>
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References