Electronic Supplementary Information

**In-situ** structural evolution of multi-site alloy electrocatalyst to manipulate intermediate for enhanced water oxidation reaction

Bingliang Wang, Kangning Zhao, Zhuo Yu, Congli Sun, Zhuo Wang, Ningning Feng, Liqiang Mai, Yonggang Wang, Yongyao Xia

**Affiliations:**

a. Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Institute of New Energy, iChEM (Collaborative Innovation Center of Chemistry for Energy Materials) Fudan University, Shanghai 200433, China.

b. State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, State Key Laboratory of Silicate Materials for Architectures, International School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, P. R. China.

c. NRC (Nanostructure Research Centre), Wuhan University of Technology, Wuhan 430070, P. R. China.

* E-mail: ygwang@fudan.edu.cn, yyxia@fudan.edu.cn
Fig. S1, The XRD pattern of MMOC.
Fig. S2. FT-IR spectrum of MMOC and H$_2$DHBD ligand.
Fig. S3. (a-b) SEM images of MMOC. (c) TEM image of MMOC. (d) HRTEM image of MMOC, Inset image: corresponding SAED pattern. (e) HAADF-STEM images and corresponding EDS mapping analysis of MMOC. Scale bar: (a) 1 μm, (b) 500 nm, (c) 200 nm, (d) 10 nm inset image: 5 1/nm and (e) 200 nm.
Fig. S4. SEM images of MsA. Scale bar: (a) 1 μm and (b) 500 nm.
Fig. S5. CV curves of electrochemical dealloying process for Ni foam. (Cycle 1, 100, 1000 and 3000 were selected, all CV curves without iR-correction) scan rate:100 mV s$^{-1}$. 
Fig. S6. HAADF-STEM images and corresponding EDS elemental mapping analysis of (a) 1st CV (b) 100th CV (c) 1000th CV. Scale bar: (a) 100 nm, (b) 50 nm and (c) 50 nm.
Fig. S7. SAED pattern of (a) 1st CV (b) 100th CV (c) 1000th CV. Scale bar: 5 nm⁻¹
**Fig. S8.** LSV curve of Ni foam after 3000 cycles. Scan rate: 5 mV s$^{-1}$.
Fig. S9. CV tests at various scan rates for calculating the ECSA.
Fig. S10. EIS analysis performed at the potential corresponding with 100 mA cm$^{-2}$ of LSV curves. (a) DMsA, (b) MsA and (c) commercial RuO$_2$ catalyst.
Fig. S11. 2D contour image of operando ATR FT-IR spectrum for DMsA electrocatalyst in 1 M KOH in H$_2^{18}$O at the potential range from 1.4 to 1.8 V vs RHE.
Fig. S12. 2D contour image of operando ATR FT-IR spectrum for MsA electrocatalyst in 1 M KOH in H₂O at the potential range from 1.4 to 1.8 V vs RHE.
<table>
<thead>
<tr>
<th>Sample name</th>
<th>Element</th>
<th>Concentrate (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MsA</td>
<td>Ni</td>
<td>15.23</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>5.042</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>4.805</td>
</tr>
<tr>
<td>DMsA</td>
<td>Ni</td>
<td>72.69</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>17.11</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>13.13</td>
</tr>
</tbody>
</table>
Table S2. OER performance comparison with recently reported results

<table>
<thead>
<tr>
<th>Electrocatalysts</th>
<th>Current density (mA cm$^{-2}$)</th>
<th>Corresponding Overpotential (mV)</th>
<th>Tafel slope (mV dec$^{-1}$)</th>
<th>Cycling performance</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMsA</td>
<td>10</td>
<td>~170</td>
<td>34</td>
<td>200 h at 100 mA cm$^{-2}$</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>250</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>$\text{NiN}_x$-PC/EG $^1$</td>
<td>10</td>
<td>280</td>
<td>45</td>
<td>10 h at 100 mA cm$^{-2}$</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>330</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G-$\text{FeCoW}^2$</td>
<td>10</td>
<td>191</td>
<td>—</td>
<td>500 h at 30 mA cm$^{-2}$</td>
<td>Science 2016, 352,333-337</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>—</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe-ultrathin TiO$_2$ nanobelt (Fe-UTN) $^3$</td>
<td>10</td>
<td>270</td>
<td>37</td>
<td>10 h at 10 mA cm$^{-2}$</td>
<td>Angew. Chem. Int. Ed. 2019, 56, 2313–2317.</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>376</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Co}<em>{1.5}\text{Fe}</em>{0.5}\text{P}^4$</td>
<td>10</td>
<td>278</td>
<td>57</td>
<td>10 h at 10 mA cm$^{-2}$</td>
<td>Angew. Chem. Int. Ed. 2020, 59, 465-470.</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>330</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoBDC-NF $^5$</td>
<td>10</td>
<td>178</td>
<td>51</td>
<td>80 h at 100 mA cm$^{-2}$</td>
<td>Nat. Commun. 2019, 10,50348.</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>241</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W-$\text{Ni(OH)}_2$ $^6$</td>
<td>10</td>
<td>237</td>
<td>33</td>
<td>3 h from 50 to 100 mA cm$^{-2}$</td>
<td>Nat. Commun. 2019, 10,2149.</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>~280</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Co}_3\text{Sn}_2\text{S}_2$ sp(single particle) $^7$</td>
<td>10</td>
<td>270</td>
<td>74</td>
<td>12 h at 10 mA cm$^{-2}$</td>
<td>Sci. Adv. 2019, 5, eaaw9867.</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>~390</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>amorphous LaNiFe hydroxide (a-LNF(t-d)) $^8$</td>
<td>10</td>
<td>189</td>
<td>36</td>
<td>100 h at 10 mA cm$^{-2}$</td>
<td>Adv. Mater. 2019, 31, 1900883.</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>310</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeOOH (Se)/IF $^9$</td>
<td>10</td>
<td>287</td>
<td>54</td>
<td>14 h at 10 mA cm$^{-2}$</td>
<td>J. Am. Chem. Soc. 2019, 141, 7005–7013.</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>364</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiFe-LDH@NiCu $^{10}$</td>
<td>10</td>
<td>218</td>
<td>57</td>
<td>6 h at 320 mV (~45 mA cm$^{-2}$)</td>
<td>Adv. Mater. 2019, 31, 1806769.</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>~370</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AN-CuNiFe $^{11}$</td>
<td>10</td>
<td>224</td>
<td>44</td>
<td>12 h at 10 mA cm$^{-2}$</td>
<td>Angew. Chem. Int. Ed. 2019, 131, 4233–4238.</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>330</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
References:


