Electronic Supplementary Information

Capturing the Active Sites of Multimetallic (Oxy)Hydroxides for Oxygen Evolution Reactions

Xin Bo, a Rosalie K Hocking, b Si Zhou, c, d Yibing Li, a Xianjue Chen, a Jincheng Zhuang, a Yi Du, c, e and Chuan Zhao **

a School of Chemistry, The University of New South Wales, Sydney, Australia, 2052. E-mail: chuan.zhao@unsw.edu.au.

b Department of Chemistry and Biotechnology and Centre for Translational Atomaterials, CTAM, Swinburne University of Technology, Hawthorn, VIC, Australia, 3122.

c Institute for Superconducting and Electronic Materials (ISEM), Australian Institute for Innovative Materials (AIIM), University of Wollongong, Wollongong, NSW, 2522.

d Key Laboratory of Materials Modification by Laser, Ion and Electron Beams (Dalian University of Technology), Ministry of Education, Dalian, China, 116024.

e BUAA-UOW Joint Research Center and School of Physics, Beihang University, Beijing, China, 100191.
**Fig. S1.** The cell (a) was filled with 1.0 M KOH electrolyte and bubbled with hydrogen for 30 min. Then the Pt foils (exposed area, 1.0 × 1.0 cm$^2$) were applied as both working and counter electrodes and the Hg/HgO or Ag/AgCl electrode as the reference electrodes. Then CVs (b, c) were carried out at a scan rate of 1.0 mV·s$^{-1}$ and the average of the two interconversion point values was taken as the thermodynamic potential.$^1$

The pH of 1.0 M KOH (13.7) was measured by using a pH meter (PHS-3, LEICI), which was calibrated with the standard references of pH = 4, 6 and 13. As read from **Fig. S1b–c**, the potential values can be converted by the following equations: $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.926$ and $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 1.037$.

**Fig. S2.** (a–d) Atomic structures of various Cr and/or Fe substituted β-NiOOH models for DFT calculations. The (101) surfaces are exposed and covered by OH groups in alkaline media. The H, O, Cr, Fe and Ni atoms are shown in white, red, green, cyan and blue colours, respectively. Of note: model (d) was used to fit FTs for operando Fe-sub-β-NiOOH under the applied potential of 0.70 V.
Fig. S3. Scaling relations between calculated binding energies of OOH*, O* and OH* species on various metal sites of the Cr and/or Fe substituted β-NiOOH models described in Table S7. The dashed lines are linear fitting of the data points, and the fitting equations are given.

Fig. S4. Overall XPS surveys of NiFeCr/NF and NiFe/NF.
Fig. S5. HRTEM (a), SAED patterns (b) and EDS mapping (c: Fe, d: Ni, e: O) of NiFe (oxy)hydroxide catalyst on TEM copper grid.

Fig. S6. (a) SEM for NiFeCr/CF and relevant Ni (b), Fe (c), Cr (d), O (e) EDS mappings and statistics (f).
Fig. S7. (a) SEM for NiFe/CF and relevant Ni (b), Fe (c), O (d) mappings and EDS statistics (e).

Fig. S8. Reversal LSV scans (a) at the scanning rate of 5.0 mV·s$^{-1}$ in 1.0 M KOH electrolyte with 80 % iR-compensation and the derived Tafel slopes (b).
**Fig. S9.** Color change on NiFe/NF (left: black) and NiFeCr/NF (right: gray) electrodes during water oxidation in 1 M KOH under the applied potential of 1.6 V vs RHE without iR-compensation

**Fig. S10.** CVs of NiFe/NF (a) and NiFeCr/NF (d) at the scanning rates from 100~800 mV·s⁻¹ in 1.0 M KOH without iR-compensation; (b, e) The relevant plots of the redox peak current densities vs. the square root of scanning rates; (c, f) The relevant plots of the redox peak potentials vs. the logarithm of scanning rates.
Fig. S11. CVs of NiFe/NF and NiFeCr/NF in 0.1 M (a) and 1.0 M (c) ultrapure KOH electrolyte; CVs of NiFe/NF and NiFeCr/NF in 0.1 M (b) and 1.0 M (d) unpurified KOH electrolyte; Scanning rate of 50.0 mV·s\(^{-1}\) and without iR-compensation.

Fig. S12. LSVs of Cr/CF, FeCr/CF, NiCr/NF, NiFe/NF and NiFeCr/NF at the scanning rate of 5.0 mV·s\(^{-1}\) in 1.0 M KOH electrolyte with 80% iR-compensation.

Cr/CF control sample was fabricated on copper foam substrate in the depositing bath of 6 mM Cr(NO\(_3\))\(_3\)·9H\(_2\)O via the same electrodeposition protocols in the manuscript. FeCr/CF control sample was fabricated on copper foam substrate in the depositing bath of 3 mM Fe(NO\(_3\))\(_3\)·9H\(_2\)O and 6 mM Cr(NO\(_3\))\(_3\)·9H\(_2\)O. NiCr/NF control sample was fabricated on nickel foam substrate in the depositing bath of 12 mM...
Ni(NO$_3$)$_2$·6H$_2$O and 6 mM Cr(NO$_3$)$_3$·9H$_2$O. NiCr and FeCr control samples were not tested for XAS because they show very poor OER activities, which also indicates the significant OER observed at NiFeCr is resulted from the synergistic effect from Ni, Fe and Cr dependently.

**Fig. S13.** XPS of O1s (a), Fe2p (b), Ni2p (c) and overall survey (d, insert: Cr2p) of NiFe/NF and NiFeCr/NF after OER.

**Fig. S14.** CVs of NiFe/NF electrode in 1.0 M KOH electrolyte before and after addition of 0.5 mM Cr(NO$_3$)$_3$·9H$_2$O at the scanning rate of 50 mV·s$^{-1}$ without iR-compensation. CVs were carried in an H-cell separated with Nafion 117 membrane so as to get rid of the enhancement from the counter electrode.
**Fig. S15.** TEM morphology of defective NiFeCr sheet after OER peeled from NF substrate.

**Fig. S16.** Cyclic voltammetries on NiFeCr/NF (red) and NiFe/NF (black) under various scanning rates and the relevant calculation for electrochemical surface areas.
**Fig. S17.** ECSA normalised LSVs from Fig. 2a.

**Fig. S18.** LSVs of NiFe/NF and NiFeCr/NF at the scanning rate of 5.0 mV·s⁻¹ in 0.1 M KOH electrolyte with 60 % iR-compensation.
Fig. S19. Raman of NiFe (black) and NiFeCr (red) (oxy)hydroxide compounds on SPE (gold substrate).

Fig. S20. XANES data of Fe (a), Ni (b) and Cr (c) K-edge on pristine NiFe, NiFeCr catalysts and the relevant hydroxide references; FTs from EXAFS of Fe (d), Ni (e) and Cr (f) on pristine NiFe, NiFeCr catalysts and the relevant hydroxide references.

The Ni(OH)$_2$, Fe(OH)$_3$ and Cr(OH)$_3$ references were synthesized via co-precipitation approach. For example, 3 mmol Ni(NO$_3$)$_3$·6H$_2$O (or hydrated Fe, Cr nitrate salts) were dissolved in 250 ml Ar-saturated H$_2$O. Then 0.1 M KOH was slowly
dropped into the solution with 500 rpm stirring till the pH of the suspension was adjusted to 10 and the suspension was washed and centrifuged with water and ethanol three times. The precipitate was carefully collected and dried in the vacuum oven at 60 °C for 48 hours. Finally, the dried solids were ground into powder. For XAS analysis, 5.0 mg reference powder was mixed with 95.0 mg cellulose (99.5 %, Sigma) and filled in a polymer XAS holder sealed with Kapton tap.

**Fig. S21.** EXAFS K space of Fe (a) and Ni (b) and Cr (c) in NiFe and NiFeCr catalysts (solid: measured, circle: fitting).

**Fig. S22.** Structures of OH*, O* and OOH* reaction intermediates (in the black circles) on (a) oxyhydroxide and (b) on the defective oxyhydroxide. The H, O, Cr, Fe and Ni atoms are shown in white, red, green, cyan and blue colours, respectively.
TABLES

**Table S1.** Elemental contributions on NiFe and NiFeCr electrode

<table>
<thead>
<tr>
<th></th>
<th>XPS</th>
<th>EDS</th>
<th>ICP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni in NiFe</td>
<td>6.6</td>
<td>4.0</td>
<td>6.0</td>
</tr>
<tr>
<td>Fe in NiFe</td>
<td>2.0</td>
<td>3.0</td>
<td>2.8</td>
</tr>
<tr>
<td>Ni in NiFeCr</td>
<td>6.2</td>
<td>6.7</td>
<td>6.0</td>
</tr>
<tr>
<td>Fe in NiFeCr</td>
<td>1.0</td>
<td>2.0</td>
<td>1.1</td>
</tr>
<tr>
<td>Cr in NiFeCr</td>
<td>1.1</td>
<td>2.7</td>
<td>2.6</td>
</tr>
</tbody>
</table>

From XSP fitting, as the Ni$^0$ on the substrate, Ni content should contribute more than the real content in NiFeCr and NiFe hydroxide thin film.

**Table S2.** Onset overpotential and Tafel slope values

<table>
<thead>
<tr>
<th></th>
<th>Forward</th>
<th>Backward</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiFe onset</td>
<td>260 mV</td>
<td>270 mV</td>
<td>265 mV</td>
</tr>
<tr>
<td>NiFe Tafel</td>
<td>50 mV·dec$^{-1}$</td>
<td>46 mV·dec$^{-1}$</td>
<td>48 mV·dec$^{-1}$</td>
</tr>
<tr>
<td>NiFeCr onset</td>
<td>240 mV</td>
<td>240 mV</td>
<td>240 mV</td>
</tr>
<tr>
<td>NiFeCr Tafel</td>
<td>41 mV·dec$^{-1}$</td>
<td>31 mV·dec$^{-1}$</td>
<td>36 mV·dec$^{-1}$</td>
</tr>
</tbody>
</table>

**Table S3.** EIS parameters of NiFe/NF and NiFeCr/NF

<table>
<thead>
<tr>
<th></th>
<th>$R_s$/Ω</th>
<th>$Q_1$/S·s$^0$</th>
<th>$n_1$</th>
<th>$C_{dl1}$/F</th>
<th>$R_{ct1}$</th>
<th>$Q_2$/S·s$^0$</th>
<th>$n_2$</th>
<th>$C_{dl2}$/F</th>
<th>$R_{ct2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiFe</td>
<td>2.74</td>
<td>0.04</td>
<td>0.69</td>
<td>0.0057</td>
<td>0.38</td>
<td>0.012</td>
<td>0.88</td>
<td>0.0075</td>
<td>59.93</td>
</tr>
<tr>
<td>NiFeCr</td>
<td>2.90</td>
<td>0.09</td>
<td>0.49</td>
<td>0.0016</td>
<td>0.26</td>
<td>0.011</td>
<td>0.93</td>
<td>0.0084</td>
<td>39.45</td>
</tr>
</tbody>
</table>
### Table S4. Comparison between this work and other benchmark catalysts

<table>
<thead>
<tr>
<th>Materials</th>
<th>η/mV</th>
<th>j/mA·cm⁻²</th>
<th>iR</th>
<th>Electrolyte</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiFeCr/NF</td>
<td>240</td>
<td>onset</td>
<td>Correcton</td>
<td>1 M KOH</td>
<td>this work</td>
</tr>
<tr>
<td>NiFeCr/NF</td>
<td>260</td>
<td>100</td>
<td>Correction</td>
<td>1 M KOH</td>
<td>2</td>
</tr>
<tr>
<td>NiFe/NF</td>
<td>265</td>
<td>onset</td>
<td>Correcton</td>
<td>1 M KOH</td>
<td>this work</td>
</tr>
<tr>
<td>NiFe/NF</td>
<td>290</td>
<td>100</td>
<td>Correction</td>
<td>1 M KOH</td>
<td>2</td>
</tr>
<tr>
<td>Ru</td>
<td>290</td>
<td>10</td>
<td>No</td>
<td>1 M NaOH</td>
<td>3</td>
</tr>
<tr>
<td>Ir</td>
<td>390</td>
<td>10</td>
<td>No</td>
<td>1 M NaOH</td>
<td>3</td>
</tr>
<tr>
<td>NiFe LDH</td>
<td>225</td>
<td>10</td>
<td>Correction</td>
<td>1 M KOH</td>
<td>4</td>
</tr>
<tr>
<td>NiFe₂O₄</td>
<td>410</td>
<td>5</td>
<td>--</td>
<td>0.1 M KOH</td>
<td>5</td>
</tr>
<tr>
<td>Co₃₋ₓCxO₄</td>
<td>350</td>
<td>10</td>
<td>Correction</td>
<td>1 M NaOH</td>
<td>6</td>
</tr>
<tr>
<td>NiV LDH</td>
<td>310</td>
<td>10</td>
<td>--</td>
<td>1 M KOH</td>
<td>7</td>
</tr>
<tr>
<td>CoFe LDH</td>
<td>325</td>
<td>10</td>
<td>Correction</td>
<td>0.1 M KOH</td>
<td>8</td>
</tr>
<tr>
<td>CoMn LDH</td>
<td>324</td>
<td>10</td>
<td>Correction</td>
<td>1 M KOH</td>
<td>9</td>
</tr>
<tr>
<td>NiFeV LDH</td>
<td>230</td>
<td>10</td>
<td>Correction</td>
<td>1 M KOH</td>
<td>10</td>
</tr>
<tr>
<td>CoFeW LDH</td>
<td>191</td>
<td>10</td>
<td>Correction</td>
<td>1 M KOH</td>
<td>11</td>
</tr>
<tr>
<td>NiFePi</td>
<td>290</td>
<td>10</td>
<td>Correction</td>
<td>1 M KOH</td>
<td>12</td>
</tr>
</tbody>
</table>

### Table S5. ICP-OES survey for Cr content in KOH electrolyte

<table>
<thead>
<tr>
<th>Cr content/μg·L⁻¹</th>
<th>KOH before OER</th>
<th>KOH after OER</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.78</td>
<td>144</td>
<td></td>
</tr>
</tbody>
</table>

1.0 ml fresh 1.0 M KOH was collected and diluted into 10 ml for a blank control; After OER, another 1.0 ml 1.0 M KOH was collected and diluted into 10 ml. The diluted electrolyte samples were then tested in ICP-OES system.
<table>
<thead>
<tr>
<th>Path</th>
<th>CN</th>
<th>R (Å)</th>
<th>( \sigma^2(\text{Å}^2) )</th>
<th>( E_0 ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni Pristine NiFe</td>
<td>Ni-O</td>
<td>6</td>
<td>2.06</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td>Ni-M</td>
<td>6</td>
<td>3.13</td>
<td>0.008</td>
</tr>
<tr>
<td>Fe Pristine NiFe</td>
<td>Fe-O</td>
<td>6</td>
<td>1.97</td>
<td>0.007</td>
</tr>
<tr>
<td></td>
<td>Fe-M</td>
<td>6</td>
<td>3.17</td>
<td>0.014</td>
</tr>
<tr>
<td>Ni in Pristine NiFeCr</td>
<td>Ni-O</td>
<td>6</td>
<td>2.05</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>Ni-M</td>
<td>6</td>
<td>3.14</td>
<td>0.004</td>
</tr>
<tr>
<td>Fe in Pristine NiFeCr</td>
<td>Fe-O</td>
<td>6</td>
<td>1.96</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td>Fe-M</td>
<td>6</td>
<td>3.05</td>
<td>0.006</td>
</tr>
<tr>
<td>Cr in Pristine NiFeCr</td>
<td>Cr-O</td>
<td>6</td>
<td>1.94</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>Cr-M</td>
<td>6</td>
<td>3.00</td>
<td>0.006</td>
</tr>
<tr>
<td>Ni in NiFe 0.70</td>
<td>Ni-O</td>
<td>5*</td>
<td>1.88</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>Ni-M</td>
<td>6</td>
<td>2.81</td>
<td>0.001</td>
</tr>
<tr>
<td>Fe in NiFe 0.70</td>
<td>Fe-O</td>
<td>5*</td>
<td>2.01</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>Fe-M</td>
<td>6</td>
<td>3.22</td>
<td>0.016</td>
</tr>
<tr>
<td>Ni in NiFeCr 0.70</td>
<td>Ni-O</td>
<td>5*</td>
<td>2.04</td>
<td>0.013</td>
</tr>
<tr>
<td></td>
<td>Ni-M</td>
<td>6</td>
<td>3.04</td>
<td>0.001</td>
</tr>
<tr>
<td>Fe in NiFeCr 0.70</td>
<td>Fe-O</td>
<td>5*</td>
<td>1.97</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td>Fe-M</td>
<td>6</td>
<td>2.98</td>
<td>0.013</td>
</tr>
<tr>
<td>Cr in NiFeCr 0.70</td>
<td>Cr-O</td>
<td>5*</td>
<td>1.79</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>Cr-M</td>
<td>6</td>
<td>2.75</td>
<td>0.022</td>
</tr>
</tbody>
</table>

* The unsaturated CN number is due to the oxygen trap (vacancy) for active intermediate
Table S7. Calculated binding energies of OH*, O* and OOH* intermediates ($\Delta E_{\text{OH}^*}$, $\Delta E_{\text{O}^*}$, $\Delta E_{\text{OOH}^*}$), theoretical OER overpotential ($\eta^{\text{OER}}$), and rate-limit step (RLS) for various metal sites on the Cr and Fe doped NiOOH (101) surface. The values of RuO$_2$(110) surface are also listed for comparison. The atomic structures of all the models are shown in Fig. S22.

<table>
<thead>
<tr>
<th>site</th>
<th>system</th>
<th>$\Delta E_{\text{OH}^*}$ (eV)</th>
<th>$\Delta E_{\text{O}^*}$ (eV)</th>
<th>$\Delta E_{\text{OOH}^*}$ (eV)</th>
<th>$\eta^{\text{OER}}$ (V)</th>
<th>RLS</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-(Cr, Fe, Ni)</td>
<td></td>
<td>0.72</td>
<td>1.99</td>
<td>3.11</td>
<td>0.25</td>
<td>OOH*</td>
</tr>
<tr>
<td>b-(Cr, Fe, Ni)</td>
<td></td>
<td>1.18</td>
<td>2.56</td>
<td>3.80</td>
<td>0.37</td>
<td>OOH*</td>
</tr>
<tr>
<td>c-(Cr, Ni)</td>
<td></td>
<td>1.02</td>
<td>2.24</td>
<td>3.45</td>
<td>0.34</td>
<td>OOH*</td>
</tr>
<tr>
<td>(Cr, Fe, Ni) Cr near vacancy</td>
<td></td>
<td>0.67</td>
<td>1.61</td>
<td>3.59</td>
<td>1.11</td>
<td>OOH*</td>
</tr>
<tr>
<td>a-(Cr, Fe, Ni)</td>
<td></td>
<td>1.17</td>
<td>3.30</td>
<td>3.61</td>
<td>0.54</td>
<td>O*</td>
</tr>
<tr>
<td>b-(Cr, Fe, Ni)</td>
<td></td>
<td>1.17</td>
<td>3.45</td>
<td>3.70</td>
<td>0.68</td>
<td>O*</td>
</tr>
<tr>
<td>d-(Fe, Ni)</td>
<td></td>
<td>1.39</td>
<td>3.99</td>
<td>4.32</td>
<td>1.01</td>
<td>O*</td>
</tr>
<tr>
<td>a-(Cr, Fe, Ni)</td>
<td></td>
<td>1.97</td>
<td>4.62</td>
<td>4.07</td>
<td>1.14</td>
<td>OH*</td>
</tr>
<tr>
<td>b-(Cr, Fe, Ni)</td>
<td></td>
<td>2.00</td>
<td>4.68</td>
<td>4.6</td>
<td>1.17</td>
<td>OH*</td>
</tr>
<tr>
<td>c-(Cr, Ni)</td>
<td></td>
<td>2.01</td>
<td>4.47</td>
<td>4.55</td>
<td>1.18</td>
<td>OH*</td>
</tr>
<tr>
<td>d-(Fe, Ni)</td>
<td></td>
<td>1.70</td>
<td>4.38</td>
<td>4.34</td>
<td>1.09</td>
<td>OH*</td>
</tr>
<tr>
<td>Ru</td>
<td>RuO$_2$(110)</td>
<td>0.33</td>
<td>2.31</td>
<td>3.65</td>
<td>0.40</td>
<td>OOH*</td>
</tr>
</tbody>
</table>
References


