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Reverse Polarization Degradation of Nickel Iron Oxyhydroxide Anodes in Alkaline Water Electrolysis

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Summary

We report the effect of reverse polarization on thin-film Ni(Fe)OOH anodes in conditions that mirror those seen in commercial alkaline water electrolyzer stacks. Regardless of the extent of the reverse polarization potential, the anodic charge capacity decreases over successive cycles, indicating loss of active $\text{Ni}^{2+}/\text{Ni}^{3+}$ sites. Electrodes held for a longer period in the reduced state exhibited an accelerated catalyst loss through dissolution and structural reorganization during reverse polarization. In-situ Raman spectroscopy and X-ray photoelectron spectroscopy revealed a significant decrease in the Fe:Ni surface ratio after reverse polarization, which correlates with a measurable decline in activity towards the oxygen evolution reaction. These findings illustrate how nickel iron oxyhydroxide anodes degrade during reverse-polarization conditions and how managing the dissolved ions in the recirculating KOH improves anode lifetimes.

Keywords: electrolysis, reverse current, electrocatalysis, iron effects, electrolyte engineering

Introduction

Alkaline water electrolysis (AWE) is the most widely deployed and economical technology for water electrolysis to produce hydrogen.¹⁻³ Advanced alkaline water electrolysis (AAWE) uses a zero-gap electrode-diaphragm assembly where each cell is connected through bipolar plates.^{4,5} The use of bipolar plates and high-surface-area catalyst layers introduces design challenges associated with reverse currents, which are most problematic during interruption of power.^{6,7} Positively polarized metal oxides and negatively polarized metal hydrides generate an electromotive force which can self-discharge through manifolds required to recirculate a conductive KOH electrolyte.^{8,9} In this way, the electrolyzer acts as a galvanic cell following shutdown resulting in redox reactions at both the anode and cathode catalyst layers. During repeated oxidation-reduction cycles, both anode and cathode catalysts often experience accelerated performance decay, which could be associated with mechanical stress caused by structural transformations, enhanced dissolution, and/or passivation.¹⁰ The final resting voltage during reverse polarization is determined by the relative charge capacities of the anode and cathode. The electrode with the lowest charge capacity discharges faster, resulting in a greater change in potential relative to its operational state.⁹ The magnitude of reverse current in a practical electrolyzer depends on the stack geometry, cell position, electrode capacity, and manifold resistance, with normalized current densities in prior studies ranging from -0.25 to -10 mA cm^{-2} ; accelerated stress tests have typically applied reverse currents approximately $\sim 0.2\%$ of the operating current.^{6,11} The use of thick, porous catalyst layers where the electrochemical potential varies across the population of catalyst sites can delay the impact of reverse currents, but complicates studies on the degradation mechanism. Hence, studying the dynamic behavior of thin-film Ni-based catalyst layers in industrially relevant

conditions may clarify how the electrolyte environment can be modified to produce reverse-current-tolerant electrodes.^{9,12}

Ni(OH)₂ and Ni_{1-y}Co_y(OH)₂ films cycled in unpurified 0.1 M KOH at 20 °C under a simulated reverse current of -5 mA cm⁻² were previously found to degrade faster than films held under a steady state current.⁶ *In-situ* surface-enhanced Raman spectroscopy of these films indicated that the oxyhydroxide phase underwent structural collapse during deep discharge events and that conversion was not fully reversed after re-oxidation.⁶ Reduced Ni_(1-y)Co_y(OH)₂ films exhibited lower electronic conductivity and faster metal ion dissolution compared to the active oxygen evolution reaction (OER) catalyst.^{6,11,13} Similarly, Ni-alloy (Ni-201) anodes exposed to repeated oxidation and shutdown events showed a significant mass loss that scaled with the number and the duration of the shutdown cycle.¹¹ Ni-Fe alloy electrodes studied in 1.0 M KOH at room temperature showed that potential cycling to reduced conditions led to surface restructuring and enhanced OER activity.¹⁴ The kinetics of NiOOH self-discharge in 1.0 M KOH were recently characterized by *in-situ* Raman and UV-Vis spectroscopy, revealing that the number density of Ni³⁺ sites decays linearly with time after the polarization is removed and is governed by multiple factors, including structural re-organization and hydroxide transport.¹⁵ However, the dynamics of Ni and Fe loss during reverse currents has rarely been studied in concentrated (>1.0 M KOH with rigorous control of the concentration of dissolved transition metals).

Here we systematically investigated the factors controlling the rate of anode catalyst degradation at model thin Ni_xFe_(1-x)OOH films in industrially relevant electrolyte conditions (30% w/w KOH, 80 °C) to understand the fundamental effects of AAWE shutdown on common Ni-Fe catalyst materials. To prepare the model electrodes, Ni_xFe_(1-x)OOH was coated on an oxidatively stable and OER-inactive platinum foil substrate (**Figure S1**). This allowed us to isolate the intrinsic

(in)stability of both Ni and Fe in the oxyhydroxide as a function of the electrochemical potential. The loss of active material was quantified across cycle number, residence time in the reduced state, and discharge rate, and supported a model for reverse-current degradation in the absence of mechanical effects experienced at typically studied thick catalyst layers. The data also support a framework to mitigate the performance decay of Ni-based catalysts in AAWE systems powered by intermittent energy resources and may lead to the design of stable catalyst coatings that do not compromise the energy efficiency of hydrogen production.

Results

A detailed description of the charge-discharge analysis protocol we used can be found in the methods section. After holding the potential at $J = 1 \text{ A cm}^{-2}$ for 2.0 min, characteristic discharge curves obtained for $\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$ electrodes exhibited an extended potential plateau at $\sim 1.2 \text{ V}$ vs RHE, assigned to the reduction of Ni^{3+} to Ni^{2+} , followed by a sloped region at $E < 1.0 \text{ V}$ assigned to Pt/PtO_x redox (**Figure 1a**). Films discharged at -0.1 mA cm^{-2} showed a small-capacity plateau at $E > 1.2 \text{ V}$ vs. RHE, positive of the oxygen reduction potential, which could be associated with higher valence states within the $\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$ film.¹⁵ The time spent at the $\text{Ni}^{2+/3+}$ plateau was inversely proportional to the applied current, consistent with a nearly complete reduction of available Ni^{3+} sites independent of J_- . The two values of E_- investigated in this work occurred at a more negative E than the $\text{Ni}^{2+/3+}$ plateau, such that the catalyst layer was fully discharged. This is representative of a system where E_- is controlled by the redox properties of the cathode catalyst layer (i.e. where during reverse polarization discharge the cathode has more capacity than the anode causing the anode potential to fully discharge).

A focused-ion beam SEM (FIB- SEM) cross section of the $\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$ film supported on Pt showed that the films were uniform in coverage and $< 100 \text{ nm}$ in thickness (**Figure 1b**). This

thin-film catalyst layer was designed to avoid convoluting effects from changes in the electrical conductivity during the reoxidation of the $\text{Ni}_x\text{Fe}_{(1-x)}(\text{OH})_2$ during subsequent charging cycles. *Ex-situ* Raman spectra were collected after potentiostatic holds at $E = 1.600$ V (charge) and 0.700 V (discharge) for 1.0 min in Fe-spiked KOH (6 ppm) at 80°C . A single pair of peaks corresponding to Ni-O stretching (A_{1g}) and Ni-O bending modes (E_g) were observed for the oxidized film, assigned to the $\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$ phase (**Figure 1c**). The discharged film yielded a broad peak at a position characteristic of $\text{Ni}(\text{OH})_2$, indicating a complete conversion of the Ni-O coordination environment and a film that lacked long-range order.^{16,17}

The transition of NiOOH to $\text{Ni}(\text{OH})_2$ involves multiple polymorphs whose stability depends on the applied potential and time spent in KOH.¹⁸ The electrochemical oxidation of nickel hydroxides to nickel oxyhydroxides (nominally β and γ phases) and the subsequent reduction to the hydroxides involves two phases, α and β .^{19,20} To investigate the reversibility of the nickel-iron hydroxide phase formed during discharging, two different discharge potentials were compared, corresponding to the stability window of the α (0.3 V) and β (0.7 V) phases.¹⁹ The surface density of electrochemically active Ni sites was calculated during each charge-discharge cycle from the integrated charge density, Q , passed over a potential window of 1.100 to 1.300 V vs RHE.²¹ This potential window corresponds to the Ni^{3+} to Ni^{2+} transition and is useful for monitoring Ni-redox coverage and redox reversibility; it should not be interpreted as a direct measure of the OER active sites.²¹ In this way, the coverage of the $\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$ was monitored as a function of cycle number, time, and E_- . Cycling at $E_- = 0.700$ V and $E_- = 0.300$ V led to an initial steep decrease in Q followed by a gradual stabilization at ~ 1 mC cm^{-2} (**Figure 2a**). In the first 20 cycles, $>60\%$ of the total electrochemically accessible Ni sites were lost, whereas an additional 8% of the total sites were lost across the next 80 cycles. Initial results suggested that the loss of Ni sites was correlated

to the magnitude of the applied reverse current, with the slope of the decay profile increasing from $10 \mu\text{C cm}^{-2}/\text{cycle}$ to $105 \mu\text{C cm}^{-2}/\text{cycle}$ following a two order of magnitude increase in J_- (**Figure 2b**). However, when the first 100 cycles were normalized to the total time the electrode spent in the reduced state, $t_{\text{Ni}^{2+}}$, the decay profiles collapsed into a single curve (**Figure 2c**). The electrode with the highest discharge rate ($J_- = -1.0 \text{ mA cm}^{-2}$) spent four times less time in the reduced state as compared to the electrode discharged at $J_- = -0.10 \text{ mA cm}^{-2}$.

For $\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$ electrodes, the dissolved Fe concentration, $[\text{Fe}]$, in the electrolyte is a crucial factor determining the OER activity during a steady-state operation.²² $[\text{Fe}]$ exhibited a similarly impactful association with the retention of electrochemically active Ni sites over 100 charge-discharge cycles (**Figure 3a**). Although all films lost Ni sites during the initial 10 cycles, Fe-containing electrolytes retained a substantially greater fraction of electrochemically accessible Ni. At $[\text{Fe}] = 0 \text{ ppm}$, over 70% of the total active Ni sites were lost in the first 20 cycles, whereas $> 85\%$ sites were retained when $[\text{Fe}] = 24 \text{ ppm}$. Both galvanostatic discharge and CV integration techniques showed a comparable initial Ni redox charge of ~ 3.2 to 3.4 mC cm^{-2} for the Fe-free and 24 ppm Fe conditions, followed by a more rapid loss in the absence of Fe (**Figure S5**). Although the absolute charge differed between the two methods, both techniques indicated a greater retention of electrochemically accessible Ni sites in the presence of Fe (**Figure S6**). We approximated the intrinsic activity of catalyst films, the rate of oxygen generation per electrochemically accessible catalyst site, by normalizing the OER activity at 1.55 V vs RHE to the cathodic charge during reduction of NiOOH to Ni(OH)_2 , J/Q . J/Q for electrodes operated in $[\text{Fe}] = 6$ or 24 ppm , showed an initial decline that plateaued after the first ~ 30 cycles. $[\text{Fe}] = 0 \text{ ppm}$ showed a prominent increase in J/Q from 0.25 to $\sim 1 \text{ mA mC}^{-1}$ during the first 50 cycles (**Figure S7**). This apparent increase is due to the loss of catalytically inactive Ni sites, given that the initial OER activity is low

in the Fe-free system. Cyclic voltammograms collected after each cycle reflected changes to OER activity during continuous restructuring of the catalyst layer. In the Fe-free system, a sharp $\text{Ni}^{2+/3+}$ oxidation peak was observed at $E = 1.35$ V vs RHE, which shifted anodically to 1.38 V upon Fe spiking, accompanied by the appearance of a second peak at 1.32 V vs RHE (**Figure 3b-c**).

The OER overpotential at $J = 10 \text{ mA cm}^{-2}$, measured at the first cycle, was decreased by >100 mV when the [Fe] was increased from 0 to 24 ppm. The well-defined $\text{Ni}^{2+/3+}$ redox feature observed in the first cycle of Fe-free KOH was fully diminished by the 100th cycle, but electrodes cycled in Fe-spiked electrolytes retained most redox features and a greater fraction of the initial OER activity at $E = 1.50$ V.

Changes in the chemical composition of catalyst films during the reverse polarization were quantified by XPS and visualized by plotting the count rate normalized to the maximum count rate from the $\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$ sample for each element. Fe content was assumed to vary continuously throughout the film and the apparent Fe content, $(1-x)$, was calculated based on the integrated Fe2p region for three independently analyzed samples for each condition, and decreased from 6% in $\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$ to <1% after reduction to $\text{Ni}_x\text{Fe}_{(1-x)}(\text{OH})$, before partially recovering to >3% upon subsequent re-oxidation. Due to uncertainty in the position and intensity of satellite peaks, the Fe2p region was not fit to individual peaks. For the $\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$ electrode, the area of the peaks in the Fe2p region diminished by over 77% following reduction to form $\text{Ni}_x\text{Fe}_{(1-x)}(\text{OH})_2$ (**Figure 4a-c, Table 1**).²³ The decrease in the Fe2p signal in the reduced phase and the incomplete recovery of Fe content in the reoxidized phase (**Figure 4a**) are associated with the loss of Fe from the anode catalyst film during reverse polarization events. The changes in the Ni2p and O1s regions further indicated that the reconstructed $\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$ layer differed from the initial structure.²⁴ We did not attempt to fit the multiplet of peaks comprising the primary Ni2p_{3/2} peak at 857 eV,²⁵

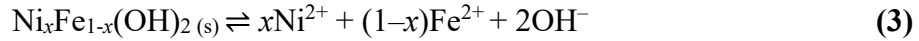
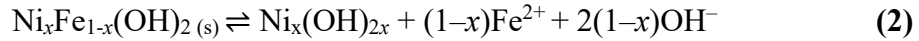
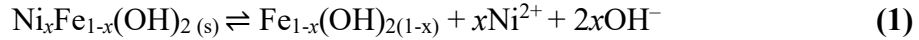
but note that the intensity relative to the Ni2p_{3/2} satellite at 861 eV increased for the reconstructed catalyst layer, and this was accompanied by a change in the relative intensity observed for the O1s region (534–529 cm⁻¹).

Raman spectroscopy of NiOOH films after testing in 30% w/w KOH containing 24 ppm Fe showed red-shifts to the A_{1g} and E_g peaks to 471 cm⁻¹ and 560 cm⁻¹ (**Figure S8**). Raman spectra collected at a controlled potential of 1.60 V showed two peaks at 477 cm⁻¹ and 560 cm⁻¹, which were assigned to the Ni_xFe_(1-x)(OOH) phase. At more negative *E*, the two well-defined peaks broadened, and at *E* = 1.30 V, the lower wavenumber A_{1g} peak shifted to ~468 cm⁻¹, which is attributed to a change in the out-of-plane vibration associated with the onset of Ni_xFe_(1-x)(OH)₂ formation. At *E* < 1.30 V, a single broad peak was observed, indicating a complete change in the predominant phase of the catalyst layer. Following reoxidation to 1.60 V, the peaks associated with Ni-O stretching and bending modes were blue-shifted. A comparable blue shift of ~2 cm⁻¹ was also observed in ex-situ Raman spectra at [Fe] = 6 ppm, whereas no measurable shift in the peaks resulted from reduction and oxidation in a Fe-free electrolyte (**Figure S9-10**). Overall, these results show that Ni_xFe_(1-x)(OOH) catalyst undergoes a structurally reversible phase transformation along with a progressive change in the surface Fe content during discharge, which is followed by a partial recovery of Fe sites upon further charging.

Changes in the catalyst composition and OER activity during repeated reverse-current discharges were dependent on the Fe content of the film and trace metal impurities within the electrolyte. OER overpotentials, *η*, were monitored at a current density where the activity was primarily controlled by kinetics and the production of gas bubbles was minimal (2 mA cm⁻²). NiOOH films in [Fe] = 0 ppm electrolyte yielded initial *η* values that were >100 mV greater than *η* for catalyst films operated in Fe-containing electrolytes (**Figure 5a**). The OER activity continued to

decrease in the absence of dissolved Fe, indicated by a further increase in η by ~ 80 mV over 100 charge-discharge cycles. NiOOH catalyst layers characterized in KOH with $[\text{Fe}] = 6$ ppm and $\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$ characterized in $[\text{Fe}] = 0$ ppm exhibited similar initial OER activities, but η in $[\text{Fe}] = 0$ ppm increased rapidly over the first 50 cycles and ultimately approached the same activity as the Fe-free NiOOH electrode by cycle 60. Repeated reconstruction of $\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$ through charge-discharge cycles led to a film that behaved similarly to NiOOH in Fe-free electrolytes.

The rate of dissolution of the reduced film formed after discharge was studied by controlling the chemical potential of Ni and Fe species in the electrolyte. The corrosion reaction for $\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$ can be represented by independent (**Equations 1–2**) or coupled (**Equation 3**) reactions



Catalysts cycled in KOH spiked with 6 ppm Fe and an excess of insoluble $\text{Ni}(\text{OH})_2$ ($\text{Ni}(\text{OH})_2$ -spiked) led to a suppression of the loss of Ni, with an average decay rate of $28 \mu\text{C cm}^{-2}/\text{cycle}$ as compared to an electrolyte with no intentional Ni addition, which decayed at $66 \mu\text{C cm}^{-2}/\text{cycle}$ (**Figure 5b**). In contrast, a $\text{Ni}(\text{NO}_3)_2$ -spiked electrolyte showed a nearly identical discharge profile compared to the system with only 6 ppm Fe, with an average decay rate of $52 \mu\text{C cm}^{-2}/\text{cycle}$, indicating no meaningful suppression of Ni dissolution. Regardless of the source of Ni added to the electrolyte, loss of $\text{Ni}^{2+/3+}$ species from the catalyst film continued to occur when held in the reduced state.

The partial stabilization of the $\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$ catalyst film in $\text{Ni}(\text{OH})_2$ -spiked electrolytes was not accompanied by a commensurate stabilization of η (**Figure S11**). $\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$ films cycled in $\text{Ni}(\text{OH})_2$ -spiked electrolytes exhibited a continuously increasing η , whereas films tested in an electrolyte without intentional Ni^{2+} additions lost Q but maintained a steady η . The OER activity of the films (measured at 1.55 V) was normalized to the charge density of electrochemically active Ni^{3+} sites, J/Q , and indicated that Ni^{2+} spiking led to an immediate loss in specific activity such that a stable charge did not result in stabilization of catalyst performance (**Figure 5c**), consistent with the loss of more active Fe sites. For both Fe-spiked and $\text{Ni}(\text{NO}_3)_2$ -spiked KOH, the J/Q value decreased by $\sim 60\%$ in the first 20 cycles, followed by a stable activity in the rest of the testing, whereas the $\text{Ni}(\text{OH})_2$ -spiked system showed a steady J/Q value throughout the testing.

The voltammetry of thin film $\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$ in $\text{Ni}(\text{OH})_2$ -spiked electrolyte was analyzed to quantify the evolution of the redox environment and number density of Ni sites in the thin-film limit. Due to shifts in the cathodic peak, a wider voltage window (1.04–1.30 V) was used when measuring Q_c . Films cycled in $\text{Ni}(\text{OH})_2$ -spiked electrolyte initially showed a cathodic peak potential, E_p^c , that was similar to those tested without added Ni^{2+} (~ 1.22 V vs RHE), but after 50 cycles, E_p^c shifted negatively to 1.19 V (**Figure S11-12**). A shoulder feature from $E = 1.06$ –1.16 V vs RHE was evident in the first cycle and was the dominant source of cathodic charge in the film after 100 cycles. The $\text{Ni}(\text{OH})_2$ -spiked electrolyte led to a greater separation in the anodic/cathodic charge capacity of $\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$ thin films correlated with an increase in the η and J/Q values for the OER. (**Figure S13**)

Finally, we characterized the performance of an electrodeposited Ni catalyst layer supported on an OER-inert conductor in a zero-gap AAWE environment coupled to a high surface-area PGM-catalyst serving as the cathode. Additions of Fe^{2+} and Ni^{2+} simulated the unavoidable

presence of dissolved transition metals resulting from recirculating KOH solutions through stainless steel or Ni-plated tubing, heat exchangers, and gas-liquid separators (**Figure 6a**), whereas addition of insoluble Ni(OH)_2 simulates the presence of delaminated catalyst from the electrodes during prior reverse current events. Electrodes were repeatedly charged at 400 mA cm^{-2} and discharged at $J_- = -0.1 \text{ mA cm}^{-2}$ to 0.700 V vs RHE. The impact of metal ion concentration in the electrolyte was monitored at $J = 400 \text{ mA cm}^{-2}$ as a function of cycle number.

The total cell voltage showed distinct trends depending on the presence of Fe, Ni, or Ni(OH)_2 . While a Fe-spiked electrolyte led to an increase in cell voltage of $\sim 140 \text{ mV}$ after 160 cycles, the Ni(OH)_2 -spiked electrolyte showed an increase of over 350 mV over the same number of cycles. The cell voltage increased rapidly during the first 40 cycles of the Ni(OH)_2 -spiked electrolyte, and the rate of degradation is significantly slower in systems containing only dissolved Fe and Ni species. This trend is consistent with the zero-gap results, where the system with dissolved Fe showed a stable and lower cell voltage despite a faster decrease in the discharge capacity (**Figure S14**). Intentional additions of Fe and Ni led to changes in the electrochemical properties of the anode catalyst that were qualitatively consistent with thin film studies. The Ni(OH)_2 -spiked electrolyte led to improved retention of electrochemically active Ni sites that were less active towards the OER, in comparison to electrolytes with only controlled Fe (**Figure 6c-d**). For Ni(OH)_2 -spiked KOH, the cyclic voltammograms showed a cathodic shift of the $\text{Ni}^{3+/2+}$ reduction peak from 1.24 V to 1.20 V by cycle 160. By cycle 50, the $\text{Ni}^{3+/2+}$ reduction peak progressively broadened and shifted cathodically, suggesting gradual modification of the local Ni-Fe coordination environment leading to a Ni-rich surface (**Figure S15**). Electrodes in the Ni(OH)_2 -spiked electrolyte showed a $\sim 70\%$ reduction in specific activity for OER compared to electrolytes spiked only with Fe,

corresponding to a 100 mV increase in η (at 5.0 mA cm⁻²) relative to the first cycle after 160 charge-discharge cycles (**Figure 6c**, **Figure S16**).

Discussion

Ni_xFe_(1-x)OOH model thin films were characterized during repeated charge-discharge cycles that mimicked the flow of charge and dissolved metal species during intermittent operation of an AAW system. During the charging process, the electrode is fully oxidized to the oxyhydroxide phase and during the discharging process, the spontaneous flow of reverse currents leads to reductive conversion of the catalyst layer into the hydroxide phase.¹³ Monitoring the characteristic discharge profile Ni_xFe_(1-x)OOH, coupled with surface-sensitive photoelectron and Raman spectroscopies, reported on the electrochemically accessible Ni³⁺ sites throughout a variety of cycling programs and in the presence of dissolved transition metal impurities (**Figure 1a**).¹⁵

Residence time in the reduced state

The nearly overlapping Q -decay profiles over 100 cycles measured during polarization to 0.7 and 0.3 V vs RHE (**Figure 1a**) indicate that the degradation of Ni_xFe_(1-x)OOH films is insensitive to the final discharge potential after complete conversion to Ni_xFe_(1-x)(OH)₂ (**Figure 1c**). This is inconsistent with a failure mode that is sensitive to the specific Ni(OH)₂ phases (α , β , or γ), instead indicating that these phases exhibit similar corrosion kinetics or else that β -Ni(OH)₂ remained as the dominant phase throughout the discharge cycle. Although the charge retention for Ni^{2+/3+} was correlated with J_- , this relationship was absent after normalizing for the total time spent at $E < 1.0$ V (**Figure 2c**).

The total residence time of the anode in the reduced state primarily determines the degradation of the anode catalyst during reverse polarization, and this result suggests that Ni²⁺ and Fe³⁺

corrosion kinetics are not dependent on applied electrochemical potential after conversion. Thus, minimizing the time that anode catalysts in the hydroxide phase are exposed to recirculating electrolyte and/or stabilizing the corrosion kinetics of Fe and Ni species from the hydroxide phase are strategies to stabilize this class of catalyst towards intermittent operation evident from this study.

Reconstruction of $\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$ catalysts

Surface-sensitive Raman and X-ray photoelectron spectroscopy characterized the composition and structure of (oxy)hydroxide catalysts during cycling. The reconstruction process to form $\text{Ni}(\text{OH})_2$ and $\text{Ni}_x\text{Fe}_{(1-x)}(\text{OH})_2$ could be monitored by Raman spectroscopy, where the peaks present at 477 and 560 cm^{-1} were replaced by a single broad peak at 509 cm^{-1} , consistent with a complete conversion of the thin-film catalyst (**Figure 4d**). In KOH electrolytes with $[\text{Fe}] = 0$ ppm, two Raman peaks remained after discharge to 0.700 V, with a lower wavenumber peak that was unchanged from the original A_{1g} mode observed for NiOOH and a higher wavenumber peak similar in energy to the peak observed for $\text{Ni}_x\text{Fe}_{(1-x)}(\text{OH})_2$. This is direct evidence of Fe^{3+} cations affecting the reconstruction pathway and modifying the environment of the reduced catalyst layer.

Surface Fe^{3+} is evidently less stable in $\text{Ni}_x\text{Fe}_{(1-x)}(\text{OH})_2$ layers than the oxidized catalyst, and the potential dependence of x was measured directly by XPS and indirectly by shifts in the in-situ Raman spectra (**Figure 4a-d**). This change is partially reversible, as the A_{1g}/E_g ratio increased from 1.01 to 1.68 when the catalyst was re-oxidized after a complete reduction to $\text{Ni}_x\text{Fe}_{(1-x)}(\text{OH})_2$. The average surface Fe content of the film ($1-x$), increased from $0.4\% \pm 0.2\%$ to $1.1\% \pm 0.4\%$ during re-oxidation, which was less than the “as-conditioned” value of $1.9\% \pm 0.6\%$, and this shows that reverse current events reduce the Fe content of the catalyst layer in a manner that is not kinetically reversible (**Table 1**). Although charging effects during XPS could lead to systematic errors in the reported Fe content of the film, the result that reduced $\text{Ni}(\text{OH})_2$ catalyst layers consistently

contained less Fe than the same catalyst layers after re-oxidation in Fe-containing electrolytes was robust. Reconstructed catalyst layers may lack Ni-Fe sites associated with the initially high OER activity, as indicated by the immediate increase in overpotential and declining J/Q over the initial cycles (**Figure 5a**).⁶

Degradation is not described exclusively by the loss of electrochemically active sites (Q) but also changes in the intrinsic catalytic activity of the film. This observation is consistent with the view that OER activity is governed primarily by dynamically evolving surface Fe sites, which can form through continuous dissolution and redeposition under operating conditions.²⁶ This behavior may differ substantially from that of bulk NiFeOOH, where Fe is incorporated throughout the catalyst structure during synthesis.²⁷ Ni-based electrodes used for intermittent AWE have been previously reported to exhibit repeated uptake and loss of Fe from the electrolyte, which was implicated as a reversible mode of degradation.²⁸ Poli et al. further showed that periodic regeneration can restore the Fe sites lost during OER and maintain extended stability for Ni anodes.²⁹ However, in our study, $\text{Ni}_x\text{Fe}_{(1-x)}(\text{OH})_2$ thin films on an inert Pt substrate appeared to be more prone to dissolution in the reduced states compared to the high valent Ni states.

The rate of Ni and Fe dissolution is influenced by the chemical potential of these species within the KOH electrolyte. The number of cycles required to reach a charge capacity, Q , of 2.0 mC cm^{-2} increased from ~ 5 to 30 as $[\text{Fe}]$ was increased from 0 to 24 ppm (**Figure 3a**). Films cycled in electrolytes with $[\text{Fe}] = 0$ showed no clear redox peaks after 100 cycles, but when $[\text{Fe}]$ was increased to 24 ppm, the anodic peak potential, E_p^a shifted negatively by ~ 20 mV accompanied by a reduction of peak intensity by ~ 60 % (**Figure 3b, d**). Thus, both the rate of Fe and Ni loss is suppressed by the presence of dissolved Fe, which suppresses the net dissolution rate in the discharged state and/or accelerated recovery of $\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$ upon reoxidation. This is more

consistent with a collective corrosion mechanism (**Equation 3**), in which the kinetic stability of both metals is affected by the corrosion products of the solid phase. However, the nearly identical decay of electrochemically active Ni sites for electrolytes spiked with both Fe and Ni indicates that at industrially relevant dissolved Ni^{2+} concentrations, Ni does not meaningfully suppress metal dissolution. The $\text{Ni}(\text{OH})_2$ -spiked electrolyte further extended the cycle life of similarly prepared catalyst layers to >55 cycles to 2.0 mC cm^{-2} . However, measurements of total integrated charge do not directly correlate with the OER activity since they do not account for the adsorbed Fe content or the retention of Fe-associated active sites.³⁰

Whereas $\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$ films cycled in electrolytes spiked with only Fe showed a stable E_p^c , the presence of dissolved Ni^{2+} led to a negative shift in E_p^c and an increasing charge capacity at more negative potentials. This suggests the presence of redox-active, but OER-inactive, NiOOH sites rather than $\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$ and once again suggests that the charge capacity of $\text{Ni}^{2+/3+}$ alone is not a meaningful predictor of the stability of the original $\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$ catalyst. Fe^{3+} dissolution is relatively reversible following discharge events, but the irreversible dissolution of Ni^{2+} sites has more long-lasting consequences for catalyst activity. The continual replenishment of surface Fe from soluble Fe species creates a dynamic surface equilibrium that may protect the Ni sites from deleterious degradation processes.

Implications for zero-gap alkaline electrolyzers

The overall performance of the zero-gap cell is significantly affected by the identity and concentration of metal species in the electrolyte. Thissen *et al.* showed that the stability of a Ni-Fe anode and Ni cathode during cycling between oxidation and shutdown conditions is influenced by the Fe dissolution-intercalation mechanism, where the cathode becomes more active due to active Fe deposition and the anode becomes less active due to incomplete Fe insertion.²⁸ Here, the use of

a low-overpotential platinum-group-metal cathode minimized the impact of iron metal deposition at the cathode. We find that the intentional addition of insoluble Ni(OH)_2 , which could be a product of catalyst delamination, slowed the rate of Ni dissolution during reverse polarization in both the three-electrode and zero-gap configurations (**Figure 5b, 6c**). The thin-film $\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$ in the presence of 6 ppm Fe exhibited a $\sim 70\%$ loss of active Ni sites, which was suppressed in the Ni(OH)_2 -spiked electrolyte to $\sim 48\%$ over a similar number of cycles. However, insoluble Ni(OH)_2 also led to an increased total cell voltage, possibly due to interactions with the concentration of free $\text{Fe}^{2+/3+}$, compared to low concentrations of dissolved Fe^{3+} and Ni^{2+} in the electrolyte (**Figure 6b**).

Suspended Ni(OH)_2 and $\text{Ni}_x\text{Fe}_{(1-x)}(\text{OH})_2$ impacted the specific activity of thin film catalysts during intermittent operation. Although electrodes and electrolyzers cycled in the presence of suspended Ni(OH)_2 exhibited greater charge retention, the primary effect was a loss in specific catalyst activity, which occurred over < 20 cycles (**Figure 5c, 6d**). This could be caused by a lower activity of dissolved Fe, caused by scavenging of free Fe species by Ni(OH)_2 . The broadening of the anodic wave at $E > 1.3$ V concurrent with a $+0.040$ V shift in E_p^a (**Figure S8**), along with a negative shift in the E_p^c , is mostly consistent with $\text{Ni(OH)}_2/\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$ particles that are resistive or in poor contact with the conducting substrate, rather than indicating a change in the Fe content of the film which leads to a positive shift in both the anodic and cathodic waves. This is consistent with the preservation of Q along with declining OER activity in the presence of Ni(OH)_2 . These results suggest that the removal of these suspended catalyst particles is important for the stability of the remaining catalyst layer.

The impacts of Fe^{2+} , Ni^{2+} , and Ni(OH)_2 on the electrochemical behavior of the $\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$ films are related to the Fe content of the solid phase (**Figure 7**). $\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$ is well

known to adsorb soluble Fe from KOH electrolytes, impacting the catalyst water-oxidation activity (**Figure 7a**). The dominant effect of dissolved Fe on the OER properties of Ni-based layered oxyhydroxides is also reflected in the stability of these catalysts during repeated charge/discharge cycles. Here we report that 70% of the Fe cations are released during a 30 min hold in the reduced $\text{Ni}_x\text{Fe}_{(1-x)}(\text{OH})_2$ state, and that the addition of soluble Fe leads to improved retention of Ni sites (as measured via charge capacity). These soluble transition metals most likely stabilize the solid by reducing the *net* rate of dissolution for the mixed-metal oxyhydroxide during conversion. When the catalyst is in the reduced state (**Figure 7b**), the impact of dissolved Fe on the net corrosion rate of Ni suggests that the dissolution processes for both Ni and Fe are coupled (**Equation 3**), or that the high chemical potential of Fe in the electrolyte supports a higher surface Fe concentration, which kinetically slows the Ni^{2+} dissolution. Dissolved Ni^{2+} had a comparatively minor impact on the preservation of redox-active Ni sites, which suggests that dynamic exchange of Fe with the electrolyte is the primary driver of catalyst dissolution in Ni-based alkaline electrolyzers.

Multiple dissolved transition metal species are expected in a realistic AAWE environment due to the use of stainless steel and Ni alloys in piping and gas-liquid separators (**Figure 6a**). Bulk Ni electrodes serve as a Ni reservoir for the active catalyst layer, and this maintains a continuous supply of Ni sites that can interact with catalyst sites lost to dissolution during the discharged state. Separating and understanding catalyst degradation from the substrate is key in designing reverse current-tolerant, highly active catalyst-coated porous, practical anodes. A critical distinction of our study from many previous Ni electrode-based studies is the use of an inert and non-passivating Pt substrate which isolates the *intrinsic* catalyst-layer changes from corrosion and passivation reactions at the substrate. Interactions with Ni^{2+} and $\text{Ni}(\text{OH})_2$ are not always favorable to the total catalyst activity, and these studies quantified the chemical effects of reverse polarization at $\text{Ni}_x\text{Fe}_{(1-x)}$.

x)OOH alone. Studies involving Ni substrates are representative of typical cell constructions but may overestimate the intrinsic durability of the solid and underestimate the intrinsic OER activity because the chemical potential of Ni and Fe is poorly defined. Other transition metals, such as Co, may impact the ultimate fate of Fe. This study employed simplified shutdown transients, a thin-film catalyst layer model, and was limited to <50 h of testing. Dissolution and delamination could be distributed in a complex manner throughout a porous electrode, making the macroscopic effect of repeated shutdowns difficult to predict solely from studies at thin films. The proposed degradation mechanisms explored in this work are expected to be relevant to catalyst layers supported on Ni or stainless steels but these supports could influence the local concentration of dissolved transition metals in a manner that is difficult to predict from this study alone. Future studies should examine how dissolution and delamination occur in porous anodes under longer-term stack operations and with more realistic shutdown conditions.

$\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$ films produced from Ni coated on Pt-Ti mesh showed initial activation over the first 20 cycles, likely associated with continued formation of the layered oxyhydroxide film *in-situ* at the Ni metal surface. The mitigated decay rate (15 $\mu\text{C}/\text{cycle}$) at the zero-gap mesh, as compared to 27 $\mu\text{C}/\text{cycle}$ at the thin film $\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$, could be a balance between continued oxidation of the metallic Ni and dissolution/passivation of the catalyst layer. This configuration is representative of stability observed at Ni meshes and Ni-plated steels used as anodes in AWE cells and suggests that electrolyte engineering can benefit the system even in the presence of a large excess of solid Ni. For both thin films and zero-gap mesh electrodes, stabilization of redox active $\text{Ni}^{2+/3+}$ comes with the expense of a reduction in the charge-normalized activity of the catalyst layer and generally reduces the performance of the anode (**Figure 5c-d**, **Figure 6c**).

Here, we find that coupled interactions with dissolved Ni^{2+} have a minor impact on charge retention and that electrolytes containing $\text{Ni}(\text{OH})_2$ preserve surface charge but lower the activity of the catalyst layer. Catalyst layers have been stabilized via dynamic exchange with electrolyte impurities during the OER in neutral and acidic environments.^{31,32} Future studies on dynamically stable $\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$ films should seek to identify dissolved species that suppress the corrosion of Ni^{2+} while also maintaining a high content of Fe^{3+} sites within the catalyst layer. Recent online inductively coupled plasma mass spectrometry results from Marquez et al. show that potassium phosphate could assist in this role.⁶ Intentional control of the composition of recirculating electrolytes may lead to catalyst layers that maintain robust activity within an AWE system during repeated start-up and shut-down events.

Methods

Materials: Nickel(II) nitrate hexahydrate, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.99%), and iron(III) nitrate nonahydrate, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (> 99.95%, trace metals basis) were purchased from Sigma Aldrich. Potassium hydroxide pellets, KOH (>99.98 %, metals basis), were purchased from Thermo Fisher Scientific. Deionized water, H_2O , with a resistivity of >18.2 M Ω -cm was obtained from a Millipore Milli-Q purification system. Nickel hydroxide, $\text{Ni}(\text{OH})_2$, was prepared by precipitating 3 M $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 1.0 M KOH. The precipitate was washed three times with H_2O and dried in an oven at 50 °C. The precipitate purity was confirmed using powder x-ray diffraction (**Figure S2**).

Preparation of thin-film nickel-iron oxyhydroxide ($\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$) and nickel oxyhydroxide (NiOOH) electrodes: Platinum foil (0.8 cm^2) was cleaned using aqua regia (3:1 v/v HCl : HNO_3) and H_2O . An aqueous solution of $0.50\text{ M Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was spin-coated onto the Pt foil (3000 rpm, 15 s) and then dried on a hot plate set to $60\text{ }^\circ\text{C}$ for 5 min. The thin film was then electrochemically cycled at a constant scan rate of 50 mV s^{-1} in 30% w/w KOH at $80\text{ }^\circ\text{C}$ until a stable voltammogram was obtained. Electrodes conditioned in Fe-free KOH are referred to as NiOOH, whereas those conditioned in KOH containing 6 ppm Fe are referred to as $\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$.

For studies in the zero-gap AAWWE environments, Pt was e-beam evaporated onto a Ti mesh (Pt-Ti), and this mesh served as a substrate instead of Pt foil. A controlled amount of Ni metal was electrodeposited onto Pt-Ti mesh from a bath containing 0.50 M NiCl_2 and 0.50 M NiSO_4 at a geometric current density, $J = -50\text{ mA cm}^{-2}$ for 30 s. The electrode was then oxidized at 1.6 V for 30 min in 30% w/w KOH containing 6 ppm Fe at $80\text{ }^\circ\text{C}$. The cell was assembled with a commercial PGM-based electrode as the cathode, which we previously found to be stable against Fe plating,²² and Zirfon-220 as the separator. Both electrodes had a geometric area of 1 cm^2 , while the separator had an active area of 1.5 cm^2 . Additional details on the cell construction can be found in the supplementary information.

Charge-discharge analysis: All electrodes were “charged” at 1.0 A cm^{-2} towards the OER for 2.0 min in 30% w/w KOH at $80\text{ }^\circ\text{C}$ in a three-electrode arrangement with Ni wire serving as the counter electrode and a reversible hydrogen electrode (RHE, Gaskatel Hydroflex) as the reference electrode. Electrodes were galvanostatically “discharged” at a constant rate, J_- (-1 mA cm^{-2} , -0.1 mA cm^{-2} , and -0.01 mA cm^{-2}), to either 0.700 or 0.300 V vs RHE. Together, these charging and discharging steps constitute a single “cycle”. We chose to use a single discharge current during electrode cycling to explicitly study how the rate and duration of the anode discharge reaction

impacts catalyst lifetime.^{9,33} The discharge current-potential profile at a bipolar plate is better defined by a constant resistance, which is typically defined by the electrolyte manifold resistance and the position of the cell within the stack,^{12,34} but this leads to varied rates of discharge across the stack and even across an individual, large-area electrode. The charge-discharge studies were performed in a 1 cm² zero-gap assembly (**Figure S3**), with a commercial cathode containing a PGM mixture serving as the cathode. The electrode was charged at 400 mA cm⁻² and discharged at $J_- = -0.1 \text{ mA cm}^{-2}$ to 0.700 V vs RHE.

Zero-gap cell assembly:

A single-cell zero-gap study was conducted in a Teflon coin cell where the electrodes and separator were assembled in between two polyether ether ketone (PEEK) plates (**Figure S3**). The cell contained 20 mL of 30 w/w % KOH at 80 °C. A reversible hydrogen electrode was inserted into the anode compartment to collect 3-electrode measurements of the anode potential. The temperature was monitored with a probe inserted into the electrolyte compartment. A syringe pump replaced water lost to electrolysis and evaporation at an empirically determined rate of 46 $\mu\text{L h}^{-1}$. The electrolyte in both anode and cathode compartments was stirred to maintain a constant KOH concentration throughout the experiment.

Studies on electrolyte composition: To study the impact of dissolved metal ions on the reversible charging behavior of Ni electrodes, three different electrolyte compositions were used. Fe-spiked electrolytes were prepared by adding Fe³⁺ to 30 % w/w KOH from a standard solution containing 3.0 mM iron(III) nitrate nonahydrate solution, adjusted to pH = 2.0 using nitric acid. A Ni(NO₃)₂-spiked electrolyte was prepared using a 0.10 M Ni(NO₃)₂·6H₂O solution, which was added to 30 % w/w KOH containing 6 ppm Fe at 80 °C to a total Ni content of 6 ppm. A Ni(OH)₂-spiked electrolyte was prepared by adding ~0.025 g of Ni(OH)₂ to 6 ppm Fe containing 30 % w/w

KOH at 80 °C until a solid $\text{Ni}(\text{OH})_2$ precipitate was visible, and this precipitate was present in the cell during electrolysis (**Figure S4**).

In-situ Raman spectroscopy: A custom cell machined out of polytetrafluoroethylene (PTFE) was used for spectroscopy of $\text{Ni}_x\text{Fe}_{1-x}\text{OOH}$ films on Pt foil under controlled electrochemical potential. A Ni wire served as the counter electrode and the reference electrode was Hg/HgO. The optical objective was protected with a thin, translucent PTFE film and immersed in KOH electrolytes heated to 60 °C. A 633.78 nm red laser (5 mW) was used to acquire the spectra, and the final spectrum was averaged over 10 acquisitions of 20 s each.

X-ray photoelectron spectroscopy (XPS): XPS measurements were conducted using a Thermo-Scientific ESCALAB 250 instrument calibrated with Au 4f7/2, Ag 3d5/2, and Cu 2p3/2. A Mg-K α X-ray source was powered at 200 W, with 50 eV pass energy, and an energy resolution of approximately 0.1 eV. A low-energy electron flood source was used for charge neutralization during all high-resolution measurements. The analysis chamber pressure was maintained below 1.0×10^{-7} mbar, and the analyzer pressure was below 1.0×10^{-8} mbar. XPS spectra were collected from a $\text{Ni}_x\text{Fe}_{1-x}\text{OOH}$ sample first held at 1.600 V vs RHE for 30 min in $[\text{Fe}] = 6$ ppm KOH. Then, the same sample was held at 0.700 V vs RHE for 30 min to form nickel-iron hydroxide ($\text{Ni}_x\text{Fe}_{1-x}(\text{OH})_2$), and a second spectrum was collected. Finally, $\text{Ni}_x\text{Fe}_{1-x}(\text{OH})_2$ was again held at 1.600 V for 30 min to form reoxidized $\text{Ni}_x\text{Fe}_{1-x}\text{OOH}$, and a third spectrum was acquired. Atomic percents of Ni, Fe, and O were calculated from the total integrated peak intensity in the Ni2p, Fe2p, and O1s regions using a Shirley background.

Resource Availability

Lead Contact: Requests for further information and resources should be directed to and will be fulfilled by the lead contact, Paul Kempler (pkempler@uoregon.edu).

Materials availability: This study did not generate new unique reagents.

Data and code availability: The raw data used to prepare figures for this paper are available on GitHub (<https://github.com/Kempler-Group/ReverseCurrent2026>) and are publicly available as of the date of publication. This paper does not report original code. Any additional information required to reanalyze the data reported in this paper is available from the lead contact upon request.

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Author Contributions

Conceptualization: PAK, SWB, MR; methodology: PAK, SWB, MR, FBS; investigation: MR; Writing – Original Draft: MR, PAK, FBS; Writing – Review & Editing: MR, PAK, SWB, FBS; Visualization: MR, PAK; Supervision: PAK, SWB; Funding acquisition: PAK, SWB.

Declaration of Interests

SWB and PAK serve as advisors to and hold shares of Hgen Inc., a company developing advanced liquid alkaline water electrolyzers.

Supplementary Information

Supplementary information is available and contains materials characterization (X-ray diffraction, Raman spectroscopy), additional electrochemical data, and a schematic of the zero-gap electrolyzer used in this work

Figure 1: Behavior of thin-film nickel iron oxyhydroxide electrodes. **a)** Characteristic discharge curve of $\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$ during reverse polarization showing Ni^{3+} to Ni^{2+} transition. **b)** Platinum overlayer deposited cross-section SEM image of $\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$ coated on Pt foil. **c)** Ex-situ Raman spectra of $\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$ and $\text{Ni}_x\text{Fe}_{(1-x)}(\text{OH})_2$ polarized in 30 % w/w KOH at 80 °C.

Figure 2: Charge-decay profiles of nickel iron oxyhydroxide during repeated reverse polarization. **a)** Discharge profile of $\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$ coated on Pt foil in 6 ppm Fe containing 30 % w/w KOH at 80 °C, where the electrode was charged at 1.0 A cm^{-2} and discharged at a constant current of -0.10 mA cm^{-2} to 0.700 V and 0.300 V vs RHE. **b)** Discharge profile of $\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$ coated on Pt foil in 6 ppm Fe containing 30 % w/w KOH at 80 °C, where the electrode was charged at 1.0 A cm^{-2} and discharged at three different rates to 0.700 V vs RHE. **c)** Discharge profile as a function of the total time the electrode spent in the Ni^{2+} state.

Figure 3: Charge-decay profiles of nickel iron oxyhydroxide as a function of dissolved iron content. **a)** Discharge profile of NiOOH coated on Pt foil in intentionally Fe spiked ($[\text{Fe}] = 0, 6, \text{ and } 24 \text{ ppm}$) 30% w/w KOH at 80 °C, where the electrode was charged at 1 A cm^{-2} and discharged at a constant current of -0.1 mA cm^{-2} to 0.7 V vs RHE. Cyclic voltammograms of NiOOH at **b)** ~0, **c)** 6, and **d)** 24 ppm Fe concentrations collected after the first and the 100th discharge curve ($\nu = 50 \text{ mV s}^{-1}$).

Figure 4: Characterization of nickel iron oxyhydroxide before and after reverse polarization. XPS data for $\text{Ni}_x\text{Fe}_{(1-x)}(\text{OH})_2$, $\text{Ni}_x\text{Fe}_{(1-x)}\text{OOH}$, and reoxidized $\text{Ni}_x\text{Fe}_{(1-x)}(\text{OH})_2$ electrodes **a)** Fe2p region, **b)** Ni2p region, **c)** and O1s region. **d)** *In-situ* Raman spectra of NiFeOOH films in 30% w/w KOH at 60 °C, recorded at five potentials along the discharge curve.

Figure 5: Correlation of activity and charge capacity of nickel iron oxyhydroxide as a function of electrolyte composition. **a)** The OER overpotential at 2 mA cm^{-2} for the thin-film catalyst charged at 1.0 A

cm⁻² and discharged at -0.1 mA cm⁻² to 0.700 V vs RHE. **b)** The discharge capacity decay for NiFeOOH coated on Pt foils in Fe-spiked KOH, Ni(NO₃)₂-spiked KOH, and Ni(OH)₂-spiked KOH. **c)** Intrinsic OER activity of thin film Ni_xFe_(1-x)OOH measured at 1.55 V vs RHE normalized to the charge measured in **b)**.

Figure 6: Correlation of activity and charge capacity of nickel iron oxyhydroxide in a zero-gap environment as a function of electrolyte composition. **a)** Scheme of zero-gap cell and components operated in 30% w/w KOH with insoluble Ni(OH)₂ and 6 ppm dissolved iron, showing the dynamic behavior of anode catalyst during reverse polarization. **b)** Effect of electrolyte composition on total cell voltage at $J = 400 \text{ mA cm}^{-2}$ for thin film Ni_xFe_(1-x)OOH coated on Pt-Ti mesh anode and PGM cathode assembled in a zero-gap cell operated at 80 °C **c)** Discharge capacity decay for thin film Ni_xFe_(1-x)OOH coated on Pt-Ti mesh in a zero-gap cell with 30% w/w KOH containing 6 ppm Fe in the absence of additional Ni, Fe with 6 ppm Ni, and Fe with insoluble Ni(OH)₂. The electrode was charged at 400 mA cm⁻² and discharged at a constant current of -0.1 mA cm⁻² to 0.7 V vs RHE **d)** Intrinsic OER activity of thin film Ni_xFe_(1-x)OOH coated on Pt-Ti mesh calculated at 1.55 V vs RHE in a zero-gap cell with 30% w/w KOH containing 6 ppm Fe in the absence of additional Ni, Fe with 6 ppm Ni, and Fe with insoluble Ni(OH)₂.

Figure 7: Processes affecting anode catalyst stability during repeated charge/discharge cycles. **a)** Ni_xFe_(1-x)OOH formation leads to Fe uptake and forms an active O₂ evolving catalyst **b)** electrochemical reduction to Ni_xFe_(1-x)(OH)₂ is followed by chemical dissolution of Ni and Fe, leading to loss of Q and catalyst activity. **c)** Recirculating Ni(OH)₂ lowers the activity of soluble Fe, increasing the effective rate of dissolution and/or impeding Fe uptake.

Table 1. Surface composition (atomic %) of Ni_xFe_(1-x)OOH and Ni_xFe_(1-x)(OH)₂ films.

Element	Atomic %	Atomic %	Atomic %
	Ni _x Fe _(1-x) OOH	Ni _x Fe _(1-x) (OH) ₂	Reoxidized Ni _x Fe _(1-x) OOH
Fe	1.9(0.6)	0.4(0.2)	1.1(0.4)
Ni	29(5)	35(5)	30(6)
O	68(6)	64(5)	69(7)
Apparent Fe content (1-x)	0.06(1)	0.0093(5)	0.033(5)

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