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21 **Dynamic stability of active sites in hydr(oxy)oxides**  
22 **for the oxygen evolution reaction**

23  
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37 **Abstract**

38 The poor activity and stability of electrode materials for the oxygen evolution reaction (OER) are  
39 the main bottlenecks in the water splitting reaction for H<sub>2</sub> production. Here, by studying activity-  
40 stability trends for the OER on conductive M<sub>1</sub>O<sub>x</sub>H<sub>y</sub>, Fe-M<sub>1</sub>O<sub>x</sub>H<sub>y</sub> and Fe-M<sub>1</sub>M<sub>2</sub>O<sub>x</sub>H<sub>y</sub>  
41 hydr(oxy)oxide clusters (M<sub>1</sub>= Ni, Co, Fe; M<sub>2</sub>= Mn, Co, Cu), we show that balancing the rates of  
42 Fe dissolution and redeposition over a MO<sub>x</sub>H<sub>y</sub> host establishes dynamically stable Fe active sites.  
43 Together with tuning the Fe content of the electrolyte, the strong interaction of Fe with the  
44 MO<sub>x</sub>H<sub>y</sub> host is the key to control the average number of Fe active sites present at the solid-liquid  
45 interface. We suggest that the Fe-M adsorption energy can therefore serve as a reaction  
46 descriptor that unifies OER catalysis on 3d transition metal hydr(oxy)oxides in alkaline media.  
47 Thus, introduction of dynamically stable active sites extends the design rules for making active  
48 and stable interfaces.

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51 Progress in the fundamental understanding of electrochemical interfaces, encompassing  
52 electrode materials (catalysts) and hydrated (solvated) ions in the double layer, has begun to  
53 revolutionize the development of alternative energy systems as a viable replacement to fossil fuel  
54 technology. At the core of this transition lies the oxygen evolution reaction (OER), an important  
55 electrochemical process part of hydrogen production in water electrolyzers<sup>1</sup>, corrosion<sup>2</sup>, metal-air  
56 batteries<sup>3,4</sup>, and synthesis of new chemicals from CO<sub>2</sub> reduction<sup>5</sup>. Not surprisingly, a wide  
57 variety of materials have been evaluated as active OER catalysts for water electrolyzers, ranging  
58 from noble metal oxides (e.g., RuO<sub>2</sub>, IrO<sub>2</sub>)<sup>6,7</sup>, to transition metal oxides<sup>8-10</sup> and perovskite-type  
59 oxide structures<sup>11-12</sup> to 3d transition metal based hydr(oxy)oxides<sup>13-17</sup>. Together with changes to  
60 surface structure and composition, tuning the double layer through the use of covalent and non-  
61 covalent interactions is another effective strategy to improve catalytic activity<sup>18,19</sup>, but it has not  
62 been consistently demonstrated for the OER<sup>20,21</sup>. Despite progress in increasing the activity,  
63 much less is known about stability of these interfaces during the oxygen evolution, an important  
64 aspect to guide the practical design of OER materials that require both high activity and stability.

65 Recently it has been found that many OER active materials suffers severe dissolution  
66 during reaction<sup>21-24</sup>, which implies that high activity in OER is always accompanied by elevated  
67 metal dissolution rates (thermodynamic material instability)<sup>25, 26</sup>. In order to take into account  
68 both activity and stability, the Activity-Stability Factor (ASF)<sup>27</sup> was suggested, as a metric that  
69 evaluates the ratio between the rates of O<sub>2</sub> production (activity) and metal dissolution (stability)  
70 measured simultaneously using *in situ* inductively coupled plasma mass spectrometry (ICP-MS)  
71 method<sup>28-30</sup>. However, the fact that dissolution occurs indicates that the surface atoms are  
72 dynamic, which is inconsistent with the common view of the electrochemical interface as a static  
73 environment. The traditional view is that all the components are “frozen” in space (static active  
74 sites), and only the reactants and products are mobile. This static view has begun to change as  
75 dynamic phenomena has been observed during OER on metal oxide<sup>31,32</sup> and perovskite<sup>12,33,34</sup>  
76 surfaces, suggesting that activity and stability can be simultaneously enhanced. Thus,  
77 understanding the dynamic properties of the entire interface can open the possibility for  
78 designing materials and the interface that are no longer bound by the severe thermodynamic  
79 instability.

80 Here, by learning from the functional links between activity and stability established for  
81 monometallic (M) and Fe modified (Fe-M) hydr(oxy)oxide materials, we demonstrate that the

82 creation of a dynamically stable interface (concomitant dissolution and redeposition of active  
83 sites) is possible after manipulation of both electrode and electrolyte components. The  
84 occurrence of dynamic active sites was verified by employing several experimental methods,  
85 both *in situ* and *ex situ*, in combination with isotope labeling and ICP-MS experiments,  
86 confirming formation of a highly active and dynamically stable catalyst. Further experimental  
87 and theoretical analysis suggests that this process is most effective (high ASF) when there is an  
88 optimum electrochemical interface; a strong interaction between a stable host and a continuous  
89 exchange of active species, a concept that could be extended to other systems with modified  
90 hosts and active sites altogether.

### 91 **Activity and stability trends for monometallic $\text{MO}_x\text{H}_y$**

92 We begin by establishing *in situ* the activity-stability trend, and thus ASF values, for the OER in  
93 alkaline media (0.1 M KOH) on well-defined monometallic 3d M hydr(oxy)oxide clusters  
94 deposited over Pt(111) ( $\text{MO}_x\text{H}_y$ ; M: Ni, Co and Fe), as shown in Fig. 1. These  $\text{MO}_x\text{H}_y$  clusters  
95 have the benefits of well-defined surface area (roughness factor equals one), synthesis with good  
96 control of sub-monolayer coverages over the Pt surface (maximum at 50%, Fig. 1a);<sup>19,35,36</sup>, as  
97 well as good electronic conductivity needed for the ASF determination (supplementary Fig. 1).  
98 Because the presence of a small amount of impurities in the electrolyte can cause significant  
99 variations in the electrochemical performance, even more so in alkaline media<sup>13,37-39</sup>, we chose to  
100 purify further high purity commercial KOH by applying an electrolytic method, (see  
101 supplementary Note 1 and supplementary Fig. 2 for details).

102  
103 Figure 1b and 1c shows the results of monitoring simultaneously the rates of  $\text{O}_2$   
104 production (current densities) and the rates of metal dissolution using our stationary probe  
105 rotating disk electrode (SPRDE) coupled to an ICP-MS method<sup>28</sup>, revealing that  $\text{FeO}_x\text{H}_y$  is the  
106 most active species for OER in comparison to  $\text{CoO}_x\text{H}_y$  and  $\text{NiO}_x\text{H}_y$ <sup>40</sup>. Although activity is the  
107 highest for Fe containing sites, its potential dependent dissolution rate at OER potentials is three  
108 orders of magnitude higher than that observed for Co and Ni based hydr(oxy)oxides (Fig. 1d, ca.  
109 12.1, 0.023, and 0.004  $\text{ng}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$  respectively). By comparing activity and stability at 1.7 V, the  
110 stability trend observed is  $\text{NiO}_x\text{H}_y > \text{CoO}_x\text{H}_y \gg \text{FeO}_x\text{H}_y$  which is the exactly opposite trend  
111 measured for OER activity,  $\text{NiO}_x\text{H}_y < \text{CoO}_x\text{H}_y < \text{FeO}_x\text{H}_y$  (Fig. 1e).

112 As a consequence of higher dissolution rates, Fe hydr(oxy)oxide shows a significant  
113 OER activity drop during its initial 5 cycles (poor activity retention) followed by a decrease in  
114 the amount of Fe dissolution at every consecutive cycle (supplementary Fig. 3), a direct  
115 consequence of active site depletion from the electrode surface<sup>41,42</sup>. Similar results are obtained  
116 from chronoamperometry measurements at constant voltage (1.7 V, 1 hr), indicating that severe  
117 dissolution of Fe undermines its use as OER catalyst, while NiO<sub>x</sub>H<sub>y</sub> shows the highest stability  
118 without any appreciable activity loss (supplementary Fig. 3). These results serve as the basis for  
119 the activity-stability relationships on M hydr(oxy)oxides, best summarized by the ASF values  
120 calculated at 1.7 V (Fig. 1f). As a rule of thumb, the ASF evaluate the extent by which a material  
121 produces O<sub>2</sub> molecules (specific for OER) for a given amount of dissolution of the active site.  
122 Therefore, the higher the ASF of a material, more O<sub>2</sub> is produced per dissolved active site. The  
123 conclusion after evaluation of ASF values of FeO<sub>x</sub>H<sub>y</sub>, CoO<sub>x</sub>H<sub>y</sub> and NiO<sub>x</sub>H<sub>y</sub> sites is that Ni based  
124 hydr(oxy)oxides is the most promising durable catalyst for O<sub>2</sub> production in this series, as the  
125 elevated ASF reflects its extremely high stability despite its poor OER activity. Further  
126 evaluation of Faradaic efficiency for the O<sub>2</sub> production (FE<sub>oxygen</sub>) on MO<sub>x</sub>H<sub>y</sub> was performed by  
127 using rotating ring disk electrode method, supplementary Fig. 4). The high FE<sub>oxygen</sub> values for Ni  
128 and Co hydr(oxy)oxide (over 99 %) indicates that most of current is originated from O<sub>2</sub>  
129 evolution and not side pathways such as H<sub>2</sub>O<sub>2</sub> production or from corrosion currents. On the  
130 other hand, the measured Faradaic efficiency of FeO<sub>x</sub>H<sub>y</sub> shows poor stability (~88 %), which is  
131 well within its ASF values, and no formation of H<sub>2</sub>O<sub>2</sub> (supplementary Fig. 5).

### 133 **Activity and stability trends for Fe incorporated Fe-MO<sub>x</sub>H<sub>y</sub>**

134 As Fe incorporated Ni and Co based hydr(oxy)oxide systems have been shown to display  
135 significant activity in alkaline media<sup>13,37</sup>, we added Fe into purified electrolyte forming Fe-  
136 MO<sub>x</sub>H<sub>y</sub> (Fe-Ni and Fe-Co) and compared their activity-stability trends. Scanning tunneling  
137 microscopy (STM) reveals that the cluster height increases slightly with respect to monometallic  
138 systems (supplementary Fig. 6), suggesting that Fe is selectively adsorbed over Ni and Co  
139 hydr(oxy)oxide substrates. Further quantification of Fe incorporation reveals a Fe content  
140 spanning from 15% to 28% by weight in the Co and Ni containing MO<sub>x</sub>H<sub>y</sub> clusters, respectively  
141 (supplementary Fig. 6).

142 The OER activity trend for Fe-MO<sub>x</sub>H<sub>y</sub> sites (Fig. 2a and supplementary Fig. 7) reverses  
143 when compared to the results for monometallic systems (Fig. 1), appearing in the order Fe-  
144 NiO<sub>x</sub>H<sub>y</sub> > Fe-CoO<sub>x</sub>H<sub>y</sub> > FeO<sub>x</sub>H<sub>y</sub>. At 1.7 V, the current density on bimetallic Fe-NiO<sub>x</sub>H<sub>y</sub> is 9  
145 times higher than that observed from pure NiO<sub>x</sub>H<sub>y</sub>, and it is enhanced about 3 times on Fe-  
146 CoO<sub>x</sub>H<sub>y</sub> clusters in comparison to pure CoO<sub>x</sub>H<sub>y</sub>, highlighting that a small amount of Fe in the  
147 material can significantly enhance its OER activity and current enhancement is originated from  
148 actual O<sub>2</sub> evolution (supplementary Fig. 8). In addition, this Fe effect is observed regardless of  
149 support (Pt(111), glassy carbon, nickel or cobalt metal surfaces), indicating that MO<sub>x</sub>H<sub>y</sub>  
150 oxyhydroxide-Fe interaction is key for OER promotion (supplementary Fig. 9).

151 Together with trends in catalytic activity, it is important to establish the stability trends  
152 for bimetallic hydr(oxy)oxides so that ultimately we can determine their technological relevance  
153 based on ASF values. Surprisingly, the trend in stability as measured by activity retention for the  
154 Fe incorporated MO<sub>x</sub>H<sub>y</sub> clusters is highly dependent on the presence of trace levels of Fe in the  
155 electrolyte (Fe<sub>(aq)</sub> = 0.1 ppm). In clean KOH solutions, the activities of Fe-NiO<sub>x</sub>H<sub>y</sub> and Fe-  
156 CoO<sub>x</sub>H<sub>y</sub> samples show a remarkable deactivation after just 1 hour of potential hold at 1.7 V (Fig.  
157 2a), bringing the initial high activities down to almost the same levels as monometallic  
158 hydr(oxy)oxides (supplementary Fig. 10). However, the intentional addition of Fe<sub>(aq)</sub> in the  
159 electrolyte effectively prevents the activity loss under the same testing conditions (Fig. 2b).

160 On one hand, *in situ* measurement of dissolution rates on Fe-NiO<sub>x</sub>H<sub>y</sub> during potential  
161 cycling (supplementary Fig. 11) shows that the total amount of Ni dissolution is still negligible.  
162 However, Fe still leaches out from NiO<sub>x</sub>H<sub>y</sub> almost two orders of magnitude faster than Ni itself,  
163 even though is not as fast as observed from pure monometallic hydr(oxy)oxide systems (Fig. 1).  
164 The same trend is observed in Fe-CoO<sub>x</sub>H<sub>y</sub> (supplementary Fig. 11), suggesting that the lack of  
165 stability (poor activity retention) in the Fe-MO<sub>x</sub>H<sub>y</sub> systems when Fe<sub>(aq)</sub> is not present in the  
166 electrolyte is related to the dissolution of Fe active sites, notably due the depletion of the initial  
167 Fe content from the electrode surface. On the other hand, evaluation of Fe dissolution when the  
168 electrolyte contains Fe<sub>(aq)</sub> reveals the same dissolution process as shown in supplementary Fig.  
169 11, although OER activity levels remained elevated and unchanged throughout the experiment.

170 From the activity and stability results of M and Fe-M hydr(oxy)oxide, there are three  
171 important features to emphasize. First, during OER, Fe active sites are very unstable, regardless  
172 if they are present as Fe or as Fe-M hydr(oxy)oxides. Second, despite the high initial activity, the

173 subsequent activity decay observed on Fe-incorporated  $\text{MO}_x\text{H}_y$  systems is related to Fe depletion  
174 through dissolution. Third, preserving the high activity levels can be achieved only when the  
175 electrolyte contains  $\text{Fe}_{(\text{aq})}$  even though Fe dissolution from the surface will still occur  
176 (supplementary Fig. 12). While these results indicate that the material itself is not absolutely  
177 stable, but OER activity can be sustained over time, it implies that a significant Fe dynamic  
178 exchange is continuously taking place at the interface.

179 In order to confirm this dynamic Fe exchange at the interface we measured the total amount  
180 of  $^{56}\text{Fe}$  and  $^{57}\text{Fe}$  in the electrode using ICP-MS at different stages of chronoamperometry  
181 experiments (see details in experimental section), providing information about the kinetics of  
182 dissolution as well as the kinetics of  $\text{Fe}_{(\text{aq})}$  redeposition. Therefore, by starting with  $^{56}\text{Fe}$  in the  
183 electrode and  $^{57}\text{Fe}$  in the electrolyte, any loss of  $^{56}\text{Fe}$  and gain of  $^{57}\text{Fe}$  can be traced back to  
184 dissolution and deposition events occurring during OER, respectively. As a control experiment,  
185 Figure 2c shows potential hold experiments where a continuous decrease of Fe in the electrode  
186 during polarization is observed, followed by OER deactivation (Fig. 2e). This is in line with  
187 results in Fig. 2a, emphasizing that Fe dissolution decreases the number of active sites on the  
188 electrode surface. However, when 0.1 ppm of  $^{57}\text{Fe}$  is in the electrolyte ( $^{57}\text{Fe}_{(\text{aq})}$ ), dissolution of  
189  $^{56}\text{Fe}$  occurred at the same rates as in Fig. 2c (ca.  $0.53 \text{ ng}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ ), but the amount of  $^{57}\text{Fe}$  at the  
190 electrode increased in similar rate as  $^{56}\text{Fe}$  loss (ca.  $0.56 \text{ ng}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ , Fig. 2d). This results in an  
191 overall Fe content,  $^{56}\text{Fe} + ^{57}\text{Fe}$ , constant throughout the duration of the experiment. Note that half  
192 of the  $^{56}\text{Fe}$  in the electrode is already exchanged to  $^{57}\text{Fe}$  in less than one minute and the ratio  
193  $^{57}\text{Fe}/\text{Fe}$  reaches 70% after one hour, confirming that a vigorous Fe dissolution and redeposition  
194 happens at the interface during OER. Interestingly, as consequence of dynamic exchange, the  
195 overall Fe content at the electrode was kept constant, preserving the total number of active sites  
196 for OER, and thus eliminating any catalytic deactivation (Fig. 2f). This further supports the fact  
197 that Fe is intimately part of the active site for OER in alkaline media when combined with Ni or  
198 Co hydr(oxy)oxides.

199 The effect of Fe promoting OER activities on Ni and Co hydr(oxy)oxides has been reported  
200 before, but the origin of such activity enhancement remains elusive. Many reports identify Ni,  
201 promoted by Fe, as active sites<sup>43,44</sup> while others indicate that Fe could be the source of OER  
202 enhancement<sup>45,46</sup>, with relevant considerations on the role of plane or edge sites and  
203 substitutional doping<sup>47-50</sup>. Given the trends observed from  $\text{MO}_x\text{H}_y$  (Figure 1), it is clear that pure



204 Ni cannot be the active site, but strongly suggesting the role of Fe as the active sites. This  
205 assertion is further supported by *in situ* XANES analysis (supplementary Fig. 13), and  
206 considerations from other electrocatalytic reactions, such as HER (supplementary Fig. 14),  
207 preclude the effective role of Ni or Co (electronically modified by Fe) as active sites for the  
208 OER<sup>51</sup>. However, it is clear that Fe species at the interface together with Ni and Co oxide hosts  
209 are critical for achieving high levels of O<sub>2</sub> production.

### 211 **Dynamically stable Fe as active site for oxygen evolution**

212 By controlling the Fe<sub>(aq)</sub> concentration in electrolyte, increasing the Fe<sub>(aq)</sub> content above  
213 0.1ppm does not lead to any further increase in OER activity (Fig. 3a), nor an increase in the  
214 amount of Fe incorporated into either Ni or Co hydr(oxy)oxides (Fig. 3b). In turn, these results  
215 indicate that OER activity is linked to the amount of Fe present in the MO<sub>x</sub>H<sub>y</sub> and there is a Fe  
216 saturation coverage for each surface. The linear relationship between OER and Fe coverage  
217 reveals that the factors contributing to OER promotion on Fe-NiO<sub>x</sub>H<sub>y</sub> and Fe-CoO<sub>x</sub>H<sub>y</sub> are not  
218 unique to each bimetallic system (Fig. 3c), but rather, are part of a general description of the  
219 active sites through the number of dynamic stable sites (Fe).

220 DFT calculations reveal that the  $\Delta\bar{G}_{Fe-M}$  values (Fe average adsorption free energy on  
221 MO<sub>x</sub>H<sub>y</sub> sites) are strongly dependent on the substrate nature (supplementary Fig. 15). In simple  
222 terms, a more negative  $\Delta\bar{G}_{Fe-M}$  value implies a higher Fe saturation coverage on MO<sub>x</sub>H<sub>y</sub>.  
223 Figure 3d summarizes Fe adsorption free energy trends over Ni, Co and Fe MO<sub>x</sub>H<sub>y</sub> substrates,  
224 revealing that Fe adsorption on FeO<sub>x</sub>H<sub>y</sub> is unfavorable and NiO<sub>x</sub>H<sub>y</sub> shows the strongest  
225 interaction with Fe<sub>(aq)</sub> (-0.69 eV at a coverage of 0.25), and consequently the highest Fe coverage  
226 in this series, providing a good match with the experimental values (supplementary Fig. 16).  
227 Furthermore, the rate of Fe dissolution depending on host (FeO<sub>x</sub>H<sub>y</sub> >> CoO<sub>x</sub>H<sub>y</sub> > NiO<sub>x</sub>H<sub>y</sub>) is also  
228 affected by the Fe adsorption energy, (Fe < Co < Ni), suggesting that strong interaction of  
229 MO<sub>x</sub>H<sub>y</sub> with Fe not only leads to the higher number of active sites but also stabilizes these  
230 active sites.

231 By taking into consideration the Fe dynamic exchange (Fig. 2) and correlation of OER  
232 activity with number of Fe (Fig. 3), we propose that O<sub>2</sub> evolution catalysis occurs on a number of  
233 dynamically stable active sites ( $N^*$ ), which is distinguished from the conventional number of  
234 active site ( $N$ ) considered at static conditions (see supplemental Note 6 for details). The average

235 number of dynamically stable active Fe sites ( $N_{Fe}^*$ ) can be estimated by equation 1, where  
 236 equation 2 shows the OER activity dependence on the number of dynamically active Fe sites.

$$N_{Fe}^* = \left( \frac{1}{1 + e^{-\frac{\Delta G_{Fe-M}}{RT}}} \right) \left( \frac{r_{dep} C_{Fe}^0}{r_{dep} C_{Fe}^0 + r_{diss}} \right) \quad (1)$$

$$i_{OER} = i^0 N_{Fe}^* \exp\left(\frac{\beta F (E - E^0)}{RT}\right) \quad (2)$$

237 where  $\Delta G_{Fe-M}$  is the adsorption energy between Fe and M hydr(oxy)oxide surface, given in  
 238 eV;  $r_{dep} \cdot C_{Fe}^0$  is the overall rate of Fe deposition and  $r_{diss}$  is the rate of Fe dissolution during OER,  
 239 given in  $\text{ng} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ ;  $i_{OER}$  is the OER current density,  $i^0$  is the exchange current density;  $\beta$  is the  
 240 symmetry factor<sup>52</sup>,  $E$  is applied potential and  $E^0$  is the equilibrium potential for OER, and  $F$ ,  $R$   
 241 and  $T$  indicate faraday constant, ideal gas constant and temperature, respectively. At a given  
 242 potential, the kinetics of oxygen evolution is determined by the number of dynamic active sites  
 243  $N_{Fe}^*$ , while equation 1 incorporates the processes of Fe redeposition and interaction with the  
 244 hydr(oxy)oxide host.

245 From the equations 1 and 2, the maintenance of high  $N_{Fe}^*$  within a host that enable stable  
 246 OER activity requires two conditions. First, the electrolyte must contain  $\text{Fe}_{(aq)}$  species to a  
 247 sufficiently high degree where the rate of redeposition can be brought to the same levels as the  
 248 rate of dissolution ( $r_{diss} \ll r_{dep} \cdot C_{Fe}^0$ , Fig. 2f). This will ensure a high enough average Fe coverage  
 249 on the electrode. Second, these dynamic Fe species must interact with the clusters at the  
 250 electrode surface where they can reside and catalyze  $\text{O}_2$  production before they dissolve away. If  
 251 the rate of dissolution is too fast or the rate of Fe deposition does not reach that of dissolution,  
 252 the overall number of dynamic Fe species will decrease, resulting in activity decay ( $r_{diss} \gg$   
 253  $r_{dep} \cdot C_{Fe}^0$ , Fig. 2e).

254 Considering that continuous elemental dissolution and redeposition occurs during OER, our  
 255 ‘dynamic stable active site (Fe)/host pair’ concept could be seen similar to a self-healing  
 256 mechanism suggested in previous works<sup>31,32</sup>. Unlike self-healing, the regeneration of the active  
 257 sites in a dynamic stable state necessarily requires a ‘specific host’ with a strong interaction with  
 258 the dynamic ‘active sites’. In this scenario, Fe species would be the active sites that can be  
 259 dynamically stable only because of their interaction with stable Ni or Co  $\text{MO}_x\text{H}_y$  clusters.  
 260 Alternatively, the simple self-healing process of Fe on  $\text{FeO}_x\text{H}_y$  (Fig. 2a and 2b) is not effective to  
 261 fully incorporate Fe on the electrode surface and unleash its OER catalytic activity. Unlike static

262 interfaces, the dynamic stable condition counterbalances the intrinsic high dissolution rate of  
263 active sites by promoting their redeposition through tailored electrode/electrolyte interactions.

264 From the OER activity point of view, there are two routes to maximize catalysis. First,  
265 increasing the absolute number of dynamic Fe active sites can be achieved by increasing surface  
266 area of the host material. Although this strategy seems trivial, it is the only pathway available if  
267 the material properties related to Fe adsorption ( $\Delta G_{Fe-M}$ ) cannot be tuned. This is shown when a  
268 steady increase in the amount of  $NiO_xH_y$  deposited on Pt(111), for instance, results in an increase  
269 of the absolute OER activity for both clean KOH as well as electrolyte containing  $Fe_{(aq)}$  at  
270 saturation levels. Despite this increase in absolute activities, the ratio between OER currents with  
271 and without  $Fe_{(aq)}$ , called activity enhancement factor ( $I_{Fe}/I$ ), remains the same for all amounts of  
272 Ni hydr(oxy)oxides (supplementary Fig. 18).

273 Second, the number of dynamic Fe species can be increased by tuning the Fe adsorption  
274 ( $\Delta G_{Fe-M}$ ) of host materials. Based on the DFT trend where  $\Delta G_{Fe-M}$  shows inverse relation with  
275  $\Delta G_{M-O}$  (supplementary Fig. 15), we screened other 3d transition metal to find promising  $MO_xH_y$   
276 host candidate better than  $NiO_xH_y$  (supplementary Fig. 19). Figure 4a shows that the elements to  
277 the left of Fe in the periodic table do not show any promotional OER activity enhancement with  
278 Fe. Because the bond (M-O) becomes stronger towards the left in the periodic table<sup>53</sup>, Fe  
279 adsorption is unfavorable. In the opposite direction (right from Fe), activity enhancement is  
280 clearly observable and becomes the highest for  $CuO_xH_y$ . Although Cu hydr(oxy)oxide showed  
281 the highest activity enhancement factor, its high dissolution rate prevents its utilization as a  
282 practical  $MO_xH_y$  host (supplementary Fig. 20).

283 Alternatively, by doping Ni hydr(oxy)oxide cluster with various other 3d TM as dopants  
284 (Mn, Co and Cu) we were able to further tune Fe adsorption energy, and consequently improve  
285 OER activity levels. Following the trend in enhancement factor on pure 3d  $MO_xH_y$ , doping  
286  $NiO_xH_y$  with Cu atoms ( $NiCuO_xH_y$ , see supplementary Fig. 21) leads to superior OER activity  
287 ( $40.5 \text{ mA cm}^{-2}$ ) in 0.1 ppm of Fe-containing KOH, which is 1.4 times higher than  $NiO_xH_y$  with  
288  $Fe_{(aq)}$  (Fig. 4b). Furthermore, the activity enhancement factor ( $I_{Fe}/I$ ) of NiCu hydr(oxy)oxide  
289 surpasses that of pure  $NiO_xH_y$ , albeit it is still lower than that of pure  $CuO_xH_y$ . The increase of Fe  
290 surface coverage revealed by ICP-MS results and supported by DFT analysis suggests that high  
291 activity of  $NiCuO_xH_y$  clusters are originated from the increase in Fe adsorption energy, an  
292 consequently higher average Fe coverage, making it the most suitable Fe host (supplementary

293 Fig. 22). This trend is further validated by the observed linear relationship between OER activity  
294 and the number of dynamic Fe species measured on the other NiMn and NiCo hydr(oxy)oxides  
295 (Fig. 4c and supplementary Fig. 23). While further promotion of OER activity can occur through  
296 a synergistic support interaction ( $\text{MO}_x\text{H}_y$ ) with Fe caused by electronic (or geometric) effects or  
297 possible new reaction mechanism/pathway<sup>45,49,50</sup>, our observations strongly support that the  
298 number of dynamic stable sites (Fe) can be regarded as a general descriptor of the active sites as  
299 described in equation 2. It is likely that the Fe-M adsorption energy which determines the  
300 saturation coverage of Fe on a given  $\text{MO}_x\text{H}_y$  can be more relevant than the M-O adsorption  
301 energy as an activity descriptor<sup>54</sup>.

302 From the stability point of view, *in situ* ICP-MS indicates that Cu in NiCu hydr(oxy)oxide  
303 becomes more stable in the OER potential window than pure  $\text{CuO}_x\text{H}_y$ , although it does start to  
304 dissolve at potentials above 2.1 V versus RHE (supplementary Fig. 24). Constant current density  
305 measurements performed at  $10 \text{ mA cm}^{-2}$ , which is considered as a benchmark for the OER  
306 stability<sup>55</sup> and high faradaic efficiency (>99 %) also indicate a superior electrochemical stability  
307 without appreciable activity loss (supplementary Fig. 24), verifying that Fe-NiCu $\text{O}_x\text{H}_y$  shows not  
308 only high material stability (decreased rates of dissolution) but also superior catalytic stability  
309 (stable chronoamperometry).

310 Finally, our observations suggest a way to maximize the ASF values for OER materials to  
311 achieve high activity and stability simultaneously (Fig. 4d). First, Fe-containing samples (red bar  
312 in Fig. 4d) show high ASF values compared to the “Fe free” samples (blue bar in Fig. 4d) due to  
313 high activity gained from hosting Fe active sites. Utilization of Ni and Cu as hydr(oxy)oxide  
314 hosts leads to better ASF values due the simultaneous improvement in the activity enhancement  
315 factor (stronger Fe adsorption), and prevention of Cu dissolution due Ni-Cu interactions. This  
316 same effect is shown on NiCo $\text{O}_x\text{H}_y$ , as it displays an elevated ASF value due to the prevention of  
317 Co dissolution by Ni $\text{O}_x\text{H}_y$ , but  $\text{CoO}_x\text{H}_y$  and NiCo $\text{O}_x\text{H}_y$  have similar OER activities  
318 (supplementary Fig. 25). As a result, active species/host pair overcomes the limitations placed on  
319 ASF by the material instability of both active sites and additional atoms present to tailor Fe-  
320  $\text{MO}_x\text{H}_y$  interactions.

## 322 Conclusions

323 In summary, we have investigated activity-stability trends for the OER on conductive M (M  
324 = Ni, Co, Fe) and Fe-M hydr(oxy)oxide clusters and found dynamically stable Fe as a result of  
325 dissolution and redeposition at the electrolyte/host interface that provides a general description  
326 for OER activity and stability. By realizing that this dynamic stability overcomes the limitations  
327 imposed by the thermodynamic instability of oxide materials at OER potentials, we propose that  
328 design of new materials should be focused on attaining a high number of dynamically stable  
329 active sites within a stable host under solid/liquid interfacial control. We have demonstrated an  
330 example of how these design rules can increase Fe utilization, by preparing Fe-NiCu  
331 hydr(oxy)oxide with higher OER activity than Cu-free material. In the future, design of new  
332 active site/host pairs may lead to discovery of new (electro)chemical interfaces that are  
333 simultaneously highly active and highly stable for OER.

## 335 **Methods**

### 336 **Chemicals**

337 High purity trace analysis grade potassium hydroxide hydrate (Trace SELECT<sup>®</sup>, Fluka) was further purified as  
338 discussed next. All transition metal used here, (Ni, Co, and Fe) nitrate hexahydrates and (Cu and Mn) nitrate  
339 hydrates (99.995% metal basis, Sigma Aldrich) were employed as is. Electrolytes were prepared with Milli-Q  
340 Millipore deionized (DI) water. All gases (argon, oxygen, hydrogen) were of 6N quality (Airgas).

### 342 **Electrolyte purification and confirmation of electrolyte purity**

343 Electrolyte (KOH) purification to control the cation concentration was conducted by prolonged electrolysis (5 days)  
344 using Ni wire (3.925 cm<sup>2</sup>, Puratronic<sup>®</sup>, 99.999%, Alfa Aesar) as both working and counter electrode motivated by  
345 previous reports<sup>13,37</sup>. Electrolysis purification was conducted inside a plastic cell made out of fluoropolymer material  
346 to avoid contamination from glass components. We confirm the purity of electrolyte by electrochemical method  
347 using Pt (111) CV. Based on previous paper<sup>38</sup>, small amounts of cation (Ni, Co and Fe) in alkaline electrolyte affect  
348 the CV shape of Pt (111) significantly. Inspired by high sensitivity and clear observation of cation effect for  
349 electrochemical performances, we compared CV of Pt (111) after 10 potential cycles from 0.05 to 0.9 V with the  
350 initial CV of Pt (111) obtained by our purified electrolyte (Detail information is in supplementary figure 2 and  
351 supplementary Note 1). To maximize the mass transport of any possible impurities in electrolyte, CV was measured  
352 under the rotating electrode with 1600 rpm. In purified KOH by our method, there is no change before and after CV  
353 cycles, indicating that our method can efficiently remove any trace level of impurity that can affect electrochemical  
354 performance.

### 356 **Extended surface electrode preparation and metal hydroxide deposition**

357 Pt(111) single crystal electrode (6 mm diameter) was prepared by inductive heating for 7 min at ~1100 °C in an  
358 argon hydrogen flow (3% hydrogen). The annealed crystal was cooled slowly to room temperature under an inert  
359 atmosphere and immediately covered with a droplet of DI water. To screen the candidate for host materials, 6 mm  
360 diameter metal electrode was used. Before experiment, the electrode was prepared mirror polishing with alumina  
361 powder and immersed in KOH to reach saturate condition. Electrodes were then assembled into a rotating disk  
362 electrode (RDE). Polarization curves were recorded in argon-saturated electrolyte. By potential cycling between  
363  $H_{\text{upd}}$  and  $OH_{\text{ad}}$  region with 1-100 ppm of transition metal nitrate, metal hydr(oxy)oxide layers were deposited on  
364 Pt(111). The surface coverage of  $MO_xH_y$  layer was controlled by the number of potential cycles and concentration of  
365 cation. The mass loading of hydr(oxy)oxide was confirmed by ICP-MS and repetitive analysis at least three times  
366 for each element was conducted. Fe-M hydroxide samples were prepared by spike experiment of 0.1 ppm of Fe  
367 nitrate hexahydrate ( $^{56}\text{Fe}/^{57}\text{Fe}$  ratio is 92/2 and denoted as  $^{56}\text{Fe}$  in manuscript) in electrolyte. Surface coverage of Fe  
368 on Fe-M hydr(oxy)oxide was calculated by the mass ratio between Fe and M (Ni Co, Cu and Mn) based on STM  
369 results. The mass ratio (%) of dopant (M) in NiM samples is as follows (Cu: 25.8, Co:26.2 and Mn: 24.8).

### 370 371 **Electrochemical measurement**

372 Electrochemical measurements were controlled using an Autolab PGSTAT 302N potentiostat. A typical three-  
373 electrode configuration with fluoropolymer based cell was used to avoid contamination from glass components in  
374 alkaline media. To avoid any contamination from previous experiment conditions, the cell was thoroughly rinsed by  
375 DI water and boiled in DI water before every experiment. Glassy carbon rod and Ag/AgCl were used as counter and  
376 reference electrode, respectively. To avoid any contamination from glassy carbon counter electrode by previous  
377 experimental condition, glassy carbon was thoroughly washed by 1 M HCl and boiled in DI water before every  
378 experiment. OER measurements were carried out cycling the electrode up to 1.7 V versus RHE. The  $iR$  drop  
379 compensation was conducted during measurement. The current density in our paper was normalized by the  
380 geometric area of Pt(111) substrate ( $0.283 \text{ cm}^2$ ). Potential hold experiments were also carried out for the  
381 hydroxide/Pt(111) systems to study the stability at 1.7 V versus RHE. Constant current measurement of Fe-NiCu  
382 hydr(oxy)oxide was conducted in 0.1 ppm of Fe containing KOH at  $10 \text{ mA cm}^{-2}$ . All electrochemical measurements  
383 were conducted in 'Fe free' electrolyte purified by our protocol except as indicated certain condition in manuscript.  
384 For isotope labeling experiment, 0.1 ppm of Fe in KOH was prepared by  $^{57}\text{Fe}$  precursor from Alfa Aesar ( $^{56}\text{Fe}/^{57}\text{Fe}$   
385 ratio is 3/95.5 and denoted as  $^{57}\text{Fe}$  in manuscript). Because the background value is too high to observe Fe dynamics  
386 if 0.1 ppm of Fe is present in electrolyte, we conduct Fe isotope analysis in Fe-M hydr(oxy)oxide preparing  
387 electrode with  $^{56}\text{Fe}$  and conducting electrochemical analysis in  $^{57}\text{Fe}$  containing KOH electrolyte. For quantifying the  
388 amount of Fe ( $^{56}\text{Fe}$  and  $^{57}\text{Fe}$ ) in electrode during chronoamperometry, the electrode (Fe-M hydr(oxy)oxide) was  
389 thoroughly dissolved in 0.1 M  $\text{HNO}_3$  and measured ICP-MS. All electrochemical measurement was done at least  
390 three times and average values are presented with standard error bar.

### 391 392 **STM and AFM measurement**

393 For cluster shape and height information analysis, the STM images were acquired with a Digital Instruments Multi-  
394 Mode Dimension STM controlled by a Nanoscope III control station using the Pt (111), Ni hydr(oxy)oxide on  
395 Pt(111) and Fe-Ni hydr(oxy)oxide on Pt (111). During STM measurement, the microscope with the sample was  
396 enclosed in a pressurized cylinder with a CO atmosphere. AFM image was collected by soft tapping mode (Bruker  
397 dimension ICON, MA) was used to measure the topography NiCu hydr(oxy)oxide deposition on Pt(111). The AFM  
398 data were processed using the Gwyddion software package.

#### 400 **In situ XANES measurement**

401 X-ray absorption near edge structure (XANES) measurement was performed at the 12 ID-C beamline, advanced  
402 photon source (APS) in Argonne national laboratory (ANL). A custom-made in situ electrochemical X-ray cell with  
403 a 6 mm diameter of Pt (111) single crystal and Ag/AgCl reference electrode was used in grazing-incidence geometry  
404 (Digital photograph images for *in situ* set-up in Fig. S9A). The experimental geometry is similar to the previous  
405 grazing-incidence fluorescence x-ray absorption spectroscopy (GIF-XAS)<sup>56</sup>. The glazing angle of incidence was  
406 fixed at the total external reflection angle of x-ray (~0.5°) for Pt(111) substrate. In this condition, the electric field at  
407 the surface is enhanced to achieve a maximum sensitivity of the elements on the surface. A Vortex<sup>®</sup> detector (Hitach  
408 High-technologies Science America, Inc) with an active area of 1 cm and an energy resolution of ~120 eV was used.  
409 A cobalt filter for Ni K edge and a Mn filter for Fe K edge were used and the detector was positioned at 90° to the  
410 horizontally polarized incoming x-rays to suppress the elastic scattering. Then, detector distance was set to ~3 cm  
411 from the surface to optimize the signal-to-background ratio. The spectra were normalized by the incident X-ray  
412 intensity and processed by ATHENA software.

#### 414 **XPS analysis**

415 X-ray photoelectron spectroscopy (XPS) analysis was conducted using Ommicron EA-125 hemispherical energy  
416 analyzer with Al K- $\alpha$  X-ray source.

#### 418 **In situ ICP-MS by SPRDE**

419 The set-up for ICP-MS with SPRDE method is followed by previous report<sup>28</sup>. The metal ions such as Fe (56 and 57  
420 a.m.u), Co (59 a.m.u), Mn (55 a.m.u.), Cu (64 a.m.u.) and Ni (60 a.m.u) were detected with a PerkinElmer NexION  
421 350S coupled to a stationary probe rotating disk electrode setup. Electrochemical measurement was conducted the  
422 same way as described in electrochemical measurement section.

#### 424 **Activity stability factor (ASF)**

425 Activity stability factor (ASF) was calculated based on our previous paper<sup>27</sup> as follows.

$$ASF = \left. \frac{J - S}{S} \right|_{\eta}$$

428 Where  $J$  indicates rate of  $O_2$  production (equivalent to OER current density) and  $S$  indicates rate of host metal  
429 dissolution (equivalent to dissolution current density) at constant overpotential ( $\eta$ ). When dynamic stable Fe is  
430 incorporated in host materials (Fe containing in KOH), ASF (Dynamic Fe-M hydr(oxy)oxide) are simply the ASF  
431 values obtained for the corresponding values without Fe multiplied by the activity enhancement factor ( $\frac{J_{Fe}}{J}$ ).

$$\text{ASF (Dynamic Fe - M hydr(oxy)oxide)} = \text{ASF (without Fe)} \times \left(\frac{J_{Fe}}{J}\right)$$

433

#### 434 **RRDE measurement for quantifying $O_2$ production and calculation of Faradaic efficiency of $O_2$ ( $FE_{Oxygen}$ )**

435 To quantify actual production of  $O_2$  and calculate Faradaic efficiency of  $O_2$  ( $FE_{Oxygen}$ ), we conducted rotating ring  
436 disk electrode (RRDE) method using Pt ring. For calibration of collection efficiency in gas evolving reaction,  
437 hydrogen evolution reaction (HER) is used (see detail discussion in supplementary Note 2). For calculation of  
438 Faradaic efficiency of  $O_2$  ( $FE_{Oxygen}$ ), we measured 2 times in each sample with different ring potential (for  $H_2O_2$ ; 1.1  
439 V and for  $O_2$ ; 0.4 V). The production of  $O_2$  is monitored using ring potential at 0.4 V (versus RHE) (Note: we  
440 choose 0.4 V as the ORR is in diffusional control, while preventing  $H_{upd}$  region that would allow the  $2e^-$  pathway  
441 during  $O_2$  reduction). For  $H_2O_2$ , we choose 1.1 V which is high enough potential for  $H_2O_2$  oxidation (diffusion  
442 limiting region) while it is below thermodynamic potential of  $O_2$  evolution (1.23 V). Faradaic efficiency of  $O_2$   
443 production is defined as follows.

444

$$\text{Faradaic efficiency of oxygen } (FE_{Oxygen}) = \frac{\text{O}_2 \text{ evolution current (ring current)}}{\text{Total current (disk current)}} \times \text{collection efficiency}$$

445

#### 446 **Computational Methods**

447 Electronic structure calculations were done within the framework of the density functional theory (DFT) with  
448 periodic boundary conditions using the VASP program<sup>57</sup>. All surface calculations were done using the implicit  
449 solvation model, which is implemented in the package VASPsol and includes the effect of electrostatics, cavitation,  
450 and dispersion on the interaction between a solute and solvent<sup>58,59</sup>. The PBE exchange-correlation functional<sup>60</sup> and  
451 the van der Waals (vdW) interactions described via a pair-wise force field using the DFT-D2 method of Grimme<sup>61</sup>  
452 were used for all calculations. The projector augmented wave (PAW) method and plane wave basis sets were used  
453 with energy cutoffs of 520 eV for full cell geometry optimization and 400 eV for geometry optimization with fixed  
454 cell parameters. Transition metal elements are treated by the PBE+U method with  $U_{\text{eff}} = 5.5$  eV, 4.4 eV and 3.3 eV  
455 for Ni, Co and Fe, respectively<sup>62</sup>. Transition metal oxyhydroxide MOOH (M=Ni, Co, Fe) monolayers were modeled  
456 by  $2 \times 4(001)$  periodic slabs using supercells (consisting of 16 MOOH units) with a vacuum layer of more than 20 Å  
457 placed along the  $z$  direction. The surface Brillouin zone is sampled with a  $3 \times 3 \times 1$  Monkhorst-Pack k-point mesh. The  
458 total energy was converged to  $10^{-5}$  eV for each electronic step using self-consistent field method. All atoms were  
459 allowed to relax during the structure optimization until the force on each atom was below 0.03 eV/Å. Bader charge  
460 analysis was conducted to analyze charge populations<sup>63</sup>. The X-ray absorption near edge structure (XANES) spectra



461 was calculated using the *ab initio* multiple scattering code FEFF9<sup>64</sup> based on optimized geometries to help  
462 interpreting experimental results.

463 In evaluating the adsorption energy of the Fe species on a surface site (denoted by \*), we have chosen the solvated  
464 Fe(OH)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub> molecular complex as a reference, where Fe has a six-fold coordination and a formal charge state of  
465 +3. The adsorption reaction can be written as:



467  
468  
469 The differential Fe adsorption energy ( $\Delta G_{Fe-M}$ ) on a metal oxyhydroxide surface is calculated as follows:

$$\Delta G_{Fe-M} = G_{(n+1)Fe*} - G_{(n)Fe*} - G_{Fe-mol} + 3G_{H_2O-mol}$$

470  
471 where  $n$  stands for the number of Fe complexes adsorbed on the surface per supercell.  $G_{(n+1)Fe*}$ ,  $G_{(n)Fe*}$ ,  $G_{Fe-mol}$ ,  
472 and  $G_{H_2O-mol}$  represent the free energies of the surface cell with  $n+1$  adsorbed Fe species, the surface cell with  $n$   
473 adsorbed Fe species, a Fe(OH)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub> molecular complex and a H<sub>2</sub>O molecule in solution at standard conditions,  
474 respectively. The average Fe adsorption energy ( $\Delta \bar{G}_{Fe-M}$ ) on a metal oxyhydroxide surface is calculated as follows:

$$475 \quad \Delta \bar{G}_{Fe-M} = (G_{(n)Fe*} - G_*)/n - G_{Fe-mol} + 3G_{H_2O-mol}$$

476  
477 where  $G_*$  stands for the free energy of the surface cell without adsorbed Fe species.

478 The total electronic energy of each system was obtained from the electronic structure calculation in VASP. The  
479 free energy was calculated by adding a Gibbs free energy correction (including contributions from zero-point  
480 energy, enthalpy and entropy) to the total energy calculated in VASP. The Gibbs free energy corrections were  
481 calculated at 25 °C using the standard statistical mechanical model after frequency calculations in VASP. For  
482 surface systems, calculated vibrational frequencies were used for the free energy correction. For the molecular Fe  
483 complex, entropy contributions including vibrational, translational and rotational contributions are taken into  
484 account. The solvation effect was taken into account using the implicit solvent model to calculate the solvation  
485 energy in VASP. For the liquid phase molecule H<sub>2</sub>O, the free energy correction was calculated using the equivalent  
486 gas phase free energy contribution at saturated vapor pressure of 3534 Pa<sup>65</sup>. The calculated free energy corrections  
487 are listed in Supplementary Tables 2-4. The structural information about the DFT calculation is shown at the end  
488 additional supplementary data1.

489

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642

### 643 **Author contributions**

644 D.Y.C., P.P.L. and N.M.M. designed the experiments. D.Y.C., P.P.L. and P.F.B.D.M. conducted  
645 electrochemical measurement and analysis. H.H. and P.Z. performed DFT calculations and  
646 analysis. D.Y.C., T.K., H.Y., S.S. and S.L. conducted *in situ* XANES measurement and analysis.  
647 D.T. and Y.Z. carried out STM and AFM analysis. D.S. and V.R.S. discussed and commented  
648 the results. D.Y.C., P.P.L., P.Z. and N.M.M. wrote the manuscript. All authors approved the final  
649 version of the manuscript.  
650

### 651 **Competing interests**

652 The authors declare no competing interest.  
653

### 654 **Data Availability**

655 All data are available in the main text, Supplementary Information and Source Data files. Data  
656 generated from DFT calculations can be found in Supplementary Data 1.  
657

### 658 **Supplementary Materials**

659 Supplementary Figure 1-25

660 Supplementary Table 1-4

661 References (01-25)

662 Supplementary Data 1 for DFT structure information  
663  
664

665

## Figure Caption

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**Fig. 1 Activity-stability trend of 3d-M hydr(oxy)oxides.** (a) STM images (40 x 40 nm) of Pt(111) and Ni(OH)<sub>2</sub>/Pt(111). Simultaneous *in situ* evaluation of (b) OER activity and (c) monitoring of metal dissolution rates in purified 0.1 M KOH revealing that Fe hydr(oxy)oxide is the most active site for OER in alkaline environment, but also the most unstable. (d-f) Summary of the activity-stability relationships obtained at 1.7 V highlighting (d) dissolution rates and (e) the current density values for all three metal hydr(oxy)oxides, suggesting that Ni hydr(oxy)oxide is the most technological relevant material within the monometallic series due its high stability, as indicated by its Activity-Stability Factor (f). The measurement was done at least three times and average values are presented with standard error bar.

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**Fig. 2 Activity-stability trend of Fe-M hydr(oxy)oxide and observation of dynamic Fe exchange by isotope labeling experiment.** Summary of activity-stability results of Fe-M hydr(oxy)oxide during chronoamperometry experiments in (a) ‘Fe free’ purified KOH, and in (b) 0.1 ppm Fe containing KOH solution under 1hr chronoamperometry at 1.7 V, revealing the high dependence of OER activity retention with the presence of Fe in the electrolyte. (c-f) Total amount of Fe in electrode (c and d) and OER activity trend (e and f) during chronoamperometry measurements at 1.7 V shows Fe dissolution from the electrode surface accompanied by OER activity loss in ‘Fe free’ electrolyte (c and e), depicting the dissolution process in the schematic diagram (inset). Similar chronoamperometry experiment done in 0.1 ppm of <sup>57</sup>Fe containing electrolyte (d and f) reveals the Fe dynamic exchange (dissolution and redeposition) at the interface during OER catalysis, as the quick dissolution of <sup>56</sup>Fe from the electrode is followed by immediate <sup>57</sup>Fe redeposition from the electrolyte. The dynamic exchange preserves the overall Fe content at the electrode surface, which is reflected in the high OER activity that does not deactivate during the course of the experiment (inset shows schematic diagram depicting both Fe dissolution and redeposition process, with balanced rates brought about by the trace level of Fe in the electrolyte).

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**Fig. 3 Dynamically stable Fe as active site for OER.** Effect of Fe concentration in the electrolyte on (a) OER activity and (b) Fe mass retained at Fe-Ni and Fe-Co hydr(oxy)oxide clusters, revealing that Fe adsorption saturates at high Fe concentrations (above 0.1ppm). (c) Correlation between absolute OER activity values with Fe coverage on both Fe-Ni and Fe-Co hydr(oxy)oxides indicates that OER catalysis enhancement increases linearly on the average Fe coverage as a result of stronger Fe-M hydr(oxy)oxide interaction. Note that the arrow indicates maximum Fe surface coverage on Ni (red) and Co (blue) substrate, respectively. The measurement was done at least three times and average values are presented with standard error bar. (d) DFT calculations of Fe average adsorption free energies at coverage of 0.25. The adsorption free energy of Fe complex on FeOOH is set to zero because it is unfavorable. (e) Schematic diagram of “dynamically stable” active site/host pair in electrode/electrolyte interface highlighting the role of M hydr(oxy)oxide as a suitable host for Fe species to stay at the interface long enough to catalyze the conversion of OH<sup>-</sup> into O<sub>2</sub> molecules, while the presence of Fe in the electrolyte ensures that Fe species can return to the interface and redeposit at hydr(oxy)oxide sites.

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710 **Fig. 4 Interface (dynamic active species/host pair) design for highly active and durable**  
711 **system** (a) Activity enhancement trend via Fe incorporation in 3d transition metal indicates that  
712 Fe interaction shows trend with M-O bond. (b) OER activity of Ni and NiCu hydr(oxy)oxide in  
713 purified and 0.1 ppm Fe containing KOH (Inset shows potential-current plot in OER region). (c)  
714 Correlation between absolute OER activity values with number of Fe surface coverage on  
715 NiM(Cu, Co, Mn) and Ni hydr(oxy)oxides indicates that OER catalysis enhancement increases  
716 linearly on the average Fe coverage. It clearly demonstrates that ‘dynamic stable Fe’ is general  
717 descriptor for OER activity. (d) Activity-Stability Factor comparison between different Fe-M and  
718 M hydr(oxy)oxide reveals that engineering dynamic active site/host pair with high number of  
719 dynamic Fe species and stable host is key design principle. The measurement was done at least  
720 three times and average values are presented with standard error bar.









