

**Supporting Information for**  
**“Nickel-Iron Oxyhydroxide Oxygen-Evolution Electrocatalysts:**  
**The Role of Intentional and Incidental Iron Incorporation”**

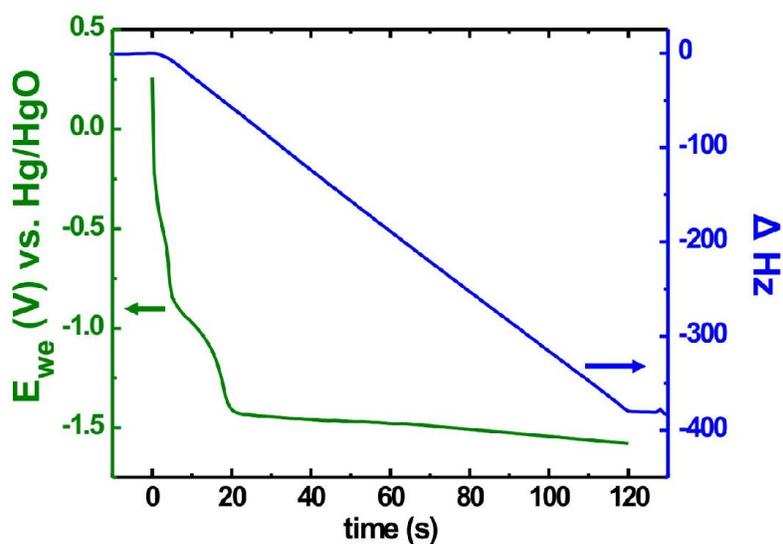
Lena Trotochaud, Samantha L. Young, James K. Ranney, and Shannon W. Boettcher

*Department of Chemistry and Biochemistry*  
*University of Oregon, Eugene, Oregon, USA 97403*

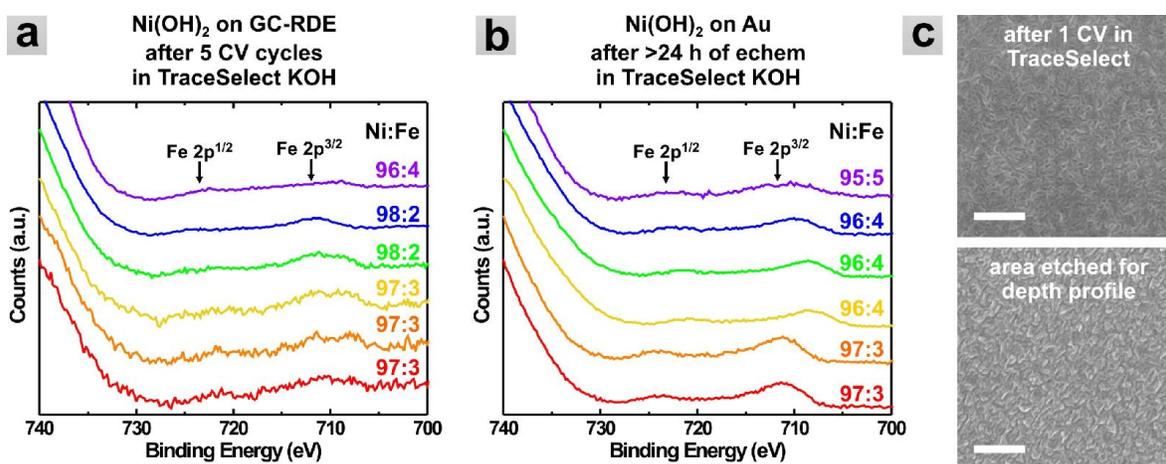
**Table S1.** Fitting Parameters for Data in Figure 5 <sup>a</sup>

| sample                                    | substrate | <i>a</i> | <i>a</i> error | <i>b</i> | <i>b</i> error | R <sup>2</sup> |
|---|-----------|----------|----------------|----------|----------------|----------------|
| NiOOH                                     | Au        | 0.152    | 0.005          | -0.562   | 0.012          | 0.999          |
|   | GC-RDE    | 0.103    | 0.004          | -0.313   | 0.018          | 0.941          |
| Ni <sub>0.75</sub> Fe <sub>0.25</sub> OOH | Au        | 1.118    | 0.059          | -0.237   | 0.034          | 0.710          |
|   | GC-RDE    | 0.064    | 0.013          | 0.172    | 0.053          | 0.411          |

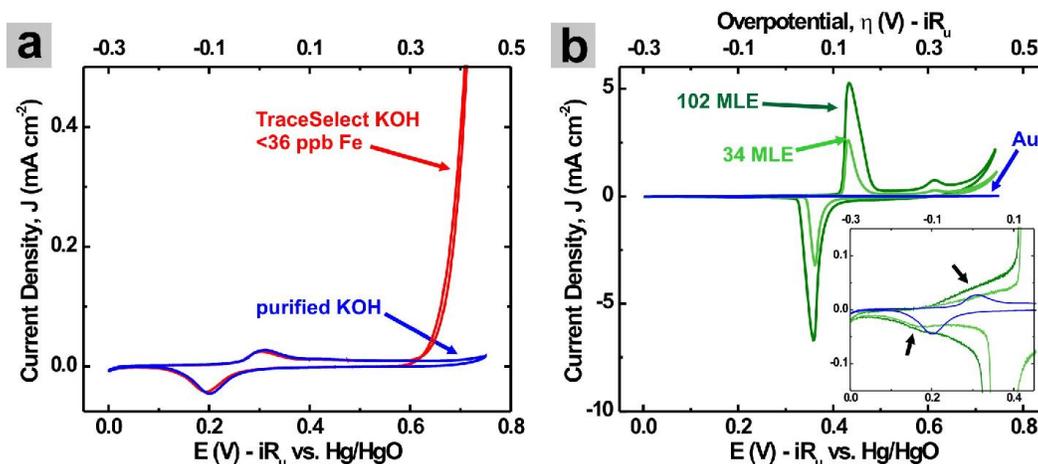
<sup>a</sup> Data were fit using Origin 8.0 to power functions with the general equation  $y = ax^b$ . The value of *b* is an indication of the degree of TOF thickness-dependence (with larger magnitude of *b* indicating greater thickness dependence).



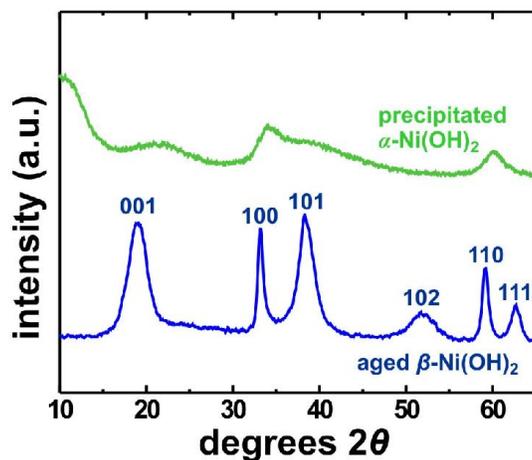
**Figure S1.** Potential vs. time deposition profile for a Ni(OH)<sub>2</sub> film deposited at 0.1 mA cm<sup>-2</sup> for 2 min and the corresponding QCM frequency change profile.



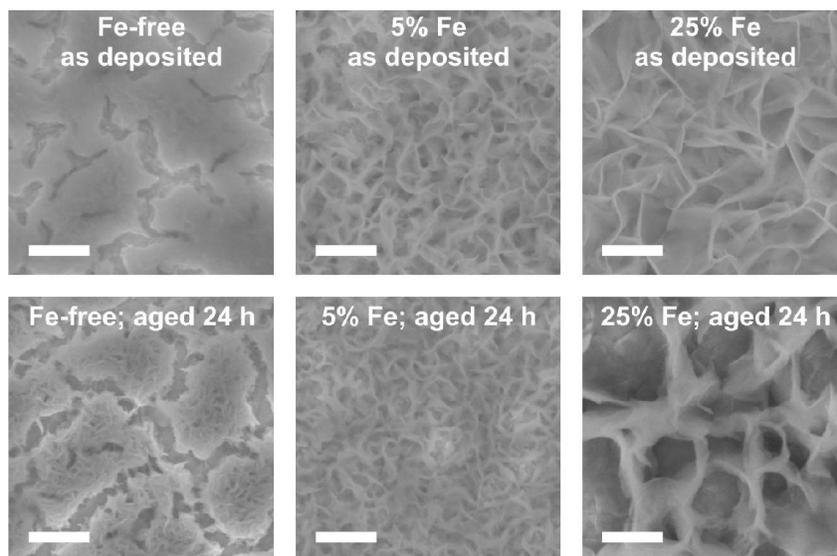
**Figure S2.** XPS depth profiles of Ni(OH)<sub>2</sub> films exposed to Fe impurities. (a) Film on GC-RDE substrate after 5 CV cycles in TraceSelect KOH. (b) Film after 1 day of electrochemical experiments in TraceSelect KOH. In each plot, the top-most spectrum is before starting the depth profile. Each subsequent spectrum is after 60 s of etching with an Ar<sup>+</sup> beam (3 kV, 2 μA) over a 4 mm × 4 mm area. (c) SEM images of a Ni(OH)<sub>2</sub> film cathodically deposited at -0.1 mA cm<sup>-2</sup> for 2 min onto Au/Ti QCM substrate before (top) and after (bottom) etching for XPS depth profile. The underlying Au substrate is apparent after Ar<sup>+</sup> etching indicating a substantial fraction of the film was etched by the ion beam. Scale bars are 200 nm.



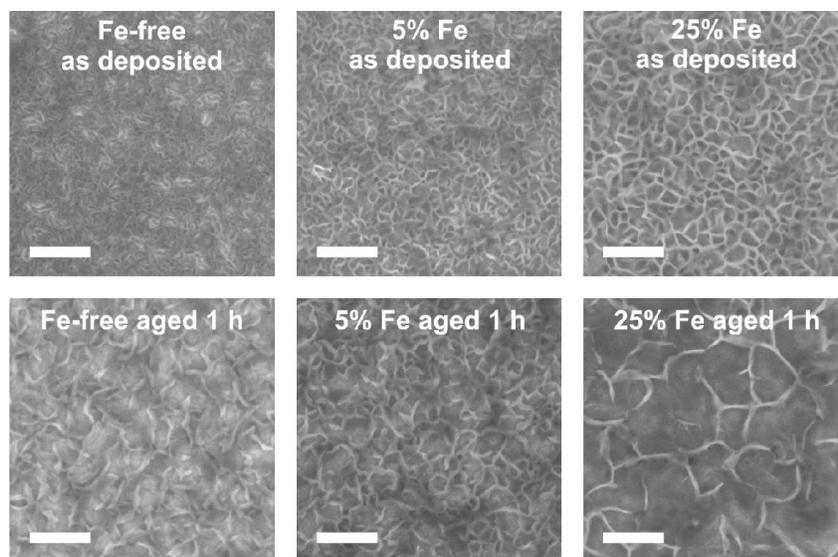
**Figure S3.** (a) Voltammograms collected using a bare Au/Ti QCM electrode (10 mV s<sup>-1</sup>). The redox waves are due to oxidation and reduction of the Au surface. The presence of Fe in the TraceSelect KOH electrolyte apparently affects the OER activity of the bare Au substrate, as indicated by the changes in OER current magnitude and onset potential. (b) Voltammograms collected for Ni(OH)<sub>2</sub> films on Au/Ti QCM electrodes (10 mV s<sup>-1</sup>). Magnification in inset shows that even for the thick films of Ni(OH)<sub>2</sub> deposited (here, 102 and 34 monolayer-equivalents, or ~82 and ~27 nm), the Au redox wave (indicated by arrows) is present just before the Ni oxidation and reduction waves, respectively. This is consistent with the electrolyte permeability of the hydroxide/oxyhydroxides.



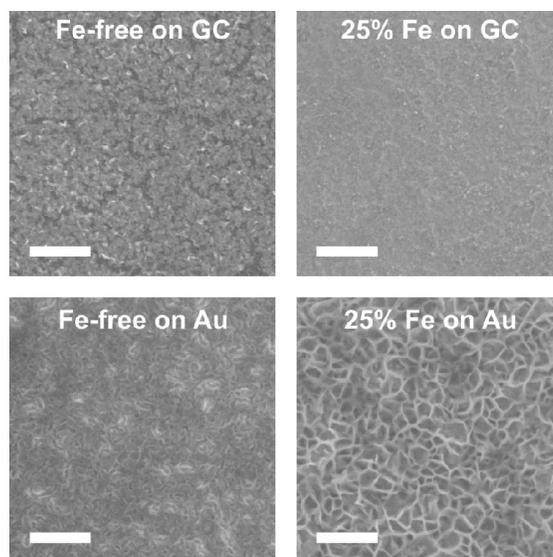
**Figure S4.** X-ray powder diffraction patterns for freshly precipitated  $\alpha$ -Ni(OH)<sub>2</sub> and aged  $\beta$ -Ni(OH)<sub>2</sub>. The powders were synthesized by precipitation of a solution of Ni(NO<sub>3</sub>)<sub>2</sub> in 18.2 MΩ cm H<sub>2</sub>O with 1 M TraceSelect KOH. The precipitates were washed 3× with ~0.1 M TraceSelect KOH solution and dried in air. Dry powders were ground and mounted onto glass slides using silicone-based vacuum grease.



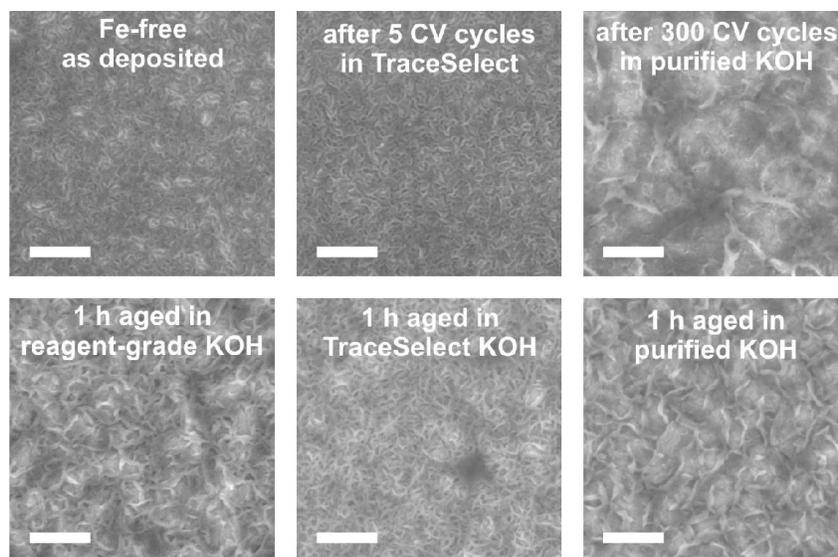
**Figure S5.** SEM images of films used for XRD experiments shown in Figure 2b. Films were cathodically deposited onto Au/Ti QCM substrates at  $-0.1 \text{ mA cm}^{-2}$  for 10 min. Films were aged in 40° C purified 1 M KOH for 24 h. Scale bars are 200 nm. (Fe-free and 25% Fe images also shown in Figure 2a.)



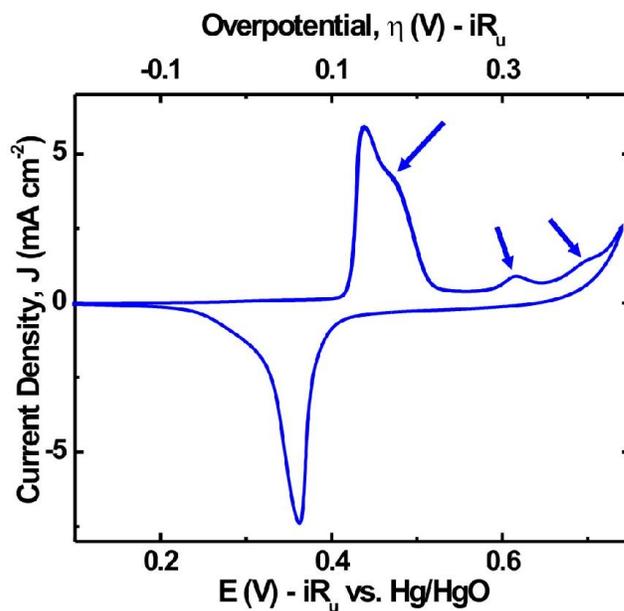
**Figure S6.** SEM images of films used for ageing experiments shown in Figure 3. Films were cathodically deposited on Au/Ti QCM substrates at  $-0.1 \text{ mA cm}^{-2}$  for 2 min. Samples were aged for 12 periods of 5 min (total ageing time of 1 h) in  $40^\circ \text{ C}$  purified 1 M KOH. Scale bars are 200 nm. (Fe-free images also shown in Figure S8.)



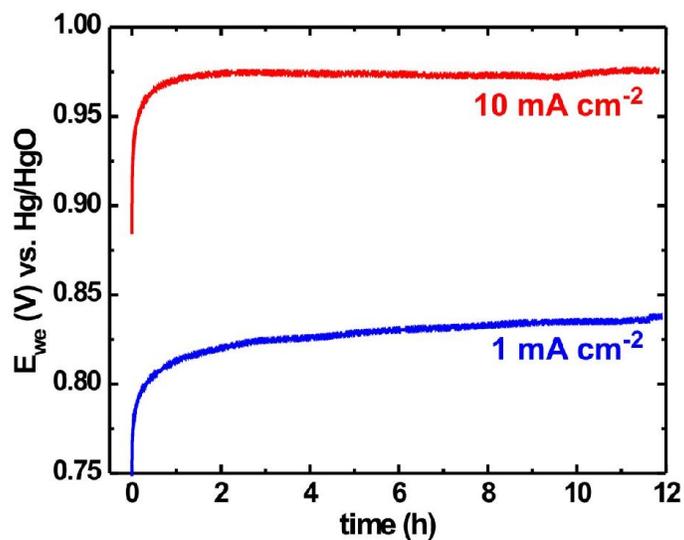
**Figure S7.** SEM images comparing film morphology on GC-RDE (top) and Au/Ti QCM (bottom) substrates. Films were cathodically deposited at  $-0.1 \text{ mA cm}^{-2}$  for 2 min. Scale bars are 200 nm. (Fe-free on Au also shown in Figure S6 and S8.)



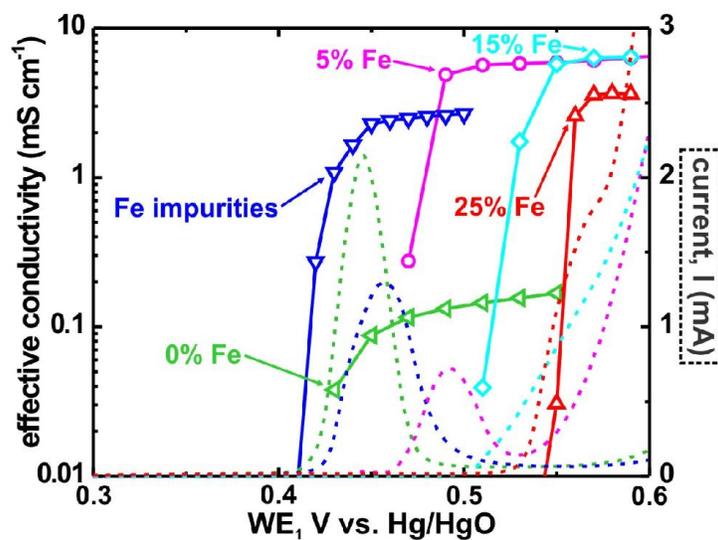
**Figure S8.** SEM images showing effects of ageing and electrochemical cycling on  $\text{Ni}(\text{OH})_2$  film morphology. Films were deposited on Au/Ti QCM substrates at  $-0.1 \text{ mA cm}^{-2}$  for 2 min. Images at top right and top left are from samples described in Figure 1a. Images on bottom from left to right are from samples whose electrochemical data are shown in Figures 3b, 3a, and 3d. Scale bars are 200 nm.



**Figure S9.** Voltammogram collected for a Fe-free  $\text{Ni}(\text{OH})_2$  film after ageing in 1 M KOH at  $40^\circ\text{C}$  for 24 h ( $10 \text{ mV s}^{-1}$ ), drying in air, performing GIXRD and XPS analysis, and then re-immersion in 1 M KOH. The waves discussed in the main text at 0.47, 0.6, and 0.7 V vs. Hg/HgO are clearly visible (indicated here by arrows).



**Figure S10.** Chronopotentiometry results for a Fe-free NiOOH film held at constant current densities of  $1 \text{ mA cm}^{-2}$  (blue curve, lower) and  $10 \text{ mA cm}^{-2}$  (red curve, upper) for  $\sim 12 \text{ h}$ . No increase in activity is observed after prolonged anodization in the purified Fe-free electrolyte.



**Figure S11.** Effective conductivity data from Figure 4d in the text shown with the y-axis on a logarithmic scale.