

UC Berkeley

UC Berkeley Previously Published Works

Title

Disentangling Catalytic Activity and Film Conductivity Reveals Temporally Decoupled Catalyst Evolution and Conductivity Artifacts

Permalink

<https://escholarship.org/uc/item/1tj7462b>

Journal

Journal of the American Chemical Society, 148(39)

ISSN

0002-7863

Authors

Kim, Sung Il
Won, Sunghwan
Park, Jinyeong
[et al.](#)

Publication Date

2026-10-07

DOI

10.1021/jacs.6c16237

Copyright Information

This work is made available under the terms of a Creative Commons Attribution License, available at <https://creativecommons.org/licenses/by/4.0/>

Peer reviewed

Disentangling Catalytic Activity and Film Conductivity Reveals Temporally Decoupled Catalyst Evolution and Conductivity Artifacts

Sung Il Kim,^{1,5} Sunghwan Won,^{1,5} Jinyeong Park,¹ Donghwi Na,¹ Shannon W. Boettcher,^{2,3} and Taek Dong Chung^{*1,4}

¹Department of Chemistry, Seoul National University, Seoul 08826, Republic of Korea.

²Departments of Chemical & Biomolecular Engineering and Chemistry, University of California, Berkeley, California 94720, United States

³Energy Technology and Systems Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States

⁴Advanced Institutes of Convergence Technology, Suwon-Si, Gyeonggi-do 16229, Republic of Korea.

⁵These authors contributed equally to this work.

ABSTRACT: Catalytic activity and electrical conductivity are critical to the performance of electrocatalysts and electrochemical devices, yet their combined assessment under operating conditions remains challenging. Here, we introduce *operando* Fourier-transform electrochemical source–drain impedance spectroscopy (FT-ESDIS), which simultaneously measures catalyst-film conductivity and charge-transfer resistance (R_{ct}) with high temporal resolution at high current densities. During Fe incorporation into nickel (oxy)hydroxide (NiO_xH_y), FT-ESDIS revealed that catalytic activation and charge transport property evolve on distinct timescales, demonstrating that activity alone cannot capture catalyst-layer evolution during operation. At higher overpotentials, nickel-containing (oxy)hydroxides ($\text{Ni(Fe)O}_x\text{H}_y$) showed an abrupt apparent conductivity increase upon oxidation, with conductivity remaining nearly unchanged thereafter, whereas iron (oxy)hydroxide (FeO_xH_y) exhibited a gradual increase in apparent conductivity. Previous reports attributed this overpotential-dependent increase to the formation of high-valent Fe species. However, we show that the increase arises predominantly from an electrolyte-mediated current artifact, in which a potential perturbation at one electrode changes the local solution potential at the neighboring electrode surface and modulates its Faradaic current, producing an apparent conductivity response without direct through-film transport. We further establish a quantitative relationship between this artifact and R_{ct} , enabling its estimation and subtraction from the apparent conductivity. The corrected FeO_xH_y conductivity exhibits substantially weaker potential dependence, suggesting that charge transport involving high-valent Fe species, if present, contributes much less than inferred from the uncorrected response. By resolving kinetic and transport properties under operating conditions, FT-ESDIS provides a more comprehensive basis for interpreting electrocatalyst behavior and establishes transport and reactivity as complementary descriptors for electrochemical energy-conversion systems.

1. INTRODUCTION

The design of efficient porous electrode structures and electrocatalysts is crucial for electricity-driven production of chemical fuels and feedstocks.^{1,2} Electrolytic hydrogen is the simplest chemical product to produce electrochemically and has broad utility as a fuel, energy storage medium, and chemical reactant.³ Anion-exchange-membrane water electrolysis (AEMWE) is an emerging technology in which advanced electrode and electrocatalyst design is central to meeting practical performance and durability metrics.^{4–7} AEMWE is of particular interest because the local alkaline operating environment enables the use of earth-abundant, non-precious transition metal catalysts, while the membrane electrode architecture offers, in principle, high current densities and good product separation.

However, the poor electrical conductivity of non-precious transition-metal-oxide oxygen evolution catalysts (OECs) complicates electrode design for industrial electrolysis (i.e., $> 1 \text{ A cm}^{-2}$), where conventional conductive carbon additives are generally avoided under OER conditions because of their limited oxidative stability.^{8–12} Previous work has also demonstrated that the electrical conductivity

of the catalyst layer modulates the apparent degradation rates of ionomers.¹³

Accurate assessment of conductivity is particularly important for thick, resistive electrocatalyst layers designed to increase catalyst loading and the number of nominally available active sites.^{14,15} Insufficient electronic connectivity can render a substantial fraction of the catalyst layer electrochemically inaccessible, limiting catalyst utilization and electrode performance. Moreover, the charge-transfer resistance (R_{ct}), typically derived from impedance measurements at a particular current or potential, generally reflects the average catalytic charge-transfer kinetics at the catalyst–electrolyte interface, and is often convoluted with porous electrode conductivity effects. Therefore, simultaneous measurement of electrical conductivity and R_{ct} would facilitate deciphering the microscopic events occurring within the electrocatalyst during its operation.

Nevertheless, current methods address these parameters separately, and the measurements are often conducted at low overpotentials and local current densities not representative of industrial conditions. For catalytic-activity evaluation, frequency response analysis

(FRA)-based electrochemical impedance spectroscopy (EIS) is widely employed to extract R_{ct} .^{16–20} In contrast, catalyst-film conductivity is not typically obtained from conventional EIS, but is instead commonly evaluated by measuring the current generated upon application of a DC bias across the electrocatalyst film. Accurate characterization of catalyst matrix conductivity is particularly important for porous electrocatalysts because, when the matrix is poorly conductive, a substantial fraction of the catalyst layer may remain electronically inaccessible, confining catalytic turnover to regions that are sufficiently connected to the current collector.¹²

The conductivity of dry catalyst layers can be measured simply in air using a two-electrode setup²¹ or a four-point probe in the appropriate geometry.²² However, measurements under dry conditions often do not reflect catalyst conductivity under operational conditions, as ionic transport in the electrolyte solution, such as proton or hydroxide transport, is coupled with electron transfer. The conductivity of the catalyst itself often also depends on the catalyst oxidation state.²³

Current methods for measuring catalyst conductivity in electrolyte solutions typically employ interdigitated array (IDA) electrodes. The IDA is coated with the catalyst layer, as illustrated in **Scheme 1a** (IDA-DC).^{24–27} A small DC potential difference ($\Delta V = 5\text{--}10\text{ mV}$) is applied between the two working electrodes (WEs) to probe current flow through the catalyst film while the common WE potential is swept. However, this offset also places the two catalyst/electrolyte interfaces at slightly different OER overpotentials. Consequently, $I_{WE1} - I_{WE2}$ contains contributions from not only the film conduction current (I_{film}) but also the ΔV -induced difference in catalytic OER current ($I_{OER,\Delta V}$). Conventional IDA-DC measurements assume that $I_{OER,\Delta V}$ is much smaller than I_{film} and estimate I_{film} as $(I_{WE1} - I_{WE2})/2$. Yet, this approximation generally breaks down at high current densities because the exponential potential dependence of OER kinetics (i.e., Tafel behavior) can translate even a small ΔV into a significant difference in catalytic currents.

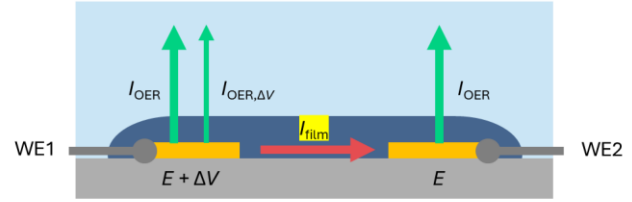
Since $I_{OER,\Delta V}$ eventually overwhelms I_{film} at high overpotentials, $I_{WE1} - I_{WE2}$ cannot accurately reflect the film's conductivity. Consequently, the IDA-DC method is inadequate for *operando* conductivity measurement at current densities relevant to electrolysis devices, creating a need for an alternative methodology capable of decoupling catalytic and transport parameters in a single *operando* measurement under realistic operating conditions.

To address these limitations, we introduce an *operando* impedance-based methodology termed Fourier-transform electrochemical source-drain impedance spectroscopy (FT-ESDIS, **Scheme 1b**), which enables quantitative and simultaneous measurement of R_{ct} and catalyst-layer conductivity. For the *operando* conductivity measurement, instead of a small DC potential offset, a multisine AC perturbation (v_{FT}) is applied to one working electrode (WE1, source), while the corresponding AC current response is monitored at a second working electrode (WE2, drain). Because both electrodes operate at the same DC potential, this configuration eliminates the DC-offset-induced difference in OER background currents, thereby enabling source-drain conductivity measurements under high-overpotential conditions. From the same measurement, the catalytic impedance is determined by separating the solution-directed current response (i.e., the AC component of I_{OER}) from the source-drain current response (i.e., the AC component of I_{film}). A full impedance

spectrum can be acquired within a second because Fourier transformation of the multisine response resolves all applied frequency components in a single acquisition.^{28,29}

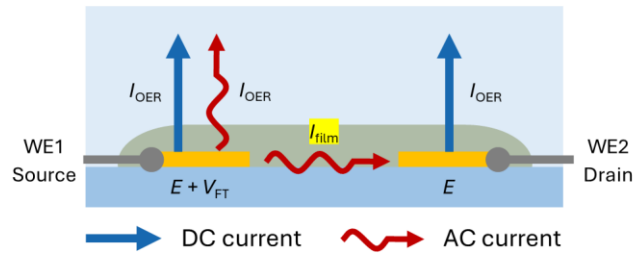
Scheme 1. Schematic representations of (a) conventional conductivity measurement technique using an IDA electrode (IDA-DC) and (b) FT-ESDIS.

(a) Conventional conductivity measurement (IDA-DC)



- $\Delta V = 5\text{--}10\text{ mV}$
 - Assumption: $I_{WE1} - I_{WE2} = 2I_{film}$ ($I_{OER,\Delta V} \approx 0$)
- The assumption is only valid under low ΔV , low I

(b) This work: Fourier-transform electrochemical source-drain impedance spectroscopy (FT-ESDIS)



- Real-time conductivity measurement at high I , η
- Simultaneous measurement of Z_{OER} and Z_{film}

The high temporal resolution of FT-ESDIS, its compatibility with high-overpotential operation, and its ability to assess both catalytic and transport parameters enable comprehensive analysis of porous electrocatalysts. First, we demonstrate that, when soluble iron (Fe) species are incorporated into a nickel (oxy)hydroxide (NiO_xH_y) matrix, catalytic activity and film transport properties evolve on different time scales, a distinction that can be resolved only by simultaneously monitoring R_{ct} and conductivity. Second, we find that the apparent conductivity of NiO_xH_y does not continue to increase at high overpotentials once the film has been oxidized to the conductive NiOOH phase, whereas FeO_xH_y exhibits a gradual increase in apparent conductivity. Most importantly, we show that the apparent conductivity increase of FeO_xH_y at high overpotentials, which has previously been attributed to the formation of high-valent conductive species,²³ does not primarily arise from genuine enhancement of through-film conductivity. Instead, it mainly originates from electrolyte-mediated current interference, which we refer to as “through-solution conduction.” Because this interference becomes increasingly significant for poorly conductive electrocatalysts, we develop a quantitative correction procedure to estimate and subtract the through-solution contribution from the apparent response. The corrected conductivity of FeO_xH_y exhibits substantially weaker potential dependence, suggesting that the contribution of higher-valent Fe

sites, if formed, is likely much smaller than inferred from the uncorrected conductivity response. This work highlights the importance of disentangling catalytic kinetics, charge transport, and measurement-induced artifacts when assigning structure–property relationships in porous electrocatalysts, providing a more reliable basis for catalyst and electrode design under realistic operating conditions.

2. RESULTS AND DISCUSSION

2.1. AC perturbation decouples charge-transfer impedance and through-film conductivity

Scheme 1a illustrates the operating principle of the conventional IDA-DC method. When the two electrodes of an IDA are bridged by an electrically conductive OEC layer, applying a small DC potential offset (ΔV) between them while sweeping the common WE potential drives I_{film} . Assuming that the increase in OER current induced by ΔV ($I_{\text{OER},\Delta V}$) is negligible, $I_{\text{WE1}} - I_{\text{WE2}}$ represents conduction through the catalyst film as follows^{23–25,27,30} (see **Note S1** in the Supporting Information for the derivation of the following Equations 1–4):

$$I_{\text{film}} = \frac{I_{\text{WE1}} - I_{\text{WE2}}}{2} \quad (1)$$

However, this equation is only valid when $I_{\text{OER},\Delta V} \approx 0$. This assumption breaks down at high overpotentials due to the exponential dependence of OER current on electrode potential. In the Tafel regime, a small potential increment ΔV can induce a disproportionately large change in catalytic current: for first-row transition metal (oxy)hydroxide OECs with typical Tafel slopes of 30–60 mV dec^{−1}, a ΔV of merely 10 mV can result in a 1.5- to 2-fold increase in catalytic current.²⁴ Consequently, at industrially relevant current densities, $I_{\text{OER},\Delta V}$ becomes comparable to or exceeds I_{film} , rendering Equation 1 unable to accurately isolate the through-film conduction current. The interference from the background OER current can be partially corrected by reversing the sign of ΔV and comparing the resulting current response.²³ However, this approach exhibits limited temporal resolution and may therefore be unsuitable for real-time tracking of the catalyst state, because it requires sequential potential-offset steps and sufficient time to obtain steady-state current.

To overcome the limitations of the conventional IDA-DC approach, we employ a multisine AC perturbation instead of a DC potential offset. This approach avoids the OER current imbalance induced by a DC potential offset, thereby enabling more reliable measurements of catalyst-film conductivity. Importantly, the same multisine AC perturbation also provides access to the catalytic response, allowing catalyst-film conductivity and catalytic activity to be measured simultaneously with high temporal resolution. Although the following description is given in the context of water oxidation catalysts, the technique is general to any electrocatalytic system.

Scheme 1b illustrates the AC and DC current components in the electrochemical system when a multisine AC perturbation (v_{FT}) is applied to WE1. Since the AC perturbation contains both positive and negative signs, the time-averaged potentials applied to WE1 and WE2 are identical. In FT-ESDIS, WE1 acts as the source electrode, to which a multisine AC perturbation is applied, while WE2 serves as the drain electrode, where the transmitted AC current is collected. Unlike conventional FRA-EIS, which sequentially imposes single-

frequency sinusoidal perturbations, FT-ESDIS applies a multisine waveform generated by superimposing sine waves at selected angular frequencies, ω_k . Fourier transformation of the recorded voltage and current signals then yields the impedance response at all applied frequency components at once.^{28,29,31} This approach enables much faster data acquisition than FRA, allowing impedance spectra to be acquired *operando*. **Figure 1a, b** illustrates a practical FT-ESDIS configuration for OEC films, showing an IDA electrode coated with an electrodeposited OEC film.

Because the AC voltage perturbation is superimposed only on WE1, WE2 should not exhibit a film-mediated AC current component unless WE1 and WE2 are electronically connected. When the two electrodes are bridged by a conductive OEC film, however, AC current can flow from WE1 to WE2 through the film. Under this ideal source–drain assignment, the AC component of I_{WE2} is attributed to the current transmitted from WE1 to WE2 through the conductive film, allowing the through-film current (I_{film}) to be selectively extracted by Fourier transformation while eliminating the DC current contribution:

$$\tilde{I}_{\text{film}}(\omega_k) = -\mathcal{F}\{I_{\text{WE2}}\}(\omega_k) \quad (2)$$

where $\mathcal{F}\{X\}$ denotes the Fourier transform of X . The negative sign accounts for the current convention at WE2. The corresponding film impedance (Z_{film}) measured between WE1 and WE2 through the catalyst film can then be expressed as follows (for detailed derivation, see **Note S1** in the Supporting Information):

$$Z_{\text{film}}(\omega_k) = \frac{v_{\text{FT}}(\omega_k)}{\tilde{I}_{\text{film}}(\omega_k)} = -\frac{\mathcal{F}\{v_{\text{FT}}\}(\omega_k)}{\mathcal{F}\{I_{\text{WE2}}\}(\omega_k)} \quad (3)$$

Therefore, Z_{film} provides a measure of the through-film impedance of the electronically connected catalyst layer.

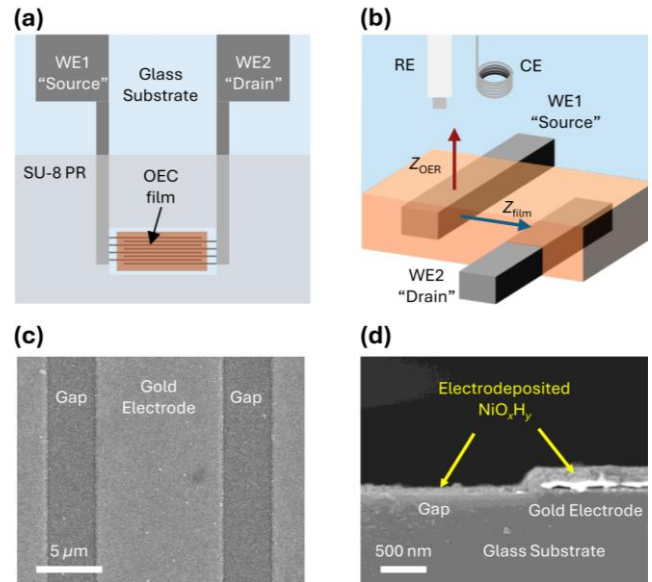


Figure 1. (a) Schematic illustration of the IDA electrode coated with an electrodeposited OEC film and (b) the corresponding current pathways probed by FT-ESDIS, yielding Z_{film} and Z_{OER} . (c) Top-view and (d) cross-sectional SEM images of NiO_xH_y film electrodeposited at -0.1 mA cm^{-2} for 20 min.

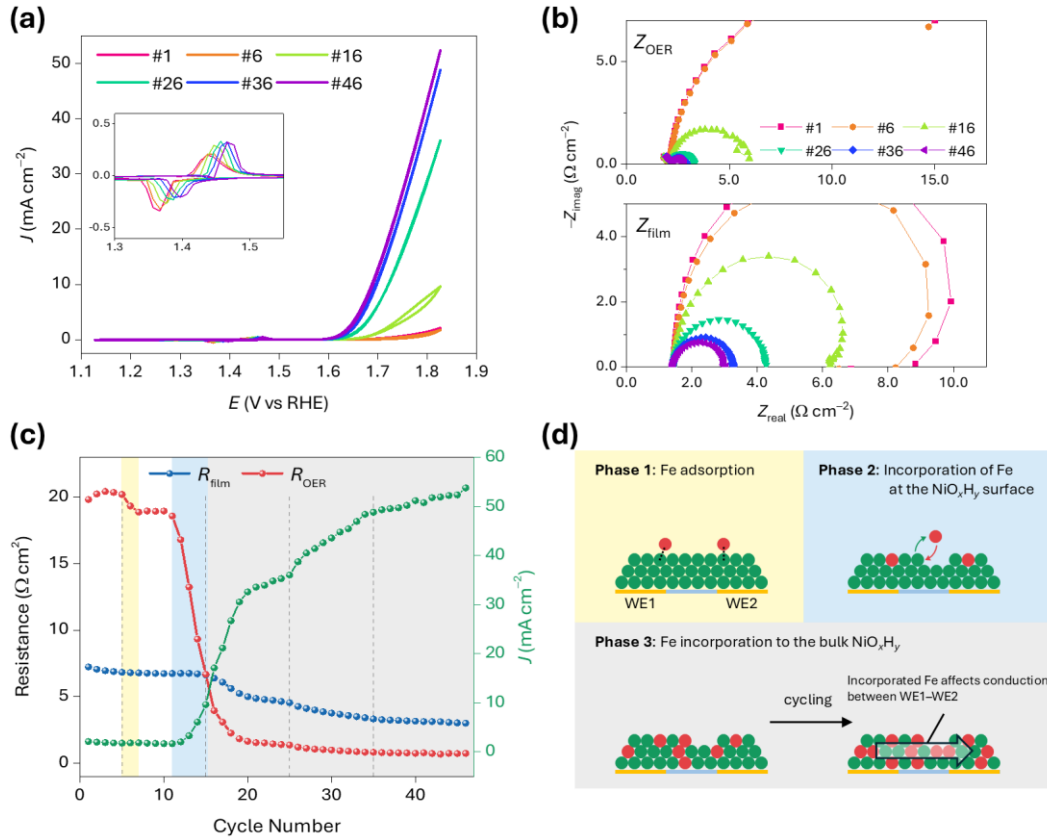


Figure 2. Simultaneous monitoring of the catalyst film impedance (Z_{film}) and OER impedance (Z_{OER}) during Fe incorporation into NiO_xH_y. Fe(NO₃)₃ was spiked after the 5th, 15th, 25th, and 35th cycles and the final concentration of Fe was 8 μM . (a) CVs of NiO_xH_y in 1.0 M KOH at the first cycle and after each Fe addition at a scan rate of 10 mV s⁻¹. The inset shows a magnified view of the nominal Ni^{2+/3+} redox window. (b) Representative Nyquist plots of Z_{OER} and Z_{film} at 1.826 V vs RHE for selected cycles during Fe incorporation. (c) Evolution of catalyst film resistance (R_{film}), charge-transfer resistance for OER (R_{OER}), and current density at 1.826 V vs. RHE during the potential cycling. (d) Schematic illustration of the proposed three-phase model for Fe incorporation into the electrodeposited NiO_xH_y layer.

At the same time, FT-ESDIS also provides access to the OER impedance (Z_{OER}). The AC current directed from WE1 toward the electrolyte, which corresponds to the AC OER current, can be extracted by summing the currents measured at WE1 and WE2, $I_{\text{WE1}} + I_{\text{WE2}}$, because this summation cancels out the through-film current contribution. Analogous to the extraction of Z_{film} , Z_{OER} can be obtained from this electrolyte-directed current as follows (**Note S1**):

$$Z_{\text{OER}}(\omega_k) = \frac{\mathcal{F}\{v_{\text{FT}}\}(\omega_k)}{\mathcal{F}\{I_{\text{WE1}} + I_{\text{WE2}}\}(\omega_k)} \quad (4)$$

Equations 3 and 4 show that applying an AC perturbation to WE1 enables simultaneous evaluation of complex, frequency-dependent Z_{film} and Z_{OER} , while maintaining the average potential of the two working electrodes identical. Therefore, the catalytic parameters can be extracted reliably even under high-overpotential conditions. The current pathways associated with Z_{OER} and Z_{film} are indicated in **Figure 1b**.

In the low-frequency limit, Z_{film} converges to a real resistance R_{film} , corresponding to the DC resistance of the catalyst film. This can be further converted to effective film conductivity as $\sigma = d/(R_{\text{film}}A)$, where d is the IDA gap distance and A is the electroactive surface area of one IDA electrode (see **Note S1** for derivation).^{23–25,27,30} Because this conversion employs a simplified geometric approximation using the projected IDA area rather than the true current-carrying cross-sectional area of the porous and nonuniform catalyst film, the resulting value should be regarded as an effective conductivity rather than an intrinsic bulk conductivity. Accordingly, throughout this

work, σ denotes effective conductivity, which is referred to simply as “conductivity” unless otherwise specified.

For the experimental implementation of FT-ESDIS, OECs were electrodeposited on Au IDA electrodes to form catalyst films that electronically connect the two working electrodes. The OEC films were electrodeposited at -0.1 mA cm^{-2} for 20 min to ensure electrical connection between the two working electrodes. As a representative example, **Figure 1c, d** show the top-view and cross-sectional scanning electron microscopy (SEM) images of an electrodeposited NiO_xH_y film, which confirm that the film bridges the IDA fingers. The composition of the film was also confirmed by EDS mapping (**Figure S4**).

To validate the FT-ESDIS system, the impedance of a dummy cell was first measured (**Note S1, Figure S2**). The resulting Nyquist plot shows clear separation between the impedances measured across WE1–WE2 and those measured between WE1 and RE/CE, where CE denotes a counter electrode. The applicability of FT-ESDIS was then evaluated using a bare Au IDA in an aqueous electrochemical system containing potassium ferri/ferrocyanide ($\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$). The WE1–WE2 impedance reached a minimum near the formal potential of the redox couple, where the coexistence of the oxidized and reduced forms facilitates electrical conduction between the working electrodes, as discussed in detail in **Note S2**.

2.2. Simultaneous, high time-resolution measurement of catalytic activity and conductivity

We applied FT-ESDIS to monitor the dynamic evolution of electrodeposited NiO_xH_y OECs during real-time Fe incorporation (**Figure 2**). This electrocatalytic system requires *operando* analysis because soluble Fe^{3+} progressively incorporates into the NiO_xH_y matrix during potential cycling.³² We deconvoluted the effects of Fe incorporation on catalytic activity and electrical conductivity during catalyst operation.

The NiO_xH_y film was electrodeposited across the IDA to electrically connect the two working electrodes (**Figures 1 and S4**). Typically, the thickness of the NiO_xH_y layer bridging the gap is ~ 100 – 200 nm. Electrodeposited NiO_xH_y films were subjected to continuous potential cycling in 1.0 M KOH. Following a pre-conditioning period of 5 cycles, $\text{Fe}(\text{NO}_3)_3$ was spiked into the electrolyte at the end of cycles 5, 15, 25, and 35, progressively increasing the total Fe concentration by $2\ \mu\text{M}$ with each addition. **Figure 2a** displays the cyclic voltammograms (CVs) of the first and the last (46th) cycle, as well as the cycles immediately after each Fe-spiking event. A pronounced increase in the OER current and a characteristic anodic shift of the $\text{Ni}^{2+/3+}$ redox peak were observed, consistent with the progressive uptake of Fe into the catalyst matrix.^{23,32}

The rapid data acquisition capability of FT-ESDIS enabled full impedance spectra to be collected in real time during potential cycling. **Figure 2b** shows representative Nyquist plots of the film impedance (Z_{film}) and OER impedance (Z_{OER}) acquired at 1.826 V vs RHE during selected cycles throughout Fe incorporation. The potential-dependent evolution of Z_{film} and Z_{OER} within a representative cycle (26th cycle) is provided in **Figure S8**. The DC film resistance (R_{film}) was obtained from the low-frequency limit of the real component of Z_{film} , whereas the OER charge-transfer resistance (R_{OER}) was determined by fitting Z_{OER} to an $R_s(QR_{\text{OER}})$ equivalent circuit (**Figure S6 and S7; Table S3**). The resulting cycle-dependent evolutions of R_{film} , R_{OER} , and the OER current density (J) at 1.826 V vs RHE are presented in **Figure 2c**, where the dashed lines indicate Fe additions after cycles 5, 15, 25, and 35. Both R_{OER} and R_{film} exhibited an overall decrease with successive Fe addition and potential cycling, revealing concurrent improvements in OER kinetics and charge-transport through the catalyst film, respectively.

Based on the trends in catalyst properties obtained *operando*, we identified three phases of the catalyst's evolution (**Figure 2c and d**). In phase 1 (cycles 5–7), a slight decrease in R_{OER} was observed while no apparent shifts were detected for R_{film} , J , and the $\text{Ni}^{2+/3+}$ redox potential. This subtle change is attributed to the adsorption of Fe species on the catalyst surface, which can enhance catalytic activity but has minimal effect on the electronic properties of the overall NiO_xH_y film.

In phase 2 (cycles 11–16), a drastic decrease in R_{OER} accompanied by a noticeable surge in OER current was observed. At the same time, a characteristic anodic shift in the $\text{Ni}^{2+/3+}$ redox peak became prominent (**Figure 2a**, inset). These changes, which emerged during continuous cycling in the Fe-containing electrolyte rather than immediately upon Fe addition, are consistent with the progressive incorporation of Fe species into the NiO_xH_y lattice, along with the formation of surface-active FeO_xH_y species.³² In contrast, R_{film} still remained essentially unchanged.

In phase 3 (from cycle 16 and onward), R_{film} finally began to decrease, while R_{OER} and $\text{Ni}^{2+/3+}$ redox peak continued to follow the trends observed in the previous phase. This temporal lag is likely associated with different spatial sensitivities of R_{OER} and R_{film} within the porous catalyst layer. While R_{OER} can decrease readily upon adsorption of Fe species at the NiO_xH_y surface, likely beginning at the film–electrolyte interface, R_{film} reflects effective lateral electronic transport through the catalyst layer between the IDA electrodes located beneath the film. Consequently, R_{film} may be weighted toward transport pathways connected to the deeper, near-electrode region rather than uniformly reflecting the entire film thickness. The delayed decrease in R_{film} is therefore hypothesized to reflect the slower incorporation of Fe into electrically relevant transport pathways within the catalyst layer.

Because R_{OER} is more sensitive to interfacial catalytic events, whereas R_{film} reflects changes in the electronically connected transport network between the IDA fingers, simultaneous monitoring of these two parameters enables more comprehensive diagnosis of catalyst evolution under operating conditions. The proposed time-dependent Fe incorporation scenario is summarized in **Figure 2d**.

Subsequent Fe additions continued to induce improvements in both conductivity and activity. Although the magnitude of these changes was less pronounced compared to the transition near cycle 16, both properties progressively improved with increasing Fe concentration (**Figure S9**). FT-ESDIS confirmed that Fe spiking induces a conductivity increase analogous to that observed in co-deposited NiFeO_xH_y films.³⁰

2.3. Assessing the conductivity of poorly conductive OEC films at high current densities

Leveraging the capability of FT-ESDIS to monitor the catalyst evolution and dynamics by simultaneously measuring its R_{ct} and electrical conductivity, we next investigated poorly conductive OECs, of which electrical conductivity has a large influence on overall performance.^{12,33} In general, understanding through-film electronic charge-transport and heterogeneous charge-transfer kinetics at the catalyst/electrolyte interface under *operando* conditions is crucial, as unwanted electron transfer pathways may lead to catalyst dissolution and/or degradation of the electrolyzer structure.¹³ Hereafter, conductivity derived directly from the source–drain response is termed “apparent conductivity”, because, as demonstrated below, the electrolyte phase adjacent to a poorly conductive catalyst film can contribute significantly to the measured conductance, leading to an overestimation of through-film conductivity. Sections 2.3 and 2.4 characterize the origin of this contribution and describe its correction, respectively.

We used FT-ESDIS to characterize the conductivity of $\text{Ni}(\text{Fe})\text{O}_x\text{H}_y$ and FeO_xH_y at current densities up to $0.6\ \text{A cm}^{-2}$, substantially expanding the accessible current density range of previous characterizations (typically below $20\ \text{mA cm}^{-2}$).²⁷ Electrodeposited $\text{Ni}(\text{Fe})\text{O}_x\text{H}_y$ and FeO_xH_y films were selected as model systems because the low conductivity of Fe-rich oxyhydroxides, particularly at Fe contents above ca. 25%, can limit catalyst-layer utilization despite the proposed favorable OER energetics of Fe sites.³⁴

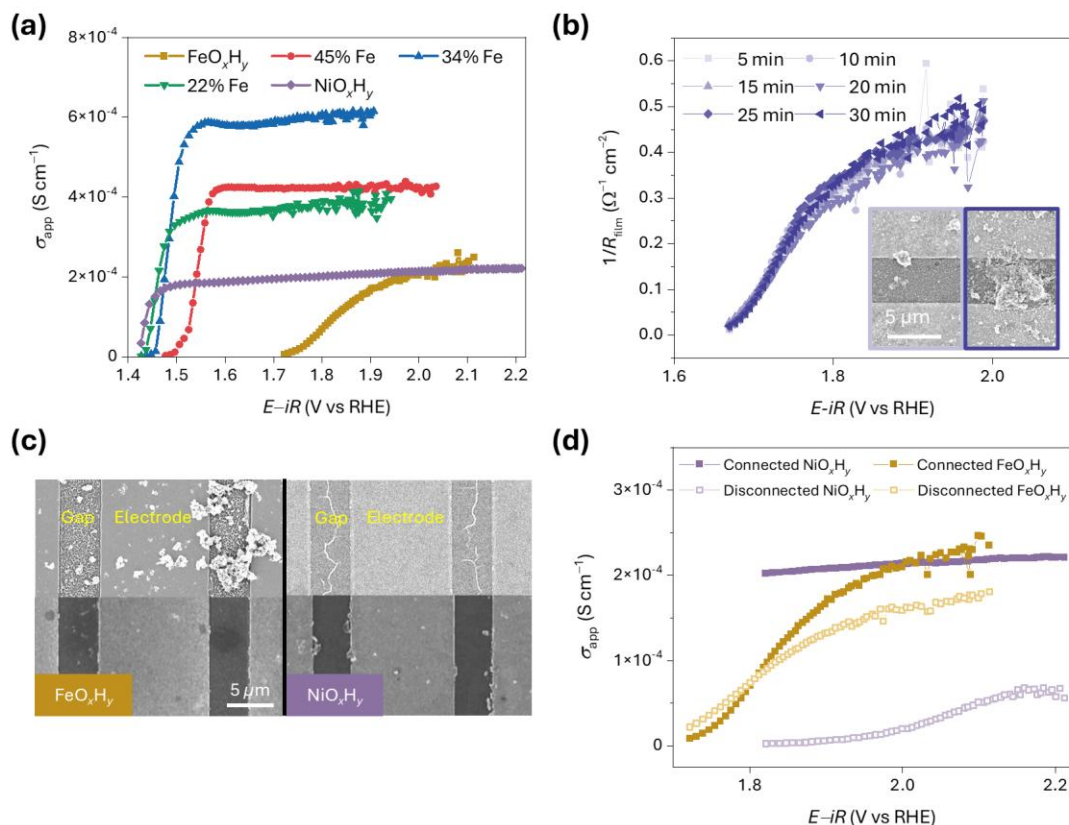


Figure 3. (a) Evolution of apparent conductivity, σ_{app} , of electrodeposited NiO_xH_y, FeO_xH_y, and NiFeO_xH_y films as a function of iR -corrected potential. (b) $1/R_{film}$ of FeO_xH_y films as a function of iR -corrected potential for varying deposition times (5–30 min). Inset shows top-view SEM images of FeO_xH_y films deposited for 10 and 30 min. (c) Top-view SEM images of connected (upper row) and disconnected (lower row) FeO_xH_y and NiO_xH_y films on Au IDA electrodes. (d) σ_{app} of connected (filled symbols) and disconnected (open symbols) NiO_xH_y and FeO_xH_y films as a function of iR -corrected potential.

FeO_xH_y and Ni(Fe)O_xH_y films with varying Fe contents were electrodeposited onto IDA electrodes. Their CVs revealed a progressive anodic shift of the Ni^{2+/3+} redox peak with increasing Fe fraction (**Figure S10**), consistent with previously reported electronic interactions between Ni and Fe centers.²⁴ The Ni-containing electrodeposited films exhibited comparable loadings, as the integrated charges of the nominal Ni^{2+/3+} redox waves ranged from 8.25×10^{-3} to 2.01×10^{-2} C cm⁻², corresponding to 5.15×10^{16} – 1.25×10^{17} cm⁻² nominal redox-accessible site densities, assuming a one-electron Ni^{2+/3+} process (**Table S4**). Fe incorporation markedly increased OER activity, as reflected by an increase in $1/R_{OER}$ (**Figure S11**).

Figure 3a summarizes the potential-dependent apparent conductivities (σ_{app}) of electrodeposited NiO_xH_y, Ni(Fe)O_xH_y, and FeO_xH_y films measured by FT-ESDIS over a broad iR -corrected potential range. The maximum σ_{app} values of NiO_xH_y and FeO_xH_y within the measured potential window were ca. 2×10^{-4} S cm⁻¹, indicating that both films are relatively resistive.^{23,24,35} The apparent conductivity of Ni(Fe)O_xH_y increased with Fe content up to 34% Fe, reaching ca. 6×10^{-4} S cm⁻¹, but decreased at 45% Fe (**Figure 3a**), consistent with previous reports.^{30,36} This decrease at high Fe content may be due, at least in part, to the increasing formation of a separate γ -FeOOH phase above the Fe solubility limit in NiOOH, as previously reported by operando XAS studies.³⁷ Overall, the measured σ_{app} values were on the order of 10^{-4} S cm⁻¹, within one order of magnitude of previously reported values.^{24,30}

The apparent conductivity data obtained by FT-ESDIS further revealed distinct potential-dependent behaviors for Ni-containing and Fe-only oxides. In Ni(Fe)O_xH_y, the apparent conductivity exhibited a clear “turn-on” behavior, surging at the Ni^{2+/3+} oxidation potential and then remaining nearly unchanged at higher potentials (**Figures 3a, S12**). Such behavior can be explained by oxidation of the nominal Ni(OH)₂ into the more-conductive NiOOH phase.^{38,39} Once the nickel-based oxides are oxidized, their apparent conductivity is not significantly affected by further increase in applied potential, even under high current densities over 0.1 A cm⁻².

In contrast, FeO_xH_y displayed a qualitatively different trend. Rather than showing an abrupt increase, its apparent conductivity gradually increased with overpotential. When the OER current density is plotted together with σ_{app} , the gradual increase in σ_{app} is found to coincide with the rise in OER current density (**Figure S13**). A similar trend was reported by Burke et al.²³ and Zhang et al.²⁷ Burke and colleagues showed that the *apparent* conductivity of FeOOH increased with overpotential, from below 10^{-7} S cm⁻¹ at $\eta = 350$ mV to 2.2×10^{-5} S cm⁻¹ at $\eta = 500$ mV, and attributed this increase to the formation of high-valent Fe species. Separately, Zou and coworkers proposed that such increase in conductivity could expand the electronically-accessible layer and thereby enhance the OER current.³⁵ However, here we show that this gradual increase in apparent conductivity instead reflects a measurement artifact rather than a genuine enhancement of the material’s intrinsic conductivity.

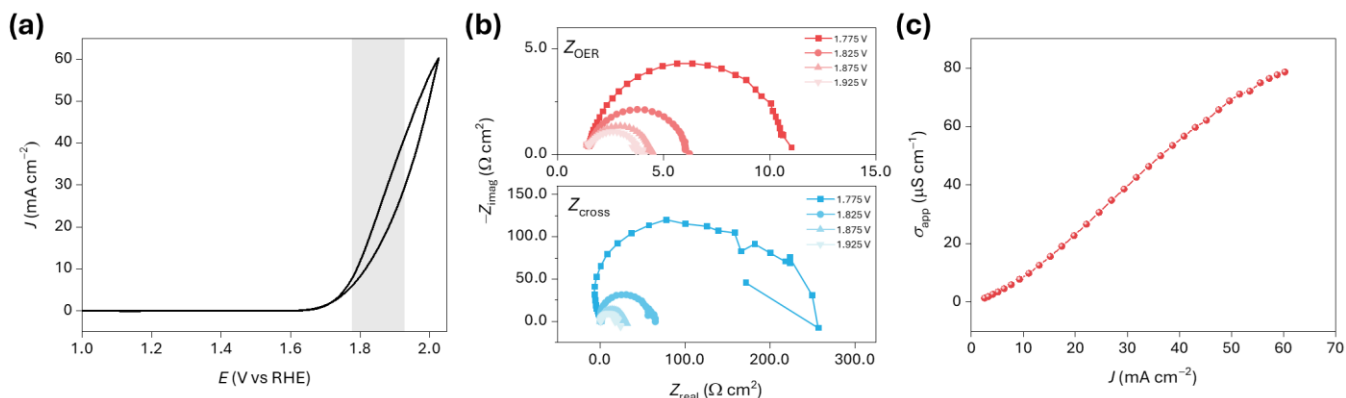


Figure 4. (a) CV of a bare gold IDA in 0.10 mM $\text{Fe}(\text{NO}_3)_3$ + 1.0 M KOH. (b) Nyquist plots of Z_{cross} and Z_{OER} measured at selected potentials from 1.775 to 1.925 V vs RHE (shaded region in (a)). (c) Apparent conductivity calculated from the low-frequency real component of Z_{cross} as a function of OER current density.

To examine the origin of this distinct apparent conductivity behavior of FeO_xH_y , we first investigated the relationship between R_{film} and the amount of electrodeposited FeO_xH_y (**Figure 3b**). Despite increasing the deposition time from 5 to 30 min, the measured R_{film} remained nearly unchanged. If the measured response were dominated by conduction through the FeO_xH_y film, increasing the catalyst loading would be expected to decrease R_{film} . Therefore, this observation suggests that a substantial fraction of the additionally deposited FeO_xH_y does not contribute to this lateral conduction pathway.

Because the additionally deposited FeO_xH_y did not appear to contribute substantially to the film-mediated conduction, we next examined another limiting case. We prepared electrodeposited IDA electrodes in which the electrocatalyst film does not fully span the interelectrode gap (termed “disconnected”) and compared their apparent conductivity behavior with that of normal samples in which WEs are connected by the catalyst film (termed “connected”). The physical connectivity of each film was verified by SEM imaging (**Figure 3c**).

Surprisingly, the disconnected FeO_xH_y film exhibited measurable apparent conductivity at high overpotentials, comparable to that of the connected FeO_xH_y (**Figure 3d**). In contrast, the disconnected NiO_xH_y film displayed negligible apparent conductivity relative to its connected counterpart, as expected for through-film conduction mechanism. If the apparent conductivity increase of FeO_xH_y at high overpotentials originated from direct through-film conduction, it should be significantly suppressed when the film is disconnected, as observed for NiO_xH_y . These unexpected observations suggest that the apparent conductivity measured for FeO_xH_y does not arise solely from direct through-film conduction.

We therefore hypothesized that the WE1–WE2 AC current response observed for the “disconnected” FeO_xH_y was mediated by the electrolyte phase rather than the solid film. To examine this possibility, we employed a homogeneous electrocatalytic system using a bare gold IDA electrode, thereby completely excluding solid-film conduction. The bare gold IDA was immersed in a 1.0 M KOH solution containing 0.10 mM $\text{Fe}(\text{NO}_3)_3$ to drive OER. Upon introduction into the alkaline electrolyte, Fe^{3+} rapidly hydrolyzes and precipitates as amorphous $\text{Fe}(\text{III})$ (oxy)hydroxide species, which subsequently transform into FeOOH phases.⁴⁰ While these precipitates actively catalyze OER, they cannot form a continuous FeOOH net-

work bridging the 5 μm gap between the IDA fingers as the precipitates form via a homogeneous reaction between Fe^{3+} and OH^- and adsorb only on the surface of the Au fingers.

Figure 4a shows the CV of a gold IDA immersed in 0.10 mM $\text{Fe}(\text{NO}_3)_3$ in 1.0 M KOH, exhibiting a moderate OER current. As previously defined, when the IDA is coated with a conductive film, Z_{film} is obtained by dividing the AC perturbation voltage by the AC current measured at WE2, $Z_{\text{film}} = -\mathcal{F}\{v_{\text{FT}}\}/\mathcal{F}\{I_{\text{WE2}}\}$ (Equation 3). However, in the present bare-IDA system, as well as in IDAs with disconnected films, no continuous solid pathway bridges the two working electrodes. Therefore, we analyze the WE2 current response in the same manner but denote the resulting impedance as Z_{cross} rather than Z_{film} .

Figure 4b shows representative Nyquist plots of Z_{cross} and Z_{OER} measured at selected potentials from 1.775 to 1.925 V vs RHE (shaded region in **Figure 4a**). Across this potential range, Z_{cross} exhibits a finite, semicircular Nyquist response similar to Z_{OER} . Thus, the AC perturbation applied to WE1 generates a measurable AC current response at WE2 even in the absence of a conductive solid bridge. Here, Z_{cross} converges to a finite real impedance (R_{cross}) as $\omega \rightarrow 0$, suggesting that this electrolyte-mediated apparent conduction also persists under a DC bias. As the overpotential increases, both Z_{OER} and Z_{cross} decrease (**Figure 4b**), while the apparent conductivity calculated from R_{cross} increases with the catalytic OER current (**Figure 4c**), suggesting that the magnitude of this “through-solution conduction” is amplified as Faradaic current increases. Notably, this behavior closely resembles the increase in σ_{app} observed for FeO_xH_y in parallel with the rise in OER current (**Figure S13**).

The “through-solution” conduction is not limited to oxidation reactions but is also observed in reduction reactions. When a bare gold IDA was biased negatively in 0.50 M H_2SO_4 to drive HER, a semicircular Z_{cross} response was likewise observed upon the onset of HER current (**Figure S14a, b**). Consistent with the OER system, the apparent conductivity derived from the low-frequency real component of Z_{cross} increased with the catalytic HER current (**Figure S14c**). Together, these results indicate that the apparent conductivity of poorly conductive porous electrocatalysts may have been substantially overestimated because of electrolyte-mediated non-film contributions.

Importantly, we find that this electrolyte-mediated conduction pathway also interferes with the conductivity measurement under DC bias, which is the basis of the traditional IDA-DC method (**Scheme 1a**). If a potential offset applied to WE1 also perturbs the

current at WE2 in the absence of a conductive film, such a response would introduce an additional component into $I_{WE1}-I_{WE2}$ and mimic through-film conduction. To examine this possibility, WE1 and WE2 were initially held at -0.41 V vs RHE, after which the potential of WE1 was stepped by ± 10 mV on a bare Au IDA in 0.50 M H_2SO_4 under HER conditions (**Figure S15**). Despite the absence of a conductive film bridging the two electrodes, the current at WE2 changed reproducibly in response to potential steps applied only to WE1. This result demonstrates that a DC perturbation at WE1 can modulate the WE2 current through a non-film pathway.

To assess the impact of this non-film response on conventional IDA-DC measurements, we estimated the purely catalytic $I_{WE1}-I_{WE2}$ expected from the HER Tafel relationship derived from the averaged current, $(I_{WE1}+I_{WE2})/2$, in which the through-solution contribution cancels out (**Note S3**). The experimentally measured $I_{WE1}-I_{WE2}$ was larger than the purely catalytic $I_{WE1}-I_{WE2}$, and the deviation increased with overpotential (**Figure S16**). COMSOL simulations reproduced a similar trend under a 10 mV DC potential offset (**Figure S17, Note S3**). These results show that a non-film contribution can increase $I_{WE1}-I_{WE2}$ beyond that expected from catalytic kinetics alone.

2.4. Mechanistic origin and quantitative correction of the through-solution conduction

In the previous section, we showed that an apparent WE1–WE2 conduction response can be detected even in the absence of a conductive solid material directly bridging the two electrodes. Although the electrolyte is ionically conductive, ionic conduction alone does not provide a steady-state DC interelectrode pathway unless charge transfer occurs at both electrode/electrolyte interfaces through complementary Faradaic reactions, as in redox cycling. Under the strongly anodic OER or cathodic HER conditions examined here, both WEs are biased to drive the same Faradaic reaction rather than toward complementary oxidation and reduction reactions. Thus, conventional redox-cycling-mediated interelectrode charge transport cannot be sustained. The key mechanistic question is therefore how a voltage perturbation at WE1 can modulate the WE2 current, even in the low-frequency/DC limit, in the absence of direct through-film conduction or redox-cycling-mediated charge transport. Here, we examine potential-mediated coupling as the origin of this apparent “through-solution conduction.” We then establish a step-by-step procedure to estimate and subtract the contribution of this coupling from the apparent conductivity response and obtain a corrected estimate of the effective film conductivity of resistive catalysts.

To describe this coupling, we derived an analytical expression for the through-solution impedance (see **Note S4** for details). Briefly, when both WE1 and WE2 operate in a Faradaic regime, a potential perturbation (either DC or AC) at WE1 generates a current, which in turn perturbs the local solution-phase potential at the WE2 surface (ϕ_{WE2}^S). Since the perturbation is applied only to WE1, the electrode potential of WE2 (ϕ_{WE2}^M) remains unchanged. Because heterogeneous electron transfer is governed by the interfacial potential difference ($\phi^M - \phi^S$), any perturbation of ϕ_{WE2}^S directly modulates the charge-transfer kinetics at WE2 even when ϕ_{WE2}^M is constant. Consequently, the potential perturbation applied to WE1 can change the current at WE2, producing an apparent WE1–WE2 current response even in the absence of direct through-film conduction.

The physical relevance of this potential-mediated coupling model is supported by comparing the calculated and experimentally observed Z_{cross} responses in two limiting potential regions: the double-

layer region, where no Faradaic current flows, and the Faradaic region, where catalytic currents flow. In 1.0 M KOH containing 0.10 mM $Fe(NO_3)_3$, the experimentally measured Z_{cross} in the double-layer region appeared in the second quadrant of the Nyquist plot, with a divergent trajectory toward negative real impedance at low frequency, a feature that is not typically observed in conventional three-electrode EIS. The theoretically derived Z_{cross} response calculated using representative R_s and C_{dl} values also showed a divergent trajectory toward the second quadrant, consistent with the limit $Z_{cross} \rightarrow -\infty$ as $\omega \rightarrow 0$ (**Figure S18**). Similar second-quadrant Z_{cross} responses were also observed for heterogeneous electrocatalysts, specifically $Ni(Fe)O_xH_y$ before its apparent conductivity turn-on and FeO_xH_y before its OER onset (**Figure S19**), demonstrating that this behavior is not limited to homogeneous catalytic systems. This low-frequency divergence indicates that, in the non-Faradaic regime, the voltage perturbation at WE1 cannot induce a steady-state current response at WE2 in the DC limit.

In the Faradaic OER region, the experimentally measured Z_{cross} responses for both disconnected catalyst films and homogeneous electrocatalytic systems exhibited a semicircular response in the first quadrant and converged to a finite real resistance at low frequency. The analytical expression derived for the Faradaic regime likewise produced a similar semicircular response and converged to a real low-frequency resistance, R_{cross} , as $\omega \rightarrow 0$ (**Figure S20**). This finite low-frequency limit has direct physical significance: by definition, a finite R_{cross} means that a voltage perturbation applied to WE1 produces a finite current response at WE2 even in the low-frequency/DC limit. Thus, in the Faradaic regime, perturbing WE1 can change the steady-state current at WE2 through potential-mediated coupling. **Figure S21** further shows the continuous evolution of Z_{cross} from the second-quadrant response in the double-layer region to the first-quadrant semicircular response in the OER regime. The agreement between the analytical prediction and experimental observations in both the double-layer and Faradaic regimes supports the conclusion that the apparent through-solution conduction response arises from potential-mediated coupling.

To further test this scenario, we compared the experimentally estimated shift in ϕ_{WE2}^S induced by the voltage perturbation applied to WE1 ($\Delta\phi_{WE2}^S$) with the calculated values obtained from COMSOL simulations for the disconnected FeO_xH_y system (**Figure S22, Note S5**). The experimental estimate was obtained from the measured R_{ct} and R_{cross} values using a small-signal approximation which relates the WE2 current response to the change in the local interfacial potential at WE2 (see **Note S5** for derivation):

$$|\Delta\phi_{WE2}^S| \approx \Delta V_{WE1} \cdot \frac{R_{ct}}{R_{cross}} \quad (5)$$

In the COMSOL simulations, $\Delta\phi_{WE2}^S$ was obtained by comparing the electrolyte-phase potential at the WE2 surface with and without a voltage perturbation applied to WE1. The experimentally inferred and simulated $\Delta\phi_{WE2}^S$ values were of the same order of magnitude (**Figure S22d**), supporting that a potential perturbation at WE1 can modulate the interfacial potential at WE2 through the electrolyte under OER operating conditions. Additional COMSOL simulations further showed that increasing the IDA gap width progressively reduced both the WE1-induced solution-potential perturbation near WE2 and the resulting WE2 Faradaic current modulation (**Figure S23**), demonstrating the geometry dependence of potential-mediated coupling. Taken together, these results support potential-mediated coupling as the origin of the apparent WE1–WE2 conduction

response. Although this response does not represent direct electronic conduction through the solution, it is experimentally manifested as a conduction-like WE1–WE2 response. For consistency with the terminology used in the previous section, we continue to refer to this potential-mediated contribution as “through-solution conduction.”

Having established that ΔV_{WE1} can modulate $\phi_{\text{WE2}}^{\text{S}}$, we next sought a quantitative relationship to estimate and subtract the resulting through-solution contribution from the measured apparent conductivity response and thereby obtain a corrected estimate of the effective conductivity of heterogeneous electrocatalysts. The analytical derivation of the potential-mediated coupling model shows that, in the low-frequency limit, R_{cross} depends on the charge-transfer resistance R_{ct} (denoted as R_{OER} for OEC measurements) according to the quadratic functional form (Note S4):

$$R_{\text{cross}} = AR_{\text{ct}}^2 + BR_{\text{ct}} + C \quad (6)$$

where A , B , and C are coefficients determined by fitting experimental data. This quadratic dependence agrees well with the experimental data obtained from both the homogeneous HER and OER systems described above, with R^2 values close to unity (Note S6, Figure S24). This relationship provides the basis for estimating the through-solution contribution from the measured R_{ct} .

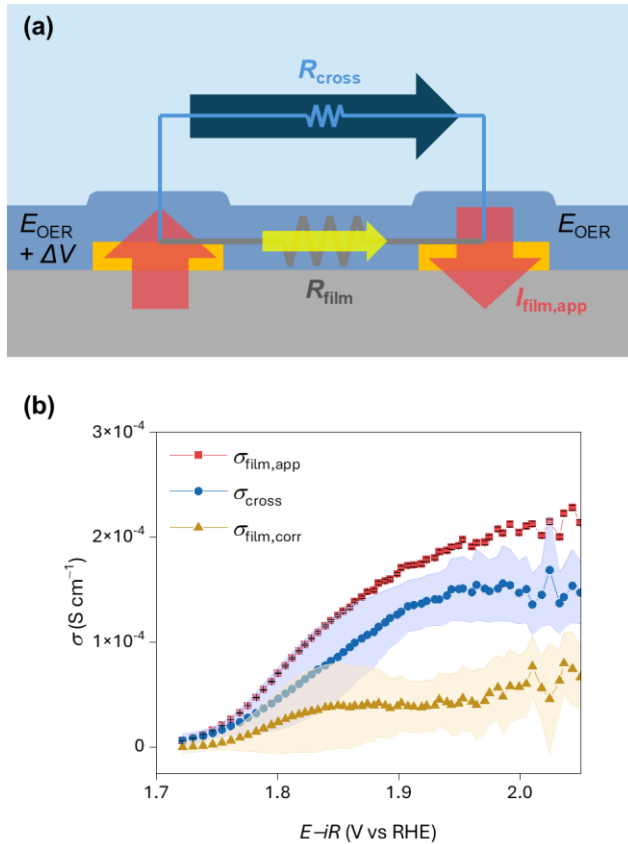


Figure 5. (a) Schematic illustration of the parallel conduction pathways: through-solution and through-film, both contributing to the measured apparent current. (b) Apparent film conductivity, estimated through-solution conductivity, and corrected effective film conductivity of connected FeO_xH_y as a function of applied potential. Shaded regions represent standard deviations obtained by uncertainty propagation.

We then revisited the conductivity measurements for FeO_xH_y films presented in Figure 3. The measured WE1–WE2 response contains a substantial through-solution contribution and therefore does not solely reflect through-film conduction. Therefore, this contribution must be estimated and subtracted to obtain a corrected estimate of the effective film conductivity. By modeling the through-film and through-solution pathways as parallel resistors (Figure 5a), the corrected film resistance ($R_{\text{film,corr}}$) can be estimated from the apparent film resistance ($R_{\text{film,app}}$) as follows (Note S6):

$$\frac{1}{R_{\text{film,corr}}} = \frac{1}{R_{\text{film,app}}} - \frac{1}{R_{\text{cross}}} \quad (7)$$

When the intrinsic film conductivity is sufficiently low, as in the case of FeO_xH_y , the apparent WE1–WE2 conduction signal measured by either conventional IDA-DC or FT-ESDIS can be dominated by through-solution conduction rather than through-film transport. Unlike conventional IDA-DC measurements, however, FT-ESDIS simultaneously provides the corresponding R_{ct} (or R_{OER}), enabling this contribution to be subtracted from the apparent response. To correct for this through-solution conduction contribution when evaluating poorly conductive “connected” films, we applied a two-step correction procedure. First, we determined the coefficients A , B , and C by fitting the R_{cross} and R_{ct} values obtained from the “disconnected” reference film, which excludes any through-film conduction, to the theoretically predicted quadratic relationship $R_{\text{cross}} = AR_{\text{ct}}^2 + BR_{\text{ct}} + C$ (Figure S25). Second, we substituted the measured R_{ct} of the “connected” film into this established equation to calculate its corresponding R_{cross} , allowing us to estimate $R_{\text{film,corr}}$ using Equation 7 (Note S6).

Using the relationship $\sigma = d/(RA)$ to convert resistance to effective conductivity, Equation 7 can be rewritten as:

$$\sigma_{\text{film,corr}} = \sigma_{\text{film,app}} - \sigma_{\text{cross}} \quad (8)$$

where $\sigma_{\text{film,corr}}$, $\sigma_{\text{film,app}}$, and σ_{cross} denote the corrected effective film conductivity, apparent film conductivity, and through-solution conductivity, respectively. Figure 5b shows these three parameters for the connected FeO_xH_y film. Notably, $\sigma_{\text{film,app}}$ is largely dominated by σ_{cross} , indicating that the uncorrected, apparent conductivity of FeO_xH_y primarily reflects an artifact arising from the through-solution conduction rather than film-mediated conduction. Furthermore, while both $\sigma_{\text{film,app}}$ and σ_{cross} increase markedly with applied potential, $\sigma_{\text{film,corr}}$ exhibits a substantially weaker potential dependence, especially after ~ 1.8 V vs RHE. Although previous reports attributed the potential-dependent conductivity increase of FeO_xH_y to the formation of high-valent Fe species,^{23,24,41} the data in Figure 5b suggest that most of this trend may instead reflect potential-dependent through-solution conduction rather than a genuine enhancement of the material’s intrinsic electrical conductivity.

Nevertheless, because the corrected conductivity is obtained by subtracting two comparable contributions, its absolute magnitude and residual potential dependence should be regarded as estimates rather than exact values. The calibration process may also be sensitive to differences in catalyst morphology, surface coverage, and interfacial properties between the connected and disconnected films. Accordingly, the resulting empirical coefficients are most appropriately applied within the same catalyst system and IDA geometry, with the connected and disconnected films prepared under comparable conditions. Quantitatively resolving the effects of the remaining morphological differences will require further systematic investigation. The remaining potential-dependent response may arise from

genuine through-film transport, potentially involving redox-mediated hopping associated with high-valent Fe species, although residual artifactual contributions cannot be excluded.

This distinction has important implications for interpreting catalyst utilization in FeO_xH_y films under OER conditions. If $\sigma_{\text{film,corr}}$ provides a reasonable estimate of the intrinsic film conductivity, electronic transport through the catalyst film may be strongly limited even at high overpotentials, implying that only a portion of the deposited film, rather than the entire porous film, is electronically accessible during catalysis (**Figure 3b**).^{34,35} Therefore, to fully utilize the catalytic capacity of poorly conductive electrocatalysts, electronically conductive components should be incorporated to expand the electrically accessible—and thus potentially electrochemically active—region of the catalyst layer.

To assess whether the through-solution artifact identified for FeO_xH_y also contributes to apparent conductivity measurements of other resistive OECs, we extended our investigation to electrodeposited MnO_xH_y . Previous studies reported that the conductivity of MnO_xH_y becomes measurable near the OER onset, analogous to FeO_xH_y , with reported values remaining in a similarly low-conductivity range.²⁴ During our FT-ESDIS conductivity measurements, large anodic peaks were observed at approximately 1.0 V and 1.4 V vs. RHE, followed by the physical detachment of the catalyst film from the electrode surface (**Figures S26 and S27**). These peaks disappeared after detachment, and no evidence of electrical connectivity between the two IDA fingers was detected in the CV, even under excess catalyst loading (**Figures S26 and S28a**). This loss of film connectivity precluded the connected/disconnected analysis and therefore prevented quantitative correction of the MnO_xH_y film conductivity. Nevertheless, a potential-dependent apparent conductivity increase was still recorded via FT-ESDIS in the high-overpotential region, similar to that observed for FeO_xH_y (**Figure S28b**). The persistence of this response despite the absence of electrical connectivity through the MnO_xH_y film indicates that the measured signal cannot originate from through-film conduction and instead predominantly reflects through-solution conduction. These results also suggest that previously reported onset-associated conductivity increases for MnO_xH_y may likewise have arisen from the through-solution artifact.

Taken together, these results demonstrate that for poorly conductive catalyst films, apparent conductivity values obtained by conventional IDA-DC methods may not reflect the intrinsic film conductivity, as the measured signal can be substantially contaminated by through-solution conduction. While $\sigma_{\text{film,corr}}$ obtained here represents a corrected estimate rather than an absolute intrinsic conductivity, it provides a more physically grounded basis for assessing film conductivity in poorly conductive OECs under operating conditions. Moreover, this information offers practical insight into how resistive transport may limit electronic accessibility and catalyst utilization in thick catalyst layers encountered in practical electrocatalytic devices.

3. CONCLUSION

In this study, we developed FT-ESDIS for the simultaneous, time-resolved measurement of catalytic activity and catalyst-film conductivity under operating conditions. By replacing the conventional DC offset with a multisine AC perturbation, FT-ESDIS enables the decoupled evaluation of R_{ct} and film conductivity even at high overpotentials and current densities. Using Fe incorporation into NiO_xH_y as a model process, we demonstrated that FT-ESDIS resolves the

distinct temporal evolution of catalytic activation and effective film conductivity. These results establish conductivity as a valuable descriptor of the catalyst bulk state and its dynamic evolution during operation.

Furthermore, FT-ESDIS revealed that conductivity values reported for poorly conductive catalysts can be substantially overestimated when through-solution conduction is interpreted as intrinsic through-film transport. This artifact was observed even in the absence of a physically connected catalyst film and was shown to follow a strong R_{ct} -dependent scaling, which can be rationalized by a potential-mediated coupling mechanism. Leveraging this relationship, we established a correction protocol to estimate and subtract the through-solution contribution, thereby obtaining a corrected estimate of the film conductivity of highly resistive catalysts such as FeO_xH_y . In contrast to previously reported conductivity trends, the corrected effective film conductivity, $\sigma_{\text{film,corr}}$ of FeO_xH_y , exhibits substantially weaker potential dependence than the apparent conductivity, indicating that most of the previously observed potential-dependent increase arises from through-solution coupling. Accordingly, although this increase has been attributed to charge transport involving high-valent Fe species, our results indicate that the contribution of this mechanism has likely been substantially overestimated in previous studies based on uncorrected conductivity measurements. These findings suggest that, for poorly conductive catalyst matrices, changes in metal oxidation state alone may be insufficient to substantially enhance charge transport throughout the catalyst layer. Thus, incorporating electronically conductive additives may be necessary to improve the utilization of porous electrocatalyst matrices. Overall, this study provides an operando framework for disentangling catalytic kinetics, film conduction, and electrolyte-mediated artifacts in porous electrocatalysts.

ASSOCIATED CONTENT

Supporting Information. Experimental details; theoretical considerations and conductivity measurements; validation of FT-ESDIS using a reversible solution redox couple; validation of apparent through-solution conduction under DC bias; analytical description of potential-mediated apparent conduction; COMSOL simulations of WE1–WE2 coupling; and correction of the through-solution contribution. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

Taek Dong Chung – tdchung@snu.ac.kr

Author Contributions

S.I.K. and S.W. contributed equally to this work. All the authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (No. RS-2021-NR060082 and RS-2022-NR070547). S.W.B. acknowledges funding from NSF Catalysis Program Award Number 2400195. The authors used ChatGPT (OpenAI) to assist with English-language editing and manuscript organization.

REFERENCES

- (1) Seh, Z. W.; Kibsgaard, J.; Dickens, C. F.; Chorkendorff, I.; Nørskov, J. K.; Jaramillo, T. F. Combining Theory and Experiment in Electrocatalysis: Insights into Materials Design. *Science* (80-.). **2017**, 355, eaad4998. <https://doi.org/10.1126/science.aad4998>.
- (2) Lees, E. W.; Mowbray, B. A. W.; Parlange, F. G. L.; Berlinguette, C. P. Gas Diffusion Electrodes and Membranes for CO₂ Reduction Electrolysers. *Nat. Rev. Mater.* **2022**, 7 (1), 55–64. <https://doi.org/10.1038/s41578-021-00356-2>.
- (3) Walter, M. G.; Warren, E. L.; McKone, J. R.; Boettcher, S. W.; Mi, Q.; Santori, E. A.; Lewis, N. S. Solar Water Splitting Cells. *Chem. Rev.* **2010**, 110 (11), 6446–6473. <https://doi.org/10.1021/cr1002326>.
- (4) Du, N.; Roy, C.; Peach, R.; Turnbull, M.; Thiele, S.; Bock, C. Anion-Exchange Membrane Water Electrolysers. *Chem. Rev.* **2022**, 122 (13), 11830–11895. <https://doi.org/10.1021/acs.chemrev.1c00854>.
- (5) Zheng, Y.; Ma, W.; Serban, A.; Allushi, A.; Hu, X. Anion Exchange Membrane Water Electrolysis at 10 A·cm⁻² Over 800 Hours. *Angew. Chem. Int. Ed.* **2025**, 64, e202413698. <https://doi.org/10.1002/anie.202413698>.
- (6) Li, D.; Motz, A. R.; Bae, C.; Fujimoto, C.; Yang, G.; Zhang, F. Y.; Ayers, K. E.; Kim, Y. S. Durability of Anion Exchange Membrane Water Electrolysers. *Energy Environ. Sci.* **2021**, 14 (6), 3393–3419. <https://doi.org/10.1039/d0ee04086j>.
- (7) Park, E. J.; Arges, C. G.; Xu, H.; Kim, Y. S. Membrane Strategies for Water Electrolysis. *ACS Energy Lett.* **2022**, 7 (10), 3447–3457. <https://doi.org/10.1021/acsenenergylett.2c01609>.
- (8) Möller, S.; Barwe, S.; Masa, J.; Wintrich, D.; Seisel, S.; Baltruschat, H.; Schuhmann, W. Online Monitoring of Electrochemical Carbon Corrosion in Alkaline Electrolytes by Differential Electrochemical Mass Spectrometry. *Angew. Chem. Int. Ed.* **2020**, 59 (4), 1585–1589. <https://doi.org/10.1002/anie.201909475>.
- (9) Möller, S.; Barwe, S.; Dieckhöfer, S.; Masa, J.; Andronesco, C.; Schuhmann, W. Differentiation between Carbon Corrosion and Oxygen Evolution Catalyzed by Ni₂B/C Hybrid Electrocatalysts in Alkaline Solution Using Differential Electrochemical Mass Spectrometry. *ChemElectroChem* **2020**, 7 (12), 2680–2686. <https://doi.org/10.1002/celc.202000697>.
- (10) Filimonenkov, I. S.; Bouillet, C.; Kéranguéven, G.; Simonov, P. A.; Tsirlina, G. A.; Savinova, E. R. Carbon Materials as Additives to the OER Catalysts: RRDE Study of Carbon Corrosion at High Anodic Potentials. *Electrochim. Acta* **2019**, 321, 134657. <https://doi.org/10.1016/j.electacta.2019.134657>.
- (11) Yi, Y.; Weinberg, G.; Prenzel, M.; Greiner, M.; Heumann, S.; Becker, S.; Schlögl, R. Electrochemical Corrosion of a Glassy Carbon Electrode. *Catal. Today* **2017**, 295 (July), 32–40. <https://doi.org/10.1016/j.cattod.2017.07.013>.
- (12) Kreider, M. E.; Yu, H.; Osmieri, L.; Parimuha, M. R.; Reeves, K. S.; Marin, D. H.; Hannagan, R. T.; Volk, E. K.; Jaramillo, T. F.; Young, J. L.; Zelenay, P.; Alia, S. M. Understanding the Effects of Anode Catalyst Conductivity and Loading on Catalyst Layer Utilization and Performance for Anion Exchange Membrane Water Electrolysis. *ACS Catal.* **2024**, 14 (14), 10806–10819. <https://doi.org/10.1021/acscatal.4c02932>.
- (13) Krivina, R. A.; Lindquist, G. A.; Beaudoin, S. R.; Stovall, T. N.; Thompson, W. L.; Twight, L. P.; Marsh, D.; Grzyb, J.; Fabrizio, K.; Hutchison, J. E.; Boettcher, S. W. Anode Catalysts in Anion-Exchange-Membrane Electrolysis without Supporting Electrolyte: Conductivity, Dynamics, and Ionomer Degradation. *Adv. Mater.* **2022**, 34 (35), 2203033. <https://doi.org/10.1002/adma.202203033>.
- (14) Hochfilzer, D.; Chorkendorff, I.; Kibsgaard, J. Catalyst Stability Considerations for Electrochemical Energy Conversion with Non-Noble Metals: Do We Measure on What We Synthesized? *ACS Energy Lett.* **2023**, 8 (3), 1607–1612. <https://doi.org/10.1021/acsenenergylett.3c00021>.
- (15) Kim, Y. T.; Lopes, P. P.; Park, S. A.; Lee, A. Y.; Lim, J.; Lee, H.; Back, S.; Jung, Y.; Danilovic, N.; Stamenkovic, V.; Erlebacher, J.; Snyder, J.; Markovic, N. M. Balancing Activity, Stability and Conductivity of Nanoporous Core-Shell Iridium/Iridium Oxide Oxygen Evolution Catalysts. *Nat. Commun.* **2017**, 8, 1449. <https://doi.org/10.1038/s41467-017-01734-7>.
- (16) Zhao, Y.; Adiyeri Saseendran, D. P.; Huang, C.; Triana, C. A.; Marks, W. R.; Chen, H.; Zhao, H.; Patzke, G. R. Oxygen Evolution/Reduction Reaction Catalysts: From In Situ Monitoring and Reaction Mechanisms to Rational Design. *Chem. Rev.* **2023**, 123 (9), 6257–6358. <https://doi.org/10.1021/acs.chemrev.2c00515>.
- (17) Wang, P.; Yan, M.; Meng, J.; Jiang, G.; Qu, L.; Pan, X.; Liu, J. Z.; Mai, L. Oxygen Evolution Reaction Dynamics Monitored by an Individual Nanosheet-Based Electronic Circuit. *Nat. Commun.* **2017**, 8, 64. <https://doi.org/10.1038/s41467-017-00778-z>.
- (18) Zhai, P.; Wang, C.; Zhao, Y.; Zhang, Y.; Gao, J.; Sun, L.; Hou, J. Regulating Electronic States of Nitride/Hydroxide to Accelerate Kinetics for Oxygen Evolution at Large Current Density. *Nat. Commun.* **2023**, 14, 1873. <https://doi.org/10.1038/s41467-023-37091-x>.
- (19) Sunde, S. Use of Electrochemical Impedance Spectroscopy in the Analysis of the Oxygen Evolution Reaction. *Curr. Opin. Electrochem.* **2026**, 55, 101786. <https://doi.org/10.1016/j.coelec.2025.101786>.
- (20) Lu, Y.; Wang, W.; Xie, F. Investigation of Oxygen Evolution Reaction Kinetic Process and Kinetic Parameters on Iridium Electrode by Electrochemistry Impedance Spectroscopy Analysis. *J. Electroanal. Chem.* **2020**, 871, 114281. <https://doi.org/10.1016/j.jelechem.2020.114281>.
- (21) Xu, D.; Stevens, M. B.; Cosby, M. R.; Oener, S. Z.; Smith, A. M.; Enman, L. J.; Ayers, K. E.; Capuano, C. B.; Renner, J. N.; Danilovic, N.; Li, Y.; Wang, H.; Zhang, Q.; Boettcher, S. W. Earth-Abundant Oxygen Electrocatalysts for Alkaline Anion-Exchange-Membrane Water Electrolysis: Effects of Catalyst Conductivity and Comparison with Performance in Three-Electrode Cells. *ACS Catal.* **2019**, 9 (1), 7–15. <https://doi.org/10.1021/acscatal.8b04001>.
- (22) Parra-Puerto, A.; Ng, K. L.; Fahy, K.; Goode, A. E.; Ryan, M. P.; Kucernak, A. Supported Transition Metal Phosphides: Activity Survey for HER, ORR, OER, and Corrosion Resistance in Acid and Alkaline Electrolytes. *ACS Catal.* **2019**, 9 (12), 11515–11529. <https://doi.org/10.1021/acscatal.9b03359>.
- (23) Burke, M. S.; Kast, M. G.; Trotochaud, L.; Smith, A. M.; Boettcher, S. W. Cobalt-Iron (Oxy)Hydroxide Oxygen Evolution Electrocatalysts: The Role of Structure and Composition on Activity, Stability, and Mechanism. *J. Am. Chem. Soc.* **2015**, 137 (10), 3638–3648. <https://doi.org/10.1021/jacs.5b00281>.
- (24) Burke, M. S.; Zou, S.; Enman, L. J.; Kellon, J. E.; Gabor, C. A.; Pledger, E.; Boettcher, S. W. Revised Oxygen Evolution Reaction Activity Trends for First-Row Transition-Metal (Oxy)Hydroxides in Alkaline Media. *J. Phys. Chem. Lett.* **2015**, 6 (18), 3737–3742. <https://doi.org/10.1021/acs.jpcclett.5b01650>.
- (25) Brodsky, C. N.; Bediako, D. K.; Shi, C.; Keane, T. P.; Costentin, C.; Billinge, S. J. L.; Nocera, D. G. Proton–Electron Conductivity in Thin Films of a Cobalt–Oxygen Evolving Catalyst. *ACS Appl. Energy Mater.* **2019**, 2 (1), 3–12. <https://doi.org/10.1021/acsaem.8b00785>.
- (26) Gu, H.; Shi, G.; Chen, H. C.; Xie, S.; Li, Y.; Tong, H.; Yang, C.; Zhu, C.; Mefford, J. T.; Xia, H.; Chueh, W. C.; Chen, H. M.; Zhang, L. Strong Catalyst-Support Interactions in Electrochemical Oxygen Evolution on Ni-Fe Layered Double Hydroxide. *ACS Energy Lett.* **2020**, 5 (10), 3185–3194. <https://doi.org/10.1021/acsenenergylett.0c01584>.
- (27) Zhang, H.; Wu, L.; Ni, Y.; Feng, J.; Jiang, Q.; Zhang, C.; Ahmad, A.; Majeed, A.; Li, Y.; Guo, C.; Zhang, W.; Song, F. Effect of Transport Properties of Crystalline Transition Metal (Oxy)Hydroxides on Oxygen Evolution Reaction. *ACS Appl. Mater. Interfaces* **2023**, 15 (21), 25575–25583. <https://doi.org/10.1021/acsami.3c03270>.
- (28) Kim, S. Il; Chung, T. D. In Situ Real-Time Dendritic Growth Determination of Electrodeposits on Ultramicroelectrodes. *Anal. Chem.* **2024**, 96, 3096–3106. <https://doi.org/10.1021/acs.analchem.3c05239>.
- (29) Han, S. H.; Rho, J.; Lee, S.; Kim, M.; Kim, S. Il; Park, S.; Jang, W.; Lee, C. H.; Chang, B. Y.; Chung, T. D. In Situ Real-Time Monitoring of ITO Film under a Chemical Etching Process Using Fourier Transform Electrochemical Impedance Spectroscopy. *Anal. Chem.* **2020**, 92 (15), 10504–10511. <https://doi.org/10.1021/acs.analchem.0c01294>.
- (30) Trotochaud, L.; Young, S. L.; Ranney, J. K.; Boettcher, S. W. Nickel-Iron Oxyhydroxide Oxygen-Evolution Electrocatalysts: The Role of

- Intentional and Incidental Iron Incorporation. *J. Am. Chem. Soc.* **2014**, *136* (18), 6744–6753. <https://doi.org/10.1021/ja502379c>.
- (31) Kim, S. Il; Shin, K.; Kang, H.; Han, S. H.; Kim, H. T.; Chung, T. D. Asymmetric Mass Transport in Polybromide Ionic Liquids and Its Impact on Dual-Plating Zinc Bromine Batteries. *Adv. Sci.* **2026**, *13*, e22078. <https://doi.org/10.1002/advs.202522078>.
- (32) Ou, Y.; Twight, L. P.; Samanta, B.; Liu, L.; Biswas, S.; Fehrs, J. L.; Sagui, N. A.; Villalobos, J.; Morales-Santelices, J.; Antipin, D.; Risch, M.; Toroker, M. C.; Boettcher, S. W. Cooperative Fe Sites on Transition Metal (Oxy)Hydroxides Drive High Oxygen Evolution Activity in Base. *Nat. Commun.* **2023**, *14*, 7688. <https://doi.org/10.1038/s41467-023-43305-z>.
- (33) Chung, D. Y.; Park, S.; Lopes, P. P.; Stamenkovic, V. R.; Sung, Y. E.; Markovic, N. M.; Strmcnik, D. Electrokinetic Analysis of Poorly Conductive Electrocatalytic Materials. *ACS Catal.* **2020**, *10* (9), 4990–4996. <https://doi.org/10.1021/acscatal.0c00960>.
- (34) Morales-Guio, C. G.; Liardet, L.; Hu, X. Oxidatively Electrodeposited Thin-Film Transition Metal (Oxy)Hydroxides as Oxygen Evolution Catalysts. *J. Am. Chem. Soc.* **2016**, *138* (28), 8946–8957. <https://doi.org/10.1021/jacs.6b05196>.
- (35) Zou, S.; Burke, M. S.; Kast, M. G.; Fan, J.; Danilovic, N.; Boettcher, S. W. Fe (Oxy)Hydroxide Oxygen Evolution Reaction Electrocatalysis: Intrinsic Activity and the Roles of Electrical Conductivity, Substrate, and Dissolution. *Chem. Mater.* **2015**, *27* (23), 8011–8020. <https://doi.org/10.1021/acs.chemmater.5b03404>.
- (36) Corrigan, D. A. The Catalysis of the Oxygen Evolution Reaction by Iron Impurities in Thin Film Nickel Oxide Electrodes. *J. Electrochem. Soc.* **1987**, *134* (2), 377–384. <https://doi.org/10.1149/1.2100463>.
- (37) Friebe, D.; Louie, M. W.; Bajdich, M.; Sanwald, K. E.; Cai, Y.; Wise, A. M.; Cheng, M. J.; Sokaras, D.; Weng, T. C.; Alonso-Mori, R.; Davis, R. C.; Bargar, J. R.; Nørskov, J. K.; Nilsson, A.; Bell, A. T. Identification of Highly Active Fe Sites in (Ni,Fe)OOH for Electrocatalytic Water Splitting. *J. Am. Chem. Soc.* **2015**, *137* (3), 1305–1313. <https://doi.org/10.1021/ja511559d>.
- (38) Haghverdi Khamene, S.; van Helvoirt, C.; Tsampas, M. N.; Creatore, M. Electrochemical Activation of Atomic-Layer-Deposited Nickel Oxide for Water Oxidation. *J. Phys. Chem. C* **2023**, *127* (46), 22570–22582. <https://doi.org/10.1021/acs.jpcc.3c05002>.
- (39) Treps, L.; Ermacora, T.; Giacomelli, A.; Michel, C.; Steinmann, S. N. Surface State of NiOOH under Oxidative Conditions: Can Dopants Induce Surface Oxidation? *Electrochim. Acta* **2025**, *524* (December 2024), 145960. <https://doi.org/10.1016/j.electacta.2025.145960>.
- (40) Furcas, F. E.; Lothenbach, B.; Mundra, S.; Borca, C. N.; Albert, C. C.; Isgor, O. B.; Huthwelker, T.; Angst, U. M. Transformation of 2-Line Ferrihydrite to Goethite at Alkaline PH. *Environ. Sci. Technol.* **2023**, *57* (42), 16097–16108. <https://doi.org/10.1021/acs.est.3c05260>.
- (41) Lin, F.; Bachman, B. F.; Boettcher, S. W. Impact of Electrocatalyst Activity and Ion Permeability on Water-Splitting Photoanodes. *J. Phys. Chem. Lett.* **2015**, *6* (13), 2427–2433. <https://doi.org/10.1021/acs.jpclett.5b00904>.

