Mechanism and Kinetics of HER and OER on NiFe LDH Films in an Alkaline Electrolyte

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The mechanism and kinetics of hydrogen evolution (HER) and oxygen evolution (OER) reactions on nickel iron layered double hydroxide (NiFe LDH) in a basic electrolyte are investigated. The deposited film reported an overpotential of 247 and 245 mV at 10 mA/cm² toward the HER and OER, respectively. A least squares procedure was performed to fit a theoretical current density model with experimental linear sweep voltammetry (LSV) results, and the chemical reaction rate constants for the OER and HER steps were identified. Electrochemical impedance spectroscopy (EIS) measurements were taken at different potentials, and the resulting kinetic model demonstrates a good agreement between theoretically calculated faradic resistance and experimental EIS results. The HER results indicated the Heyrovsky step as rate controlling, with a dependence of reaction mechanism on potential. At low potential, the mechanism begins with a Volmer step, followed by parallel Tafel and Heyrovsky steps. At higher potential, the mechanism becomes consecutive combination of the Volmer and Heyrovsky steps. The OER data point to the formation of the adsorbed peroxide as rate controlling. The HER and OER kinetic data were combined into a model capable of predicting the electrocatalysis cell current-potential characteristics, which can be used for design process and optimization.

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Hydrogen is perceived as a promising energy carrier for the future. As a fuel, hydrogen has a large energy content per unit mass with a higher heating value (HHV) of 39.42 kWh/kg, which is more than double and triple the energy content of methane and gasoline, respectively. Currently, up to 96% of the hydrogen economy is based on its production from fossil fuels, which poses significant long-term environmental threats. Hydrogen production from water electrolysis is widely accepted to be the most sustainable source of hydrogen production, particularly when integrated with sustainable energy sources such as solar or wind energy.

Understanding the mechanism of the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) is a fundamental step toward optimizing electrocatalytic activity, which is essential for optimal process design and operations. Integrating a classical steady-state polarization technique with electrochemical impedance spectroscopy has been shown to be effective in providing kinetic analysis of electrochemical reactions. Numerous efforts have been made to investigate the kinetics of OER and HER on a range of promising catalyst materials. Krsztajc et al. used the combination of classical steady-state voltammetry and impedance spectroscopy to understand the HER mechanism on Ni electrodes in an alkali medium. They demonstrated that at low overpotential values the HER proceeds with a combination of a Volmer step, followed by a rate-controlling Tafel step. The mechanism at higher overpotential, however, was shown to be a consecutive combination of a Volmer step followed by a rate controlling Heyrovsky step. Doyle et al. examined the OER kinetics on hydrous iron oxides in a basic electrolyte. In low overpotential regions, the reported Tafel slope values were found to be 40 and 60 mV/dec under different oxide growth conditions.

In practice, the efficiency of water electrolysis is limited by the large anodic overpotential of the OER. Over the last few decades, considerable research effort has been dedicated to the design and synthesis of new anodic materials with greater electrocatalytic activity relative to conventional, low Earth-abundant noble metals. Among these new anodic materials are transitional metal based materials which offer high catalytic activity and low cost.

Nickel-Iron Layered Double Hydroxide (NiFe LDH) and other transition metal layered materials have attracted enormous attention owing to their high electrocatalytic activity toward both OER and HER, as well as their low cost, simple preparation methods, and Earth abundance. Nickel is known to be an active material that resists corrosion better than other transition metals. In addition, NiFe LDH can be deposited on Ni foam, and the resulting electrode can be used for OER and HER applications as it offers high electrocatalytic activity toward both catalytic reactions in an alkaline electrolyte. Although it is not the optimal catalyst for the HER, it offers economic benefits arising from the use of the same material for both electrodes while maintaining high catalytic activity.

Lu et al. examined the electrocatalytic activity of NiFe LDH electrode toward OER in an alkaline electrolyte. Their electrode demonstrated a Tafel slope of 50 mV/dec and an overpotential of 280 mV to achieve a current density of 30 mA/cm². Luo et al. reported the performance of NiFe LDH films, with overpotentials of 240 and 210 mV toward the OER and HER, respectively, at a current density of 10 mA/cm². Fan et al. reported an active nickel–vanadium monolayer double hydroxide for OER, with a Tafel slope of 50 mV/dec and an overpotential of 300 mV at 10 mA/cm², which is comparable to, but does not exceed, the best-performing NiFe LDH reported in the literature.

In this paper, we investigate the mechanism and kinetics of both OER and HER on NiFe LDH material. We combine the results from analysis of linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) to reveal valuable insight into the reaction mechanism occurring on each electrode. Unlike most studies that focus on either OER or HER, we present a complete system kinetics investigation by combining results obtained from the anode and cathode to fit the electrochemical cell experimental data. The results from this work have great promise and will be used in future work for the process design and operation of an integrated electrolysis-solar energy system.

Experimental

**Electrode synthesis.**—The NiFe LDH films were deposited on Ni foam substrates via a simple one-step hydrothermal synthesis in an autoclave reactor. Ni foam substrates (2 × 1 cm) were cleaned with concentrated HCl solution for 10 minutes, followed by deionized water and ethanol each for 10 minutes in an ultrasonic bath. 0.32 g of Ni(NO₃)₂·6H₂O, 0.45 g Fe(NO₃)₃·9H₂O and 0.67 g urea were mixed
in 80 mL deionized water until dissolution. The Ni foam substrates were placed against the wall of a 100 mL autoclave, and the solution was poured into the autoclave. After allowing 12 hours of growth in an electric oven at 155 °C, the autoclave was allowed to cool naturally to room temperature, and the samples were washed with deionized water followed by ethanol, and dried at 80 °C for 6 hours.

**Electrochemical measurements.**—A conventional three-electrode electrochemical cell was used for the measurements with 1 M KOH solution as an electrolyte. The reference electrode chosen was CH Instruments Alkaline/Mercury Oxide (Hg/HgO/1M NaOH, 0.098 V vs NHE at 25 °C). A GAMRY interface 1000E potentiostat was used to perform the electrochemical measurements. LSV data were obtained for the cathode (HER electrode) at the applied potential range −0.93 to −1.7 V vs Hg/HgO, and for the anode (OER electrode) between the applied potential range 0.1 to 1.36 V vs NHE at 25 °C.

A 3D field emission scanning electron microscopy (SEM) operating at 10 kV. SEM images of pure Ni foam (a), and NiFe LDH (b), (c), and (d).

**Structural characterization.**—The size and morphology of the deposited NiFe LDH samples were characterized using a Hitachi SU-70 FESEM field-emission scanning electron microscopy (SEM) operating at 10 kV. SEM images of pure Ni-foam and NiFe LDH film deposited on Ni foam are shown in Figure 1. The morphology shown in Figure 1c and Figure 1d is in agreement with that described in previous work, which suggests a 3D vertical growth of LDH nanoplates on the Ni surface and a mesoporous structure of the LDH material. The LDH nanoplate average size is estimated to be 400 nm (Figure 1d).

In addition, X-ray photoelectron spectroscopy (XPS) data were collected with a Kratos Axis 165 operating in hybrid mode using Mg Kα X-rays (240 W). The use of Mg Kα X-rays was essential to detect the low concentrations of Fe in the sample and to overcome the total overlap of Fe 2p with the very intense Ni LMM that would have occurred if using the normally preferred monochromatic Al source. For the binding energy calibration, the C1s peak at 284.8 eV was used as a reference. Charge neutralization was required to minimize sample charging. Survey spectra and high resolution spectra were collected at pass energies of 160 eV and 40 eV, respectively.

XPS data were analyzed using CASAXPS, quantification was performed after application of a Shirley background taking into account relative sensitivity factors from the Kratos Vision Library and instrument transmission function. Quantification of the iron was complicated by overlap of the Fe 2p with the O KLL Auger. While only the 2p1/2 spin-orbit split components were overlapping, we could not use the 3/2 components alone to estimate peak area since the 3/2 and 1/2 components also overlap. The iron concentration was estimated using a constrained peak fit, using 3 spin-orbit split components with spin-orbit splitting fixed at 13.4 eV and area ratio of 2:1 for the 3/2, 1/2 components, respectively, in accordance with quantum mechanics. In addition, peak FWHMs and relative area ratios of the three sets of components were fixed, the Shirley background was then adjusted at the high binding energy side until both the 3/2 and 1/2 peaks fit the data well.

XPS results (Figure 2) show the presence of Ni, Fe, C, and O elements in the sample, with an estimated ratio of Ni:Fe of about 85.2:14.8. We also noticed by comparing the XPS results of samples prepared at different temperatures that the ratio of Ni to Fe increases as the synthesis temperature decreases, with an estimated Ni:Fe ratio of about 95.5:4.5 at 128 °C (Figure S1).

X-Ray Diffraction (XRD) patterns of NiFe LDH on Ni foam substrate were collected on a Bruker C2 Discover diffractometer using a Cu Kα source. Spectra were collected using a 2D Vantec detector in the range from 8.8° to 85.6°. XRD results in Figure 3 show the LDH reflection peaks of (003), (006), and (009), which represent the behavior of a typical LDH phase, and is in agreement with that reported in the literature.

**NiFe LDH Performance Toward HER**

**Experimental results and analysis.**—The HER mechanism starts with an electrochemical adsorption of a water molecule onto an active site on the cathode to produce the adsorbed species H (a step that is typically referred to as the Volmer step). The hydrogen gas can then be produced from two competing reaction paths: a chemical recombination of the adsorbed species H (Tafel step), and an electrochemical desorption step (Heyrovsky step). The HER mechanism is presented in Table I.

The deposited film reported a cathodic overpotential of 247 mV at a current density of 10 mA/cm² toward the HER. This value is higher than the 210 mV overpotential reported by Luo et al.,7 yet lower than the 269 mV overpotential demonstrated by Chen et al.13 Aside from providing valuable information on the catalyst activity toward an electrochemical reaction, the Tafel slope can offer valuable insight into the reaction mechanism. An experimental Tafel plot constructed from the LSV data (Figure 4) shows two distinct Tafel slopes with values of 38.4 and 71.3 mV/dec at lower and higher potential regions, respectively, demonstrating high electrocatalytic activity of the prepared film. A change in Tafel slope with increasing potential can be attributed to a reaction mechanism or pathway change, or to the changes in the surface coverage of intermediates. It is well accepted in the literature that a Tafel slope close to 120, 40, or 30 mV/dec indicates that the HER mechanism is controlled by Volmer, Heyrovsky, or Tafel steps, respectively,3,4,14,15 Hence, the Tafel slope value of 38.4 mV/dec reported in this work suggests that the Heyrovsky step is rate controlling. However, it will be difficult to draw a definitive conclusion about the mechanism based on the 71.3 mV/dec value observed in the high potential region since it is not a conventional value for the HER. Further investigation of the reaction mechanism is discussed in the HER theoretical analysis section.

To gain a better insight into the kinetic mechanism that governs the HER, EIS measurements were taken at different values within the LSV potential range. Figure 5 and Figure S2 show the Nyquist plots of the EIS measurements in the form of semi-circle shaped spectra. The diameter of the semi-circle decreases as the applied potential increases, indicating increasing HER activity. The intersection of the spectra with the real impedance axis in the high frequency range represents...
the ohmic resistance, mainly caused by the electrolyte resistance. The high frequency region of HER Nyquist plots shows a straight line or a deformed semi-circle behavior, which can be attributed to the porous structure of the active catalyst.16

The impedance results were interpreted by fitting the data to an Armstrong and Henderson equivalent electric circuit (Figure 6) using both Z-view software and EIS Spectrum Analyzer program to obtain the equivalent circuit components. In Figure 6, \( R_s \) is the ohmic electrolyte resistance measured between the working and the reference electrodes, \( C_{dl} \) is the double layer capacitance formed at the electrode/electrolyte interface, \( R_{ct} \) is the reaction charge transfer resistance across the electrode/electrolyte interface, and \( R_p \) and \( C_p \) are the pseudo-resistance and pseudo-capacitance related to the adsorption, desorption and mass transfer limitations of the adsorbed species H at the working electrode.5,17 The \( R_p \) and \( C_p \) are also associated with the relaxation of the adsorbed hydrogen surface coverage as the applied potential changes, with a relaxation time constant \( \tau = R_p C_p \).18 To obtain a better fit, an inductor was connected in series to the Armstrong and Henderson circuit, which may account for the cell wires and connection contributions at high frequencies.

The EIS fitting results for the HER are shown in Figure 5, Figure S2, and Table II. It can be seen that the solution resistance is nearly constant, while both the charge transfer and the pseudo-resistances decrease exponentially as the applied voltage increases, a result that is confirmed by the decrease in the semi-circle diameters of Figure 5.

**HER theoretical analysis.**—The electrochemical reaction rate expressions for the Volmer, Heyrovsky, and Tafel steps are given in

\[
\text{Volmer: } \quad \text{H}_2\text{O}^{(aq)} + S_{\text{HER}} + e^- \rightleftharpoons \text{H} + \text{OH}^{(aq)} \\
\text{Heyrovsky: } \quad \text{H} + \text{H}_2\text{O}^{(aq)} + e^- \rightleftharpoons \text{H}_2\text{O}^{(g)} + S_{\text{HER}} + \text{OH}^{(aq)} \\
\text{Tafel: } \quad 2\text{H} \rightleftharpoons \text{H}_2^{(g)} + 2S_{\text{HER}}
\]

---

**Table I.** HER mechanism in a basic electrolyte.5 \( S_{\text{HER}} \) represents active sites on the HER electrode. Electrons are denoted by \( e^- \), and the subscripts (aq) and (g) denote the aqueous and the gas phases, respectively. All remaining species correspond to adsorbed surface species.

Here is a table showing the XPS results for NiFe LDH and XRD characteristics of NiFe LDH deposited on Ni foam substrate:

**Figure 2.** XPS results for NiFe LDH.

**Figure 3.** XRD characteristics of NiFe LDH deposited on Ni foam substrate. The peaks marked # represent the Ni foam substrate.
Figure 4. Tafel plot for NiFe LDH as a HER electrode showing two Tafel slopes corresponding to low and high potential regions.

Equations 1, 2, and 3, respectively. In these rate expressions, \( \Theta_H \) is the fraction of the surface coverage of the adsorbed intermediate \( H \), \( k'_i \) is the electrochemical rate constant (mol cm\(^{-2}\) s\(^{-1}\)), \( k_i \) is the chemical rate constant (mol cm\(^{-2}\) s\(^{-1}\)), \( k_0 \) is the partial standard chemical rate constant (cm s\(^{-1}\)), \( \beta_i \) is a symmetry factor (assumed to be 0.5) and \( \eta \) is the overpotential (V).

\[
\nu_V = k'_V (1 - \Theta_H) - k_{-V} \Theta_H \tag{1}
\]
\[
\nu_H = k'_H \Theta_H - k_{-H} (1 - \Theta_H) \tag{2}
\]
\[
\nu_T = k_T \Theta_H^2 - k_{-T} (1 - \Theta_H)^2 \tag{3}
\]

where:

\[
k'_i = k_i \exp\left(\frac{-\beta_i F \eta}{RT}\right) = k_i[H_2O] \exp\left(\frac{-\beta_i F \eta}{RT}\right), i = V, H
\]
\[
k'_{-i} = k_{-i} \exp\left(\frac{(1 - \beta_i) F \eta}{RT}\right) = k_{-i}[OH^-] \exp\left(\frac{(1 - \beta_i) F \eta}{RT}\right), i = V, H
\]
\[
k_T = k_T^0 \frac{p_{H_2}}{p_o}
\]

The steady state kinetics of the HER can be characterized by applying a charge balance. The current density can then be given as a
The rate of change of the adsorbed hydrogen surface coverage can be obtained by performing a material balance: 20

\[ \frac{q}{F} \left( \frac{\partial \Theta_H}{\partial t} \right) = v_V - v_H - 2v_T \]  

(6)

The steady state coverage is obtained when \( r_1 \) is set to zero, facilitating the calculations of the coverage as a function of reaction rate constants. Setting \( r_1 \) to zero reveals a second order polynomial in \( \Theta_H \), which can be solved using:

\[ \Theta_H = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \]

\[ a = 2 (k_\text{T} - k_T) \]

\[ b = -(k'_V + k'_H + k''_H + 4k_{-T}) \]

\[ c = (k'_V + k'_H + 2k_{-T}) \]

Equations 1, 2, 4, and 5 show the dependency of the current density and Faradaic resistance on the Volmer and Heyrovsky reaction rate constants, the potential, along with the surface coverage, and Equation 7 represents the surface coverage as a function of all six reaction rate constants and the potential. Consequently, \( j \) and \( R_F \) can be theoretically represented as a function of all the reaction rate constants and the potential. A least squares procedure to fit the theoretical current density model with experimental results obtained from the steady state polarization curve is implemented using scipy.optimize.leastsquares package in the Python programming environment.

The chemical reaction rate constants for the individual HER mechanism steps, Tafel, Volmer, and Heyrovsky, were obtained as a result of the fitting procedure, and are shown in Table III. Figure 7a demonstrates the excellent fit of the current-voltage characteristics with experimental LSV data. The identified reaction rate model shows a good agreement between theoretically calculated Faradaic resistance and values obtained from EIS results (Figure 7b).

The set of identified reaction rate constants in Table III reveals the Heyrovsky step as the rate limiting step for the HER on the NiFe LDH electrode. Figure 8a shows the calculated Tafel, Volmer, and Heyrovsky reaction rates using the identified kinetic parameters, which reveals a dependence of the HER mechanism on the potential. At low potential range (below a compensated voltage of \(-1.31 \text{ V}\), equivalent to an applied voltage of \(-1.52 \text{ V} \) vs Hg/HgO), the HER mechanism starts with a Volmer step, followed by parallel Tafel and rate controlling Heyrovsky step. At higher potential range, the HER mechanism consists of a consecutive combination of the Volmer step, followed by a rate-controlling Heyrovsky step, with negligible contribution by the Tafel step. This result is in good agreement with the Tafel slope analysis presented earlier.

Figure 8b shows the influence of the potential on the adsorbed hydrogen surface coverage, with a noticeable high coverage value close to unity in all potential ranges. This observation is expected since the Heyrovsky is the rate controlling step. A small increase in the coverage value results with increasing potential, which is associated with the shift between Tafel and Heyrovsky reaction rate values close to \(-1.3 \text{ V}\). The Tafel step requires the presence of two adjacent adsorbed hydrogen species on the surface, resulting in an increase in the coverage as this rate becomes smaller. Ultimately, when the Tafel rate reaches a negligible value, the Volmer and Heyrovsky rates approach the same value, allowing the surface hydrogen coverage to reach a stable value (Figure S3).

When the theoretical potential range is further extended (Figure S4) the Tafel step reaction rate becomes independent of the applied potential, which can be attributed to the surface coverage of the adsorbed intermediate reaching a constant high coverage value in this potential region. This conclusion can be drawn by examining Equation 3 and the definition of its rate constants being independent of potential; however, the dependency of this rate at low potential values originates from that of the surface coverage.

### NiFe LDH Performance Toward OER

#### Experimental results and analysis

One of the main challenges of OER mechanistic analysis lies in its complexity, owing to the fact that it involves the transfer of four electrons through a multi-step reaction pathway in which various reaction intermediates are formed. As a result, a number of reaction pathways have been proposed for the OER. One of the better-accepted reaction pathways for the OER was proposed by Dong et al. 21 on a NiFe LDH electrode and is presented in Table IV. The OER mechanism starts when a hydroxide ion \( \text{OH}^- \) adsorbs onto an active site on the anode, followed by a sequence of intermediate reactions to form the adsorbed species \( \text{O} \), \( \text{HOO} \), \( \text{OO} \) before releasing oxygen gas \( \text{O}_2 \) from the adsorbed species \( \text{OO} \).

In terms of the catalytic performance toward OER, NiFe LDH demonstrated an excellent overpotential of 245 mV to reach an anodic current density of 10 mA/cm². This value is comparable to the

| \( V \) (V) | \( R_t \) (\( \Omega \)) | \( R_{ct} \) (m\( \Omega \)) | \( R_p \) (m\( \Omega \)) | \( C_H \) (\( \mu F \)) | \( C_P \) (\( \mu F \)) | \( L \) (\( \mu H \)) |
|---|---|---|---|---|---|---|
| -1.20 | 1.509 ± 0.2 | 1072 ± 5.9 | 2308 ± 2.8 | 171.6 ± 2.0 | 159.5 ± 2.7 | 0.09 ± 25.7 |
| -1.30 | 1.498 ± 0.3 | 304.3 ± 8.7 | 933.7 ± 3.2 | 107.1 ± 6.7 | 140.5 ± 2.6 | 0.22 ± 11.1 |
| -1.35 | 1.501 ± 0.3 | 267.7 ± 9.9 | 676.9 ± 4.5 | 103.5 ± 7.8 | 136.7 ± 2.6 | 0.21 ± 11.1 |
| -1.40 | 1.492 ± 0.4 | 255.6 ± 8.4 | 552.2 ± 4.3 | 89.6 ± 9.3 | 141.1 ± 2.5 | 0.24 ± 9.8 |
| -1.45 | 1.489 ± 0.4 | 205.8 ± 8.7 | 441.4 ± 5.2 | 87.1 ± 10.1 | 140.1 ± 2.4 | 0.29 ± 8.2 |
| -1.50 | 1.483 ± 0.4 | 191.8 ± 7.4 | 376.8 ± 5.3 | 81.6 ± 11.3 | 149.6 ± 2.3 | 0.30 ± 8.3 |
| -1.55 | 1.485 ± 0.3 | 206.4 ± 6.8 | 287.5 ± 6.1 | 91.5 ± 7.5 | 166.6 ± 3.9 | 0.28 ± 6.2 |
| -1.65 | 1.469 ± 0.5 | 158.9 ± 4.8 | 245.3 ± 5.9 | 67.3 ± 14.2 | 170.9 ± 2.4 | 0.33 ± 7.2 |
Table III. Chemical rate constants $k_i$ (mol cm$^{-2}$ s$^{-1}$) and partial standard chemical rate constants $k_{io}$ (cm s$^{-1}$) obtained for HER.

| $k_V$ | $k_{-V}$ | $k_H$ | $k_{-H}$ | $k_T$ | $k_{-T}$ |
|-------|----------|-------|----------|-------|----------|
| 1.38e-6 | 1.00e-10 | 1.94e-10 | 2.21e-5 | 5.52e-7 | 1.00 |
| 2.48e-5 | 1.00e-7 | 3.48e-9 | 2.21e-2 | 5.52e-7 | 1.00 |

Figure 7. Experimental and simulated results of the HER current density (a) and inverse of Faradaic resistance (b) versus potential.

Figure 8. Tafel, Volmer, and Heyrovsky reaction rates using the identified kinetic parameters (a) and hydrogen fractional surface coverage (b) versus potential.

240 mV overpotential reported by Luo et al.\textsuperscript{7} and higher than the 224 mV overpotential reported by Li et al.\textsuperscript{12} A Tafel plot (Figure 9) constructed from the experimental LSV data shows a Tafel slope of 48.4 mV/dec, which is less than the 52.8 mV/dec reported by Li et al.,\textsuperscript{12} and the 50 mV/dec reported by Lu et al.,\textsuperscript{8} demonstrating the excellent performance of our prepared electrode.

Numerous efforts have been made toward the analysis and interpretation of the Tafel slope values in terms of the OER mechanism. Doyle et al.\textsuperscript{4} suggested that either the formation of the peroxide (HOO) or the peroxo (OO) intermediates is rate limiting for a Tafel slope of 40 mV/dec on hydrous iron oxide films in basic electrolytes. Fan et al.\textsuperscript{11}

Table IV. OER mechanism in a basic electrolyte.\textsuperscript{21} $S_{OER}$ represents active sites on the OER electrode. Electrons are denoted by e$^{-}$, and the subscripts (aq) and (g) denote the aqueous and the gas phases, respectively. All remaining species correspond to adsorbed surface species.

| Step | Reaction |
|------|----------|
| 1    | $\text{OH}^{\cdot}_{(aq)} + S_{OER} \rightleftharpoons \text{HO} + e^{-}$ |
| 2    | $\text{OH}^{\cdot}_{(aq)} + \text{HO} \rightleftharpoons \text{H} + \text{H}_{2}O_{(aq)} + e^{-}$ |
| 3    | $\text{OH}^{\cdot}_{(aq)} + \text{O} \rightleftharpoons \text{HOO} + e^{-}$ |
| 4    | $\text{OH}^{\cdot}_{(aq)} + \text{HOO} \rightleftharpoons \text{OO} + \text{H}_{2}O_{(aq)} + e^{-}$ |
| 5    | $\text{OO} \rightleftharpoons \text{O}_{2(g)} + S_{OER}$ |

Figure 9. Tafel plot for NiFe LDH as a OER electrode.
indicated that the formation of HOO is rate limiting for NiV LDH with a Tafel slope of 50 mV/dec, and the formation of the O intermediate is rate limiting for NiFe LDH with a Tafel slope of 64 mV/dec. In addition, Louie et al.\textsuperscript{22} stated that a Tafel slope of 40 mV/dec is most likely associated with the formation of peroxide intermediate reaction as rate limiting. The 48.4 mV/dec Tafel slope obtained in this work may indicate that either the formation of O, HOO or OO intermediates in steps 2, 3, and 4, respectively, is the rate determining step, with step 3 being the most probable. Further investigation of the reaction mechanism is discussed in the OER theoretical analysis section.

The OER Nyquist plots in Figure 10 and Figure S5 show two distinctly identified semicircles: the former is related to the active material porous structure, arising from the resistance of the ionic conducting paths in the pores filled with the electrolyte.\textsuperscript{18} The latter semicircle in the OER Nyquist plot is related to the charge transfer limitations in the electrode/electrolyte interface.

Figure 11 shows the equivalent electrical circuit used to fit the EIS spectra,\textsuperscript{23} with the fitting results given in Table V. Ideally, the film porous structure resistance $R_f$ should be independent of potential, however, EIS fitting results (presented in Table V) demonstrated a slight decrease in the resistance of the first RC loop with increasing potential, which aids in increasing the overall OER rate as potential increase. On the other hand, $R_{ct}$ is highly dependent on the potential, suggesting that the second RC loop is related to the charge transfer limitations.

The constant phase element (CPE) in Figure 11 is introduced to improve the theoretical fit of the EIS spectra. A CPE is often used to represent a non-ideal capacitor, indicated by a depressed semi-circle behavior in Nyquist plot, which can be attributed to heterogeneities and porous surfaces.\textsuperscript{24} The CPE contains two parameters: CPE-P corresponding to its capacitance value in the absence of frequency dispersion, and an exponent CPE-T (or $\alpha$) $\leq 1$, with a value of 1 for ideal capacitors.\textsuperscript{4}

When a CPE is used in a circuit, the real capacitance value can be evaluated. The capacitance associated with the film resistance $C_f$ can
be calculated using the common Brug equation:

$$C_i = \left[ C_P E T_i \left( \frac{1}{R_a} + \frac{1}{R_i} \right)^{a-1} \right]^\frac{1}{a}$$

The double layer capacitance $C_{dl}$ can be calculated from the modified Brug equation [supplementary information of Ref. 18], for a two-CPE equivalent electric circuit similar to Figure 11:

$$C_{dl} = \left[ C_P E T_{dl} \left( \frac{1}{R_a} + \frac{1}{R_i} \right)^{a-1} \right]^\frac{1}{a}$$

The identified capacitance values $C_i$ and $C_{dl}$ are presented in Table VI.

**OER theoretical analysis.**—For the OER, the reaction rates can be expressed as:

$$\nu_i = k_i \Theta_S - k_i' \Theta_{HO}$$

where:

$$k_i = k_i \exp \left( \frac{(1 - \beta_i) F \eta}{RT} \right) = k_i' [OH^-] \exp \left( \frac{(1 - \beta_i) F \eta}{RT} \right),$$

$$k_i' = k_i' \exp \left( \frac{-\beta_i F \eta}{RT} \right) = \left\{ \begin{array}{ll} k_i' [H_2O] \exp \left( -\beta_i F \eta / RT \right), & i = 2, 4, \\ k_i' \exp \left( -\beta_i F \eta / RT \right), & i = 1, 3 \end{array} \right.$$

$$k_3 = k_3^c \frac{P_{O_2}}{P_O}$$

$$k_{-5} = k_{-5}^c \frac{P_{O_2}}{P_O}$$

Similar to the HER, the steady state current density and the inverse of Faradaic resistance of the OER can be characterized by:

$$r_2 = j / F = (v_1 + v_2 + v_3 + v_4)$$

$$R_{F-1} = \frac{\partial j}{\partial \eta} = F \left( \frac{\partial v_1}{\partial \eta} + \frac{\partial v_2}{\partial \eta} + \frac{\partial v_3}{\partial \eta} + \frac{\partial v_4}{\partial \eta} \right)$$

Due to the complex behavior of the OER in which numerous reaction intermediate species are formed, the derivation of the intermediates surface fractional coverage as a function of the reaction rate constants was challenging. A material balance is performed on each intermediate, with steady state converge assumed. Consequently, five algebraic equations are obtained, in which four are linearly independent; they can then be solved simultaneously along with

$$\Theta_S + \Theta_{HO} + \Theta_O + \Theta_{HOO} + \Theta_{OO} = 1$$

to obtain expressions for $\Theta_S$, $\Theta_{HO}$, $\Theta_O$, $\Theta_{HOO}$, and $\Theta_{OO}$ as a function of all reaction rate constants and the potential. A detailed mathematical derivation is included in the Supplemental Material.

A least squares procedure is performed to fit the theoretical current density model with experimental LSV results to obtain the chemical reaction rate constants for the OER (Table VII). The resulting kinetic model shows an excellent agreement between theoretically calculated and experimental current density and faradaic resistance values (Figure 12). Examining the kinetic parameters in Table VII reveals that step 3, formation of the peroxide intermediate HOO, is the rate limiting step, which validates the analysis performed on the measured Tafel slope.

Since a steady state coverage of the individual reaction intermediates is assumed, it follows that the five reaction rate values are equal at any potential, with an exponentially increasing behavior similar to the current-potential characteristics, as shown in Figure 13a. This is also supported by the sequential behavior of the OER, i.e., the consecutive formation of the adsorbed OER intermediates, as opposed to having two competing reaction pathways as is the case with the HER.

A plot of the surface coverage reveals a high coverage value of the adsorbed O species that is close to unity (Figure 13b), a consequence of step 3 as rate limiting. Examining Figure 13b reveals that at higher potential, $\Theta_O$ begins to decrease as a result of a small increase in $\Theta_{HOO}$ value. This result is reasonable owing to the $k_2^c$ value in Table VII being the second smallest value compared to the remaining rate constants, and the fact that the chemical rate $v_3$ is less dependent on the potential compared to the remaining electrochemical reaction rates.

**Combined Electrolysis Cell Modeling**

The anode and cathode kinetic results can be combined to represent the complete electrolysis cell using Equation 18

$$V_{cell} = 1.23 + \eta_a + \eta_c + I_{cell} \times R_{cell}$$

where $\eta_a$ and $\eta_c$ are the anode and cathode overpotentials, respectively, corrected for the IR drop, and $R_{cell}$ is the total cell electrolyte resistance. $R_{cell}$ is not the same as the solution resistance value $R_i$ obtained from the anode or cathode EIS fitting results. In fact, it can

| $V$ (V) | $C_i$ (mF) | $C_{dl}$ (mF) |
|--------|------------|--------------|
| 0.55   | 8.67       | 856.69       |
| 0.60   | 5.26       | 584.83       |
| 0.65   | 4.58       | 442.33       |
| 0.70   | 3.61       | 324.97       |
| 0.75   | 3.24       | 315.66       |
| 0.80   | 3.46       | 269.58       |
Table VII. Chemical rate constants $k_i$ (mol cm$^{-2}$ s$^{-1}$) and partial standard chemical rate constants $k^o_i$ (cm s$^{-1}$) obtained for OER.

| $k_1$  | $k_{-1}$ | $k_2$  | $k_{-2}$ | $k_3$  | $k_{-3}$ | $k_4$  | $k_{-4}$ | $k_5$  | $k_{-5}$ |
|--------|----------|--------|----------|--------|----------|--------|----------|--------|----------|
| 2.75e-4 | 1.61e-8  | 6.80e-2 | 1.0e-10  | 1.08e-9| 9.59e-1  | 1.16e-4| 1.29e-3  | 2.89e-4| 9.83e-1  |
| $k^o_1$ | $k^o_{-1}$ | $k^o_2$ | $k^o_{-2}$ | $k^o_3$ | $k^o_{-3}$ | $k^o_4$ | $k^o_{-4}$ | $k^o_5$ | $k^o_{-5}$ |
| 2.75e-1 | 1.61e-8  | 6.80e1  | 1.80e-9  | 1.08e-6| 9.59e-1  | 1.16e-1| 2.32e-2  | 2.89e-4| 9.83e-1  |

Figure 12. Experimental and simulated results of the OER current density (a) and inverse of Faradaic resistance (b) versus potential.

be assumed that $R_{cell}$ is the sum of the two resistances due to the differences in the three- and two-electrode set up used in the electrochemical measurements. To illustrate, the electrolyte resistance estimated from the three-electrode cell corresponds to the solution resistance between the working and reference electrodes,$^{27}$ which is approximately half the distance between the electrodes in the electrochemical cell used.

Figure 14 demonstrates a good agreement between experimental cell LSV results and the current-voltage characteristics resulting from Equation 18 using the identified kinetic model. It can be seen that the theoretical model deviates somewhat as the current increases, with approximately a 5%—7% difference between the experimental and theoretical current values. Since the magnitude of the current deviation increases with potential, this behavior can be attributed to overestimation of the total cell solution resistance $R_{cell}$. If the value of $R_{cell}$ is decreased by 5%, the theoretical results produce a perfect fit with experimental values, as shown in Figure S6. The overestimated $R_{cell}$ value obtained from combining the anode and cathode experimental results can be credited to the position of the reference electrode, causing a physical barrier between the two electrodes in the three-electrode cell set up. The cell LSV data, however, were measured by applying the potential directly between the anode and cathode, without the presence of the reference electrode in the cell.

The electrolysis cell characteristics reveal significant electrocatalytic activity of the prepared films toward water electrolysis. A current density of 10 and 100 mA/cm$^2$ can be reached at 1.7 and 2.1 V, respectively. This result is based on a 1 M KOH electrolyte resistance through a distance of approximately 3-4 cm between the electrodes. However, commercial electrolyzers stacks have much smaller
Figure 14. Experimental and simulated cell current versus applied potential.

decomposes, decreases as a result of increasing $\phi_{O_2}$ value, due to the low value of $k_{O_2}$, and the fact that the chemical rate $v_3$ is less dependent on the potential compared to the remaining electrochemical reactions rates.

Understanding the true kinetic behavior of a system allows for a better process design and operation control, especially when certain attributes in the process changes, such as temperature or electrolyte concentration.

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