The Electrocatalytic Evolution of Oxygen and Hydrogen by Cobalt and Nickel Compounds

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The Electrocatalytic Evolution of Oxygen and Hydrogen by Cobalt and Nickel Compounds

A dissertation presented

by

Daniel Kwabena Dakwa Bediako

to

The Department of Chemistry and Chemical Biology

in partial fulfillment of the requirements
for the degree of

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The Electrocatalytic Evolution of Oxygen and Hydrogen by Cobalt and Nickel Compounds

In order to meet the ever-increasing demand for energy, a worldwide transition away from fossil fuels to renewable solar–fuels is required. However, the intermittency of local insolation mandates a cost-effective and efficient storage scheme. Using solar-derived electricity to drive the thermodynamically uphill water splitting reaction to generate dihydrogen and dioxygen is one promising method of storing solar energy in fuels.

This “artificial photosynthesis” scheme requires the execution of two half-reactions, one involving the oxidation of water to $\text{O}_2$—the oxygen evolution reaction (OER)—and the other entailing the reduction of hydrogen ions to $\text{H}_2$—the hydrogen evolution reaction (HER). Accomplishing these electrocatalytic reactions stresses the development of catalysts that are capable of mediating reactions that are in net multi-electron, multi-proton transformations.

Transition metal oxides are known to be promising candidates for mediating the OER and their electrocatalytic properties have been studied extensively and optimized for operation at pH extremes. In contrast, intermediate pH OER has been relatively underexplored and the influence of proton-coupled electron transfer (PCET) reactions on OER kinetics of these materials at close-to-neutral pH has for long remained unclear. The OER studies described here have focused on elucidating the underlying mechanistic basis for the catalytic behavior of a class of structurally disordered first-row transition metal oxides, with an emphasis on intermediate-pH catalysis and proton–electron coupling.

At a fundamental level, understanding how protons and electrons may be managed and coupled to engender improved activity remains of great importance to the design of new electrocatalysts. To this end, the synthesis and study of homogeneous HER catalysts bearing functional groups in the second coordination sphere that can modulate proton–electron coupling is particularly interesting. The HER studies presented here discuss this important issue within the context of metalloporphyrin catalysts possessing proton relays.
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Figure 4.1. Qualitative band diagram of a double junction PV–PEC water splitting cell depicting the thermodynamic potential separation of the OER and HER (•••), and the quasi–Fermi level (•••) and bend edge positions (—) throughout the cell under illumination with sustained water splitting at current density, \(j\). The potential at each solution interface is given by the OER, \(\eta_{\text{OER}}\), and HER, \(\eta_{\text{HER}}\), overpotentials required to sustain the operating current density, \(j\). For clarity of representation, solution and contact resistance losses are omitted.

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Figure 5.1. Electrocatalytic oxidation of the substrate A into the products B in the presence of an acid-base couple ZH⁺/Z by means of an immobilized PH/Q + e⁻ catalyst couple.

Figure 5.2. Electrocatalytic oxidation of water into the products dioxygen and protons in the presence of an acid–base couple ZH⁺/Z.

Figure 5.3. Electrokinetic profile at large buffer concentrations. (a) Tafel plot trends predicted for a series of increasing thicknesses, from bottom to top. (b) Variation of the current density with the film thickness (relative to the optimal film thickness (d_f^{opt}), at η = 0. j₀ and j₀^{max} are defined in equations (5.7a & 5.7b) and (5.9a & 5.9b), respectively. For d_f see equation (5.8). (c) Concentration profile of oxidized catalyst form, Q (relative to the concentration of Q at the electrode–film interface), in the case of mixed control by the turnover-limiting reaction and the diffusion-like proton–electron hopping under pure kinetic conditions for a series of films with thicknesses equal to 0.5d_f^{opt}, d_f^{opt}, 2d_f^{opt}, and 3d_f^{opt}. (d) Concentration profile of Q (relative to total catalyst concentration in the film) as a function of increasing electrode potential (from bottom to top) for a film of thickness equal to d_f^{opt}.

Figure 5.4. Tafel data in the absence of buffer. (a) Tafel plots predicted for a series of increasing thicknesses from bottom to top. (b) Variation of the current density at η = 0 with the film thickness (relative to the optimal film thickness). j₀ and j₀^{max} are defined in equations (5.7a, 5.7b) and (5.9a, 5.9b) respectively. j_{H,out} is defined in Table 5.1.

Figure 5.5. Koutecky–Levich plots in absence of buffer: j₀/j as function of diffusion layer thickness, δ, for two different values of the overpotential: η = 0.4 (red squares) and η = 0.5 (blue dots) with j₀ = 2 × 10^{-10} A/cm², D_{H,out} = 5 × 10^{-5} cm²/s, C_{H⁺}^{0} = 10^{-6} M (pH 6). Dots correspond to typical rotation rates:
2500, 1600, 1225, 900 and 625 rpm (using equation (5.1) with \( v = 10^{-2} \text{ cm}^2/\text{s} \)). Dotted lines correspond to purposely forced linear fitting of the data corresponding to rotation rates between 625 and 2500 rpm.

**Figure 5.6.** Tafel plots (full lines) predicted for intermediate buffer concentrations, showing the passage from joint control by catalytic reaction and proton–electron hopping (blue) to joint control by catalytic reaction, proton–electron hopping and proton diffusion (red), for a series of \( j_{Z,\,\text{out}}/j_0 \) values (10, 10\(^2\), 10\(^3\), 10\(^4\), 10\(^5\) from bottom to top) corresponding to increasing values of buffer concentration (\( j_{Z,\,\text{out}} = F D_{Z,\,\text{out}} C_{Z}^0 / \delta \)). The figure has been plotted for the following values of the other parameters: \( C_{Z}^0 / C_{Z}^0 = 1 \) (the pH is equal to the p\( K_{a} \) of \( ZH^+ \)) and \( j_0/j_{H,\,\text{out}} = 100 \).

**Figure 5.7.** (a) Tafel plots of Co–P\(_i\) films operated in 0.1 M NaP\(_i\) pH 7 electrolyte with increasing film thicknesses 40 nm (blue), 120 nm (green), 400 nm (red), 1024 nm (yellow), 2665 nm (magenta) (for the estimation of the film thickness, see Section 5.6). Rotation rate: 1000 rpm. The slope of the solid lines is \( F/RT \ln 10 \). (b) Variation of the exchange current density with the film thickness. Solid line: fitting according to \( j_0 = j_0^\text{max} \tanh(d_f/d_f^{\text{opt}}) \) (eq. 5.10).

**Figure 5.8.** Tafel plots of Co–P\(_i\) films operated in 0.1 M NaClO\(_4\) pH 6 electrolyte with no buffer present as a function of approximate film thickness (in nm) 48 (red), 200 (green), 575 (blue) at two rotation rates. (a) 2500 rpm. (b) 625 rpm. The slope of the solid lines is \( F/2RT \ln 10 \).

**Figure 5.9.** (a) \( j_{H,\,\text{out}} \times j_0 \) as function of 1/\( \delta \) (using equation 5.1 with \( D = 5 \times 10^{-5} \text{ cm}^2/\text{s} \) and \( v = 10^{-2} \text{ cm}^2/\text{s} \)) for films of various estimated film thicknesses (in nm) 48 (red), 200 (green), 575 (blue). (b) Slopes, \( \Sigma \), of the straight lines in (a) as a function of film thickness relative to optimal film thickness (\( \Sigma = D_{H,\,\text{out}} C_{H}^0 j_{0,\,\text{PH6}}^\text{max} d_f/d_f^{\text{opt}} \)).

**Figure 5.10.** Tafel plots of 200 nm Co–P\(_i\) films operated in operated in 0.1 M NaClO\(_4\) with no buffer present, pH: 6.0 (blue), 6.2 (green), 6.4 (red), 6.6 (yellow), 6.8 (magenta), 7.2 (orange), at two rotation rates. (a) 2500 rpm and (b) 625 rpm. The slopes of the straight lines are \( F/2RT \ln 10 \) (1/120 mV).

**Figure 5.11.** Tafel plots of a 200 nm Co–P\(_i\) films operated in 0 (blue), 0.3 (green), 0.55 (red), 1 (yellow), 3 (magenta), 5.5 (orange), 10 (turquoise) mM NaP\(_i\) pH 6 electrolyte with 0.1 M NaClO\(_4\) as supporting electrolyte at various rotation rate. (a) 2500 rpm. b: 625 rpm data at other rotation rates are
given in the SI.3). The slopes of the straight lines are $F/RT ln 10$ (dashed black) and $F/2RT ln 10$ and (solid blue).

**Figure 5.12.** Tafel plots of Co–P films operated in 3 mM NaP, pH 6 electrolyte with 0.1 M NaClO₄ as supporting electrolyte with increasing film thicknesses 48 nm (red ■), 200 nm (green ▲), 575 nm (blue ●) at various rotation rates: (a) 2500 rpm. (b) 625 rpm. The solid colored lines correspond to fitting of data.

**Figure 6.1.** (a) Structure functions and PDFs (b, c) for Co₃O₄ (green), CoOOH (gray), Co–B (blue) and Co–P (red). In (b) PDFs of Co–B and Co–P are compared and the difference curve is shown by the lower purple trace (offset for clarity). PDFs have been truncated around $r = 20$ Å to highlight the differences.

**Figure 6.2.** Comparison between Co–OECs—blue: Co–B (a and c), red: Co–P (b and d) —and truncated PDFs of Co oxide model compounds—green: Co₃O₄ (a and b), grey: CoOOH (c and d). The model compound signals were scaled and truncated with a spherical characteristic function to simulate nanoparticle effects. The purple lines (—) represent the difference curves (offset for clarity) between the PDF of each model compound and that of the specified Co–OEC.

**Figure 6.3.** Preliminary model fits to (a) Co–B (blue) and (b) Co–P (red) data using the (top) CoOOH (gray) model and (bottom) Co₃O₄ (green) model. The difference is the purple line offset below. Goodness-of-fit, $R_w$, parameters equal (a) top: 0.307; bottom: 0.515 and (b) top: 0.336; bottom: 0.403.

**Figure 6.4.** (a) Cylindrical atomistic model fit (black lines) to the Co–B catalyst PDF data (blue circles). The difference curve is shown in purple, and is offset for clarity. (b) View of the refined model for the average coherent domain in Co–B films.

**Figure 6.5.** (a) Cylindrical atomistic model fit (black lines) to the Co–P catalyst PDF data (red circles). The difference curve is shown in purple, and is offset for clarity. (b) Two views of the refined model for the average coherent domain in Co–P films.

**Figure 6.6.** Cylindrical atomistic model fit (black lines) to Co–B data (blue lines) using a model constrained to a single layer. The difference curve is shown by the lower trace (purple line) and is offset for clarity. This fit is considerably
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**Figure 6.7.** Tafel plots ($\eta = E - E° - iR$) of (a) Co–Bi and (b) Co–Pi in 1 M KBi pH 9.2 and 1 M KPi pH 7.0, respectively. Films were prepared by passage of 5 (●), 15 (□), 50 (■), 150 (▲), and 1000 mC/cm$^2$ (▲). (c) Exchange current density, $j_0$, vs. catalyst loading plots of Co–Bi (■) and Co–Pi (●) obtained by fitting the linear regions of the Tafel plots in a and b to a straight line with a slope of $2.3 \times RT/F$ (59 mV). Lines are fits to $j_0 = j_0^{max} \tanh(d_f/d_f^{opt})$ (eq. 5.10). (d) Activity vs. catalyst loading (film thickness) plots of Co–Bi (■) and Co–Pi (●) at $\eta = 0.4$ V obtained by direct interpolation of Tafel plots in Figure 6.7a and 6.7b. Lines are drawn as guides to the eye.

**Figure 6.8.** (a) Schematic diagram showing the cross-sectional configuration of the interdigitated microsensor electrodes used in redox conductivity measurements (showing only one of 25 electrode pairs on the glass substrate). (b, c) Redox conductivity, $\sigma$, of Co–Bi (■) and Co–Pi (●) deposited by passage of 5.96 mC operated in 0.1 M KBi pH 9.2 and 0.1 M KPi pH 7, respectively, using a voltage offset of 5 mV. Each data point is the result of a 300 s step.

**Figure 7.1.** Top and Bottom: Schematics of the RIPPLE method showing a 2-compartment electrochemical cell with a Pt mesh electrode submerged in the left chamber and the working electrode, which undergoes patterning, submerged in the right chamber (together with a reference electrode, which is not shown). The working electrode, whose axial cross-section is shown at right, consists, for example, of a Ge thin film (green) that is exposed at defined sites (e.g. dots) through a resist layer (beige). Top: Both electrodes are immersed in acidic solution (blue) and a linearly ramped potential sweep (thick red line) is applied (e.g. between 0.3 and 1.4 V vs. NHE). Lateral etching of Ge proceeds underneath the resist layer. Bottom: A return potential sweep is applied leading to continued etching of Ge and site-selective formation of patterned features.

**Figure 7.2.** (a) SEM image of patterned periodic features emanating from the site of a defined (left) line and (right) dot. (b) SEM images of periodically-spaced and parallel lines patterned from a single line at 100 mV s$^{-1}$ (top) and 450 mV s$^{-1}$ (bottom). (c) SEM image (left) of a square Ge on Si platform raised 7 µm
above rest of substrate plane and (right) after patterning of the platform region highlighted with the red box in the left panel. Dashed teal line denotes site where the 2 µm wide line was defined and from which patterns emanate. (d) Left: SEM image of an array of 36 concentric rings; scale bar, 100 µm. Right: SEM image gallery of concentric ring patterns highlighted in image at left; scale bar, 10 µm. (e) Planview EDS elemental map of Ge for a feature containing 4 rings; scale bar, 2 µm. (f) AFM map of (left) periodically patterned sub-micron rings and (right) periodic concentric terraces that step down in regular 20 nm increments.

**Figure 7.3.** (a) Bright-field TEM images of the axial cross-section of a substrate patterned with concentric rings. (b) High-resolution bright-field TEM image of the interface between the patterned ring and underlying Si substrate marked by the pink box in (a). (c) From top to bottom, EDS elemental maps of Ge, O, and Si for the cross-section of a patterned ring. (e) Left: Cyclic voltammograms at 100 mV s\(^{-1}\) performed in 0.1 M H\(_2\)SO\(_4\); Right: Accompanying SEM images of patterned structures. Three CVs, each composed of a forward (solid lines) and reverse (dashed lines) sweep, were performed between 0.3 and 1.4 V.

**Figure 7.4** (a) Average period for the last ring pair within randomly sampled patterns as a function of voltage scan rate. Error bars denote % deviation from the mean and the dashed line is a power law fit to the data. Inset: Data presented on a logarithmic plot with linear fit to data. (b) Average period for the 1\(^{st}\) through 4\(^{th}\) ring pairs within randomly sampled patterns at 3 different voltage scan rates: 65 mV s\(^{-1}\) (green circle), 100 mV s\(^{-1}\) (red square), and 300 mV s\(^{-1}\) (blue triangle).

**Figure 7.5** (a) (top) Schematic of a square array of periodic ring patterns. (bottom) SEM image of the region where rings from adjacent patterns overlap with each other. Inset: EDS Ge map of the square. (b) (left) SEM image of an array of rings patterned from a Cu film on Si. (right) Composite Cu (orange) and Si (blue) EDS map of one pattern. (c) (left) High-resolution STEM image of a 60 nm thick axial cross-section of a patterned Cu ring. (middle and right) Cu (orange) and O (red) EDS maps of the same cross-section. (d) (left) Photograph of a Cu-structure patterned over a transparent substrate. (right) SEM image of periodic rings that serve as the “pixels” in design of the patterns.
Figure 7.6 (a) Top: SEM of patterned metallic Co (left), Co EDS map (middle), and O EDS map (right); scale bar, 10 µm. Bottom: Cyclic voltammogram in 0.1 M H$_2$SO$_4$ of a 250 nm metallic Co film (see Section 7.5) on a platinum/silicon substrate. The gray arrow indicates the direction of progression in the voltammograms. (b) RIPPLE-patterned cobalt phosphate (Co–P$_i$) water splitting catalyst. Top: SEM image of Co–P$_i$ catalyst patterned into concentric rings; Co (yellow) and O (red) EDS maps of a single Co–P$_i$ catalyst pattern are shown in the middle and bottom, respectively. (c) Cyclic voltammogram of a substrate bearing arrays of patterned Co–P$_i$ in 0.1 M KP$_i$ pH 7 electrolyte at a scan rate of 100 mV/s. (d) O$_2$ evolved by patterned Co–P$_i$ catalyst as measured by a fluorescent probe (red) and O$_2$ calculated from charge passed assuming a Faradaic efficiency of 100% (black).

Figure 8.1. Metalloporphyrin catalysts used in this study, including hangman complexes (1-M) and non-hangman analogs (2-M and 3-M).

Figure 8.2. (a) Overlay of representative normalized ($i_{\text{norm}} = i/v^{1/2}$) CVs taken of a 0.3 mM solution of Co(C$_6$F$_5$)$_4$ porphyrin in acetonitrile with 0.03 (■), 0.3 (●), and 3 (● •) V/s scan rates, using a glassy carbon electrode. (b) Difference between anodic or cathodic peak potential and midpoint potential ($E_p - E^\circ$) vs. log of scan rate ($E^\circ = 1.00$ V for the Co$^{II}$/I couple (●), and $-1.98$ V for the Co$^{II}$/0 couple (■)). Simulated curves are plotted for $k_d = 0.011$ cm/s (■—■) and $k_d = 0.2$ cm/s (■—■). The diffusion coefficient (D) for the Co(C$_6$F$_5$)$_4$ porphyrin was determined to be $8 \times 10^{-6}$ cm$^2$ s$^{-1}$ from the peak current, i, in the reversible limit: $i = 0.446FAC^\circ D^{1/2}(Fv/RT)^{1/2}$ (where F is the faraday constant, A is the area of the electrode and $C^\circ$ is the bulk porphyrin concentration).

Figure 8.3. (a) Concentration dependence studies of the “Co$^{+0}$” peak potential of 1-Co at scan rates of 0.03 (■), 0.3 (●), and 3 (▲) V/s. (b) Overlay of representative CVs taken of a 0.2 mM solution of 1-Co in acetonitrile at scan rates of 0.03 (● •), 0.3 (■—■), and 3 (■—■) V/s, using a glassy carbon electrode. (c) Plot of ($E_p - E^\circ$)F/RT as a function of the natural logarithm of scan rate, v ($E^\circ = -2.14$ V, taken from 2-Co). Experimental data (●), theoretically predicted line based on equation 8.3 using a $k_{PT}$ value estimated from the CV recorded with 0.03 V/s scan rate (■—■).

Figure 8.4. (a) CVs of a 0.1 mM solution of 3-Co in the absence of benzoic acid (■—■) and in the presence of 0.05 (●●●●), 0.3 (■—■), and 0.6 (■—■) mM benzoic acid.
acid. Scan rate, 30 mV/s; 0.2 M TBAPF$_6$ in acetonitrile. (b) CVs of 0.1 (---), 0.3 (----), and 1 mM (---) solutions of 3 in the absence of benzoic acid and in the presence of 0.05 (-----), 0.15 (---), and 0.5 (---) mM benzoic acid, respectively. Scan rate, 30 mV/s; 0.2 M TBAPF$_6$ in acetonitrile. Glassy carbon working electrode, Ag/AgNO$_3$ reference electrode, and Pt wire counter electrode.

Figure 8.5. Plots of $(E_p - E^0)F/RT$ vs. ln of scan rate for 1-Co ($E^0$ = –2.14 V, taken from 2-Co). Experimental data (●), simulated curves plotted for $k_s = 0.24$ cm s$^{-1}$ and $k_{PT} = 8.5 \times 10^6$ s$^{-1}$ (---), $k_s = 0.35$ cm s$^{-1}$ and $k_{PT} = 8.5 \times 10^6$ s$^{-1}$ (— —), $k_s = 0.18$ cm s$^{-1}$ and $k_{PT} = 8.5 \times 10^6$ s$^{-1}$ (•••), $k_s = 0.24$ cm s$^{-1}$ and $k_{PT} = 3 \times 10^7$ s$^{-1}$ (——), and $k_s = 0.24$ cm s$^{-1}$ and $k_{PT} = 3 \times 10^6$ s$^{-1}$ (— —).
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<td>( \text{OER} )</td>
<td>oxygen evolution reaction</td>
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<td>( \text{PCET} )</td>
<td>proton-coupled electron transfer</td>
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<td>( \text{PEC} )</td>
<td>photoelectrochemical cell</td>
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<td>( \text{PEM} )</td>
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<td>in the context of electrochemistry: the solution/series resistance</td>
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<td>( R )</td>
<td>in the context of EXAFS: the real distance between absorber–backscatterer pairs</td>
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<td>( \text{RDE} )</td>
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Over the course of my time in the Nocera group at MIT and Harvard, I have been blessed with the opportunity to work with some fantastic scientists and friends. Each of these interactions has enriched my graduate studies in some way and I am certain that the last five and a half years would have been substantially less fruitful and certainly less pleasant without these contributions.

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I, on the other hand will never forgive Casandra Cox and Nancy Li (aka Lu) for introducing me to the Serial podcast and for all the hours we have spent on whodunit debates. I am also thankful that they withstood my impromptu barges into their office to start a conversation about something scientific or an otherwise completely ridiculous topic. With a circle!

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mark on me during the first 22 years of my life that will never cease to impact me. I have
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Thank you all.

“Happy is the man who can recognize in the work of Today a connected portion of the work
of life, and an embodiment of the work of Eternity.” —James Clerk Maxwell
This dissertation is dedicated to my father
Chapter 1 — Introduction

Portions of this chapter have been published:


1.1. Challenges in solar energy storage

Based on current global trends, by the year 2050 annual energy consumption is predicted to more than double what it was at the turn of the new millennium and triple by 2100 (Figure 1.1).\textsuperscript{1-4} Rising global populations are driving this steady increase in global energy consumption,\textsuperscript{5,6} creating arguably the single most pressing global challenge of our century: to provide energy that can sustain the development of our and future generations. Over our entire history, humanity has made use of energy stored in the bonds of high-energy molecules (fuels). The precise source of these fuels has changed from wood and charcoal (biofuels) before the industrial revolution to coal, oil, and/or natural gas (fossil fuels) since. From estimations of global reserves, it is believed that sufficient resources exist for fossil fuels to meet our energy requirements for many decades.\textsuperscript{7,8} However, our near-exclusive dependence on these sources of energy is unsustainable, given pressing environmental, economical, and security concerns. In particular, the atmospheric carbon dioxide concentration is already the highest it has been in the last 650,000 years,\textsuperscript{9,10} and sustained high greenhouse gas emission rates are projected to result in a global mean temperature change of 3–5 °C by 2100 (relative to the global mean temperature between

\textbf{Figure 1.1.} Global energy consumption is predicted to have tripled by the year 2100 relative to consumption in the year 2000. Data taken from references\textsuperscript{1} and \textsuperscript{2}
1986 and 2005). In the absence of a rapid switch to alternative, carbon-neutral energy sources, the ecology of our planet is highly likely to be perturbed on a catastrophic scale over the next few decades.

Of all renewable sources, solar energy possesses the largest resource base. Indeed, the energy content of terrestrial insolation over the course of an hour is almost as much as our annual global energy consumption. Yet, local solar insolation is diurnally intermittent, highly mutable, and diffuse. This mandates a robust, highly energy-dense storage scheme that will make energy available upon demand. The absence of such a system has relegated renewable energy usage to a minuscule fraction of total energy consumption to-date. Indeed, fossil fuels ultimately represent the end products of solar energy storage itself (through primary photosynthesis and the food chain) over billions of years. The contemporary imperative is for a system that can replicate this process continuously, with high efficiency. In this regard, an artificial photosynthesis scheme that can generate fuels from solar-driven uphill chemical reactions stands as a “holy grail” of modern-day chemical science. One such endergonic reaction is the splitting of water to molecular hydrogen and oxygen:

\[
2\text{H}_2\text{O}(l) \rightarrow 2\text{H}_2(g) + \text{O}_2(g) \quad \text{E}^\circ = -1.23 \text{ V} \quad (1.1)
\]

This overall reaction can be divided into two half-reactions, one involving an oxidation process (known as the oxygen evolution reaction, OER) and the other a reduction (the hydrogen evolution reaction, HER):

\[
2\text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \quad \text{E}^\circ = (1.23 - 0.059 \times \text{pH}) \text{ V vs. NHE} \quad (1.2)
\]

\[
4\text{H}^+(aq) + 4e^- \rightarrow 2\text{H}_2(g) \quad \text{E}^\circ = (0 - 0.059 \times \text{pH}) \text{ V vs. NHE} \quad (1.3)
\]

Here, \( \text{E}^\circ \) values denote the thermodynamic potentials of the reactions.

The challenge in mimicking the essence of natural photosynthesis (in which glucose is made, instead of dihydrogen), is to develop systems in which solar photons can be captured, and their energy transferred to reaction centers that execute these electrochemical transformations. One means of accomplishing the solar-to-fuels process involves the
use of a photovoltaic assembly that generates an electric current upon irradiation with sunlight. This electric current is then wired to a separate electrolyzer where the OER and HER are carried out. \[^{16,19}\] Existing methods used to split water commercially (mainly for the production of high purity \( \text{H}_2 \)) involve the use of proton-exchange membrane (PEM) electrolyzers that operate in acidic electrolytes, alkaline electrolyzers that operate in strongly basic solution, and solid-oxide electrolyzers that operate at high temperatures of \( \sim 1000 \, ^\circ\text{C} \). \[^{17}\] In all cases, water splitting is carried out under very harsh conditions, and as a result the overall balance of systems cost is too high to allow these technologies to be economically viable renewable solar–fuels generators. \[^{20,21}\] PEM electrolyzers incur additional costs associated with the precious metals that are required as electrodes.

One approach to potentially reduce the cost of water splitting electrolysis is to develop systems that can operate under more benign conditions, such as at intermediate (close to neutral) \( \text{pH} \). Additional cost reductions may be realized by more directly integrating the electrolysis components with the light harvesting assembly in monolithic device architectures. \[^{18,22}\] In general, direct solar-driven water splitting systems can be categorized into those devices wherein the photovoltaic material makes a rectifying junction with solution as opposed to those in which the rectifying junctions are protected from solution or “buried.” In solution-junction photoelectrochemical (PEC) devices (Figure 1.2a), one or more semiconductor electrodes are exposed to an electrolyte solution such that the photo-generated carriers (electrons or holes) can be directed to the semiconductor–electrolyte interface to execute the water splitting reactions. Here, the semiconductor–solution interface is the critical determinant of the photovoltage generated and overall behavior of a PEC system, and as a result water-splitting kinetics are not necessarily the primary factors to consider in device design. \[^{23}\] Instead, it is critical to consider catalysts that are amenable to the formation of conformal coatings over the highly nanostructured surfaces that are typical of solution-junction PEC systems. \[^{24,25}\] Furthermore it is important that the catalyst should not deleteriously impact the energetics of the
In contrast, typical buried-junction photovoltaic–photoelectrochemical (PV–PEC) architectures employ a multi-junction stack of light absorbers that are connected in series using thin-film ohmic contacts or tunnel junctions to generate open circuit voltages that are large enough to drive water splitting (Figure 1.2b). Thin-film ohmic contacts are then applied to each terminus of this stack to both protect the semiconductor from corrosion and enable efficient charge transfer to catalyst overlayers, which mediate the water splitting reactions. In such a device, catalysis is separated from the current rectification, charge separation, and photovoltage generation, which occur at the internal junction. The photovoltages produced at buried junctions are not fixed relative to a material-specific flatband potential. Unlike a solution junction, therefore, there is no requirement for the buried junction device that the flatband potentials of the semiconductors result in band edges that straddle the thermodynamic potentials of the OER and HER under the conditions.
of operation. The requirement is only that the total cell photopotential is large enough (irrespective of the valence and conduction band edge positions of the constituent semiconductors themselves) to drive the water splitting reactions and overcome the ohmic losses due to cell resistance. Thus, efficient catalysis and photostability at the interfaces of the ohmic contact and catalyst are among the critical prerequisites in these systems.

1.2. Catalysis of the water splitting reactions

Irrespective of the design chosen for the solar–fuels conversion process, the potential in excess of the thermodynamic potential (i.e. the overpotential) required to drive the water splitting reactions at the desired rate is a crucial determinant of the efficiency of the overall system. The velocity of the electrochemical reaction, \( v \), is directly related to the measured current density at the electrode, \( j \) (\( v = nFv \), where \( F \) is the Faraday constant and \( n \) is the total number of electrons transferred in the reaction, i.e. 4 for the OER and 2 for the HER). The overall voltage required to drive water splitting is:

\[
V_{\text{overall}} = E^o + \eta_{\text{OER}} + |\eta_{\text{HER}}| + \eta_{\text{IR}}
\]  

(1.3)

\( E^o \) is the thermodynamic potential for water splitting (1.23 V under standard conditions), which defines the energy content of the chemical fuel formed during water splitting, and the additional overpotential (\( \eta_{\text{OER}} + |\eta_{\text{HER}}| + \eta_{\text{IR}} \)) indicates the amount of energy lost as heat to drive the reaction at the desired current density. The parameters \( \eta_{\text{OER}} \) and \( \eta_{\text{HER}} \) are the activation overpotentials for the OER and HER, respectively, and \( \eta_{\text{IR}} \) is the overpotential associated with ohmic losses in the device, including solution and contact resistances. Whereas appropriate engineering and device design can reduce \( \eta_{\text{IR}} \), the activation overpotentials relate directly to the chemical complexity of the water splitting reactions and the facility with which the oxygen evolving catalysts (OECs) and hydrogen evolving catalysts (HECs) mediate the half reactions. That is, \( \eta_{\text{OER}} \) and \( \eta_{\text{HER}} \) are directly related to the magnitude of the activation barrier(s) that must be surmounted for the reaction to proceed at any appreciable rate. As multi-electron reactions, both the OER and
HER present a significant degree of kinetic complexity associated with navigating the formation of a number of intermediate species. These reactions therefore incur significant activation overpotential penalties in actual devices.

The relationship between the activation overpotential and current density at an electrode is expressed generally in the Tafel law:

\[ \eta = b \log \left( \frac{j}{j_0} \right) \]  

The extrapolated current density at zero driving force for the overall reaction (\(\eta = 0\)) is known as the exchange current density, \(j_0\). Thus, \(j_0\) is a descriptor of the intrinsic activity of the electrode towards the reaction (at the thermodynamic potential). In the pure sense, it defines the standard electrochemical rate constant of the reaction. However, in reactions like the OER for which measurable current densities are typically only observed at overpotentials in excess of 150 mV, the value obtained by extrapolation over this large voltage range to \(\eta = 0\) is only nominally the exchange current density. Nevertheless, \(j_0\) provides a valuable metric that together with the Tafel slope, \(b\), defines the activity of the catalyst in the voltage range over which the Tafel data was acquired. The Tafel slope itself determines the extent to which changes in driving force influence the rate of the reaction via changes in the Gibbs free energy of activation, \(\Delta G^\ddagger\) (i.e. \(1/b = \partial \Delta G^\ddagger / \partial G\)). Therefore, the Tafel slope depends on the mechanism by which the reaction proceeds via the catalyst active sites. The ideal catalyst should possess a high exchange current density and low Tafel slope in order to require a low overpotential for sustaining a high current density. Since a full description of any electrocatalyst must take into account both parameters, the most useful method of describing the activity of an electrocatalyst is by plotting the overpotential as a function of the logarithm of steady state current densities (Tafel plot).

The non-trivial reaction landscape entailed in these reactions is well illustrated in a so-called Frost-Ebsworth diagram (Figure 1.3a). Here, the relative stability of several intermediate oxidation states of oxygen and hydrogen along the \(\text{H}_2\text{O} – \text{O}_2\) and \(\text{H}^+ – \text{H}_2\) reaction coordinates is displayed as a plot of the negative Gibbs free energy (relative to the
elemental form) per unit of the Faraday constant (−G/F) as a function of the oxidation state of the element in question (N). Since −G/F is numerically equal to N×E⁰, where E⁰ is the formal/equilibrium potential of the electrochemical reaction, the slope between any two species on a Frost diagram gives the formal potential.

Another diagrammatic way to highlight the challenge inherent to these transformations is to plot the equilibrium potential of intermediates on a linear scale (Figure 1.3b). Examination of these two plots reveals two important general implications for the catalysis of multi-electron transformations:

I. The average of all formal potentials encountered over the course of the transformation (E⁰₁, E⁰₂, …, and E⁰ₙ, where n is the total number of electrons transferred) must equal the reversible potential of the overall reaction, E⁰:

\[
\frac{E_{1}^{0} + E_{2}^{0} + E_{3}^{0} + \ldots + E_{n}^{0}}{n} \geq E^{0}
\]  

(1.5)

This expression may be considered as an application of the first law of thermodynamics to an electrochemical system.

Figure 1.3. Thermodynamics of intermediate species formation in water splitting at pH 7 upon sequential removal of 1 H⁺ and 1 e⁻. (a) Frost-Ebsworth diagram of the O₂/H₂O (solid lines) and H⁺/H₂ (dashed lines) reactions at pH 7. The slope of the line connecting two intermediates is the equilibrium potential for that reaction. The displacement of an intermediate above the line associated with the net reaction (dotted lines) leads to an overpotential penalty for the overall reaction. Catalysts serve to stabilize such high-energy intermediates. (b) Equilibrium potentials for the O₂/H₂O redox reaction showing the wide dispersion in equilibrium potentials over a > 2.6 V potential range. Catalysts can narrow the potential range and thereby lower the overpotential for the reaction.
II. It follows from (I) that narrowing the disparity between the highest and lowest formal potential will lead to generally lower overall overpotentials ($\eta$) for a desired turnover rate.

$$E_{\text{high}}^0 - E_{\text{low}}^0 \propto \eta \quad (1.6)$$

In order to facilitate the turnover of these reactions, it is imperative to make use of good catalysts that can lower the free energy of formation of the high-energy intermediates, by providing coordinative stability. In doing so, all formal potentials are brought closer to the equilibrium potential of the overall reaction, constrained to a narrower range. The process of narrowing the voltage range over which a series of redox reactions occurs is termed potential leveling.$^{27,28}$ The ideal catalyst will enable the reversible, rapid transfer of n/2-electrons in concert with bond formation/breaking. However no electrode or catalyst is known that can accomplish such a multi-electron transfer in a concerted step. The closest approximation to this ideal catalyst is one that will allow all individual electron transfers to exist in rapid equilibrium at an applied potential that is very close to the thermodynamic potential.

1.3. Approaches to the realization of low overpotentials

These catalytic challenges lie at the heart of photoelectrochemical water splitting. Through catalysis the one electron-hole generation attendant to light capture and conversion is aggregated and discharged towards fuel formation. In the consideration of design elements relevant for the construction of improved catalysts that operate with low overpotentials, one obvious approach is to target catalysts that possess high intrinsic activity. That is catalyst systems, which fulfill the requirements of eq. 1.5, and exploit potential leveling to yield a narrow potential range (eq. 1.6). Much inspiration for factors that are central to this effort is revealed to us upon consideration of the architecture found in the oxygen-evolving complex (OEC) of photosystem II.$^{13,28,29,30}$ However, two important assets of the OEC are of particular relevance.
The first of these is the composition and structure of the active site as an oxidic cluster of five metal ions (four Mn and one Ca). A key feature of this active site is, therefore, its ability to distribute redox demand over multiple centers in order to maintain low equilibrium potentials throughout the catalytic cycle. While a number of monometallic molecular systems have been reported to be water oxidation catalysts, all monometallic systems to-date display considerably poorer activity than their corresponding extended-solid or nanocrystalline oxides. One likely reason for this disparity is the capacity of active sites in these “solid-state” systems to more effectively delocalize accumulated charge, while retaining sufficient charge localization to drive catalytic reactivity. There continues to exist a fundamental gap in understanding the interplay between domain size, active site density, and reactivity. Yet these issues clearly lie at the heart of developing catalysts with higher intrinsic activities.

Besides redox leveling by distribution of redox demand over multiple metal centers, the design of the OEC also emphasizes the importance of proton-coupled electron transfer (PCET) in multi-electron catalytic reactions. A tyrosine is positioned proximate to the active site to shuttle protons away and facilitate sequential oxidation reactions. In the absence of proton loss, each successive oxidation would lead to intermediates that are increasingly highly charged and thermodynamically unstable. The loss of protons with electrons in PCET reactions is usually a natural consequence of the increased acidity upon oxidation of species bearing protic hydrogen atoms. However, in some instances the slow kinetics of a proton transfer can mean that even the most competitive pathway involves the formation of a thermodynamically unfavorable intermediate. In these instances incorporating a structural motif that facilitates proton transfer can greatly increase the intrinsic activity of the catalyst. In general, the study of PCET reactions and an understanding of the interplay between the factors that direct the details of these reactions remains of great fundamental interest.
Because the experimental overpotential is an extrinsic parameter that is related to the desired current per unit area of an electrode (eq. 1.4), in addition to increasing the intrinsic activity of a catalyst, lower overpotentials may be attained by creating catalyst films where multiple layers of active sites are assembled on top of one another (Figure 1.4). This creates a higher active site density per unit area and relaxes the turnover frequency (TOF) burden per active site. This design element places additional requirements on the charge and mass transport characteristics of the assembled film. Electrons, protons, counter-ions, substrate molecules, and product species must be rapidly delivered to and from each active site with sufficient rapidity that active sites throughout the film can be utilized. In the absence of rapid intra-film transport, the catalytic current density will fail to attain its maximal value because of poor utilization of the available catalyst material. Catalysts wherein such charge transport is an intrinsic property of the material are therefore highly desirable, since this ensures that the assembly of such multilayer catalysts is facile, and does not require additional processing besides catalyst synthesis itself.
1.4. Heterogeneous electrocatalysis of the OER

Of the two half reactions, the OER is the most kinetically demanding, since it requires the efficient completion of four proton-coupled redox processes, and the formation of two oxygen–oxygen bonds. Consequently, the majority of the activation overpotential in water splitting tends to arise from the OER. Transition metal oxides are known to meet the requirements for highly active oxygen evolution catalysts, with nickel-based oxides being the most attractive anode materials under alkaline conditions because of their low cost, high catalytic activity, and stability to corrosion. Catalysis development for the OER has historically focused on addressing challenges associated with electrolyzer development—operation at high current density at pH extremes—without consideration of the problems concerning light management or stability of fragile semiconductors. We have emphasized the development of heterogeneous OER catalysts targeted to PEC and PV–PEC device applications. Accordingly we have focused on investigations across a wide pH range, since the stability manifold of the optimal semiconductor(s) remains unknown. Furthermore, the development of catalysts that can operate at intermediate pH may open up new technological avenues for solar-fuels systems that may be inaccessible when water splitting is carried out at the pH extremes.

1.4.1. Electrodeposited cobalt oxide films: prior observations

Electrochemical studies of cobalt oxide-based materials can be traced back to the early 1900s with investigations into the anodic behaviour of cobalt plates, motivated primarily by the need to mitigate the corrosion of metals. These studies established that upon application of an anodic potential (particularly in basic electrolytes), an oxide layer could be formed on the surface that served to passivate the underlying metal anode against dissolution. Contemporaneous studies addressed the electrolytic purification of nickel and cobalt salts—often cross-contaminated and challenging to separate by physical methods—in aqueous sulfate, thiocyanate, or pyridine electrolytes. These studies exploited the
already established property that cobalt oxide could be electrodeposited at a lower anodic potential than nickel oxide. Other studies sought to characterize the speciation of the electrodeposited cobalt oxides and propose mechanisms for their formation. In all cases, despite the observation of oxygen evolution at the anode, the importance of cobalt oxide as an OER catalyst was not appreciated at the time.

In the late 1950s and 1960s the focus shifted to evaluating water oxidation performance of cobalt oxide materials. Since then, a plethora of preparation methods have been reported, including: thermal decomposition (including spray pyrolysis), sol-gel methods, high-temperature solid-state perovskite and spinel synthesis, electrochemical anodization of cobalt metal, reactive sputtering, and electrodeposition. Of these methods, electrodeposition is a particularly attractive synthetic route for water splitting catalysts targeted for PEC or PV–PEC constructs, since it permits direct integration into such solar–fuels devices. Cathodic electrodeposition usually involves the reduction of nitrate ions, O\(_2\), or H\(^+\) at the electrode surface to generate a high local concentration of OH\(^-\) that precipitates with the metal ion (in this case Co\(^{2+}\)) to generate a Co(OH)\(_2\) film. This method of cathodic electrodeposition does not involve a redox reaction of the metal ion itself, and is therefore widely applicable to the myriad of elements that form insoluble hydroxides in aqueous electrolyte media. Alternatively, with appropriate choice of electrolyte, direct reduction of the Co\(^{2+}\) ion itself results in metallic cobalt films, that may be subsequently anodized to generate an oxide film.

With regards to the electrosynthesis of OECs, anodic electrodeposition is arguably the ideal method for catalyst formation, since the catalyst may be applied directly to the photoanode using the photogenerated holes themselves. However, this deposition method requires oxidation of the metal ion precursors themselves, and is therefore limited to soluble metal ion compounds and complexes that possess redox couples within the accessible electrochemical window. In electrolyte solutions containing Co\(^{2+}\) ions,
deposition can be effected when an electrode is poised at sufficiently high anodic potentials, as exploited in the electrochemical separation studies described above. Prior to our work in this area, many research groups over many decades had explored a range of cobalt and nickel salts including acetate, sulfate, chloride, and nitrate compounds as precursors for the formation of oxidic films. These studies involved the deposition and operation of the catalyst in electrolyte conditions where catalyst formation was coincident with OER catalysis. Thus, film morphology and thickness could not be controlled with precision. More importantly, unless operated in highly alkaline solutions, the pH of the electrolyte was inevitably ill-defined; any protons generated as by-products of the deposition reaction or OER induce local pH drops at the electrode and large pH gradients across the cell, ultimately resulting in film corrosion.

1.4.2. Co–P<sub>i</sub> and Ni–B<sub>i</sub> OECs

With the aim of developing catalysts that are ideally suited for water oxidation under benign pH conditions, we set out to explore the aqueous electrochemistry of Co<sup>2+</sup> complexes in neutral pH buffered electrolytes. Researchers in our group discovered that OECs self-assemble as thin films upon electrolysis of aqueous solutions of Co(II) containing a good proton acceptor, like phosphate (P<sub>i</sub>) or borate (B<sub>i</sub>), pH 7–9. As amorphous oxidic catalysts based on first row transition metals that progress through low-valent, labile intermediate states during O<sub>2</sub> evolution, these materials possess a predilection for degradation back to their soluble Co<sup>2+</sup>(aq) precursors. However, a unique feature of these catalyst films is their capacity to self-repair, which ensures their indefinite functional stability notwithstanding their inherent structural fragility. Theses features also establish the functional integrity of these catalyst systems in impure water sources, making them potential targets for future cheap, distributed energy storage systems in impoverished regions. Owing to the terrestrial abundance of the starting materials for these Co–OECs and the simple conditions required for their electrosynthesis,
they have emerged as prime candidates for integration with a myriad of inorganic, and organic-inorganic hybrid light absorbers in solution-junction PEC systems (Figure 1a)\textsuperscript{107–121} as well as buried-junction PV–PEC water splitters (Figure 1b).\textsuperscript{122–124}

We sought to explore the synthesis of catalyst films based on other first-row transition metals with the goal of identifying the mechanistic basis for any differences in catalytic activity and stability. We found that controlled potential electrolysis of borate-buffered solutions of nickel salts at pH 9.2 also afforded the deposition of an OEC as a thin film.\textsuperscript{125} These so-called nickel-borate (Ni–B\textsubscript{i}) catalyst films were shown to mediate the OER with 100\% faradaic efficiency with modest overpotentials of ~0.4 V required for current densities of 1 mA/cm\textsuperscript{2}.\textsuperscript{125} In contrast to Co–P\textsubscript{i} and Co–B\textsubscript{i} catalysts, the potentials sufficient for initiating catalyst formation were not as well-separated from those required for driving oxygen evolution, suggesting disparate thermodynamics/kinetics of catalyst formation and/or differing kinetics of water oxidation compared to those of the Co–OECs. Intriguingly, Ni–B\textsubscript{i} films required extensive (12 h) pre-electrolysis treatments in order to establish reproducible steady state behavior\textsuperscript{125} unlike Co–OEC films that displayed unchanging steady state OER activity immediately following film deposition. However, Ni–B\textsubscript{i} films shared a common characteristic with Co–OEC films in that they also appeared amorphous\textsuperscript{125} obstructing a molecular-level understanding of catalyst structure, and by extension formation and function.

1.5. Homogeneous H\textsubscript{2} electrocatalysis

Notwithstanding the larger overpotentials that are typically associated with the OER as compared to those of the HER, catalytic hydrogen production is still a problem of great interest. The HER remains a key reaction in water splitting systems and from the perspective of fundamental scientific studies, it affords the opportunity to study a multi-electron transformation that is somewhat more tractable in terms of designing competent
molecular catalysts that lend themselves to detailed structural characterization tools as well as computational analysis.

A major thrust in our laboratory has entailed the study of metalloporphyrin-based molecules that can mediate the activation of small molecules. In particular, researchers in our group have devised porphyrin scaffolds that bear a pendant proton relay (“hangman” group) with the goal of facilitating PCET reactions via the shuttling of protons to and from the active site during electrocatalytic reactions. The incorporation of proton relay groups in the second coordination sphere of active sites is now a frontier area of study in molecular electrocatalysis. Key questions that remain in this area relate to how different types of concerted and stepwise PCET reactions may be triggered by poising an acidic or basic moiety in close proximity to a reaction center, the influence of the proton donor–acceptor distance and ΔpKₐ on PCET kinetics, and to what extent such molecular design elements can enhance multi-electron, multi-proton catalysis.

1.6. Scope of the thesis

The ostensibly amorphous nature of the Ni–Bi catalyst made it recalcitrant to structural characterization by conventional X-ray and electron diffraction techniques. Thus a pre-eminent question that remained was: what structural motifs are present in Ni–Bi films? We also considered: what transformations in film structure accompanied the aforementioned electrochemical treatment and how do they correlate with any activity changes that may be observed over the course of the pre-electrolysis? Chapter 2 addresses these two critical questions and shows that as-deposited catalyst films are comprised of metal oxido clusters populated by Ni(III) centers that are subsequently transformed to a mixed-valence Ni(III/IV) state during anodization, which correlates with drastic improvements in catalytic activity. The realization of Ni(IV) character is facilitated by the adsorption of iron (present at trace levels in the reagent grade electrolyte) onto the film. These results which indicate that Ni(IV) character in the resting state is paramount to high
catalytic activity stand at odds with the prevailing dogma for OER at Ni-based anodes. Chapter 3 addresses the following questions: What is the mechanism of oxygen evolution at Ni–Bi? What is the role of the buffer in the water oxidation mechanism? How does the OER kinetic profile of Ni–Bi compare with that of Co–P_i over a wide pH range? Electrokinetic studies reveal a novel mechanism of oxygen evolution and show that activity trends among OECs at pH extremes may be reversed at intermediate pH. Chapter 4 discusses the significance of the disparate OER mechanisms of Co–P_i/B_i and Ni–Bi for the development of PV–PEC devices with high solar-to-fuels efficiencies (SFEs). As porous films that display increasing activity as the catalyst loading (thickness) is increased, a crucial element of film performance is the mechanism of charge transport and the interplay between transport and turnover. Chapter 5 addresses this issue and shows that for such catalyst films an optimal film thickness exists beyond which film activity will plateau. The differences in intermediate-range structure between Co–P_i and Co–B_i that lead to different optimal thickness values are discussed in Chapter 6. Chapter 6 also reviews studies into the factors that likely play a role in the apparent templating of catalyst structure by the deposition electrolyte. Chapter 7 discusses the development of an electrochemical etching technique that allows for the rapid nanopatterning of metals and metal oxides over large areas—a process that could prove to be key in the fabrication of solar–fuels devices where light management and catalysis must be balanced. Chapter 8 is focused on the synthesis of hangman metalloporphyrins and studies of their electrocatalytic behavior towards H_2 production.

1.7. Concluding remarks

A critical challenge to the development of solar-driven water splitting systems that can meet global demands for energy is the development of catalysts that mediate the water splitting half-reactions and are properly matched to light harvesting/charge separating manifolds. HEC and OEC development thus far has focused primarily on materials that are
capable of operating at the pH extremes, however such systems are not suited for the unique requirements of solar-driven water splitting and have therefore failed to challenge the status quo of our heavy reliance on fossil fuels. New technologies are needed to meet this urgent 21st century demand. These novel systems will be based on explorations into the fundamental science of water splitting, particularly under benign conditions (such as at intermediate pH) where the structural stability of oxide materials is not guaranteed. Thus a new class of dynamic, self-healing catalyst materials is required. Simultaneously, studies into novel synthetic modifications that influence PCET in homogeneous, molecular water splitting catalysis are needed in order to provide a rational framework for the next generation of catalysts. The nickel- and cobalt-based catalysts presented here (oxides and molecules) are promising systems for the study of solar water splitting. The following chapters examine our initial forays into understanding the structural and mechanistic basis of their catalytic behavior.

1.8. References


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Chapter 2 — Structure and Valency of Nickel–Borate Oxygen Evolving Catalysts

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2.1 Introduction

In Chapter 1 the importance of highly active oxygen evolving catalysts (OECs) for solar energy storage by water splitting was underscored. In particular, we highlighted the development of OEC systems that are capable of operating under intermediate pH conditions as a critical component for the development of cheap, distributed solar-driven water splitting devices. Within the context of water splitting catalysts designed for operation at intermediate pH, we introduced amorphous nickel-based\textsuperscript{1} and cobalt-based\textsuperscript{2–4} OECs formed as thin films upon electrolyzing solutions of Ni\textsuperscript{2+}(aq) and Co\textsuperscript{2+}(aq), respectively, in the presence of a proton-accepting electrolyte such as phosphate (P\textsubscript{i}), methylphosphonate (MeP\textsubscript{i}), or borate (B\textsubscript{i}) (pH 7–9). These catalysts mediate the OER under mild conditions and at high activity,\textsuperscript{5} and accordingly they lend themselves to the construction of novel direct solar-to-fuels architectures such as the artificial leaf.\textsuperscript{6–9}

Continued development of improved catalysts requires an understanding of how catalyst structure correlates with catalytic activity. However, a challenge with constructing OER structure–function relations for solid-state materials is to observe active sites relative to the bulk.\textsuperscript{10–13} To this end, our recent discovery of such heterogeneous OEC films composed of molecular-like metal-oxido clusters\textsuperscript{14–16} offers the opportunity to begin defining OER structure-function relations because of a higher density of active site species. Nickel-borate (Ni–B\textsubscript{i}) and cobalt-phosphate/borate (Co–P\textsubscript{i}/Co–B\textsubscript{i}) catalyst films may be self-assembled under nearly identical potential and pH conditions.\textsuperscript{1} Yet the Ni–B\textsubscript{i} films are unique because they required a subsequent 12 h oxidative pretreatment or anodization in order to attain a well-defined OER activity.\textsuperscript{1} In contrast, maximal OER activity of Co–P\textsubscript{i}/Co–B\textsubscript{i} is observed immediately following electrodeposition and remains unchanged indefinitely.\textsuperscript{17} The requirement for anodic pre–treatment in the case of Ni–B\textsubscript{i} led us to postulate that an underlying structure and/or valency change was accompanying the marked increase in catalytic activity during the anodization process. This observation
permits a structure–function correlation of OER activity to be undertaken with unprecedented fidelity. Because Ni–B\textsubscript{i} is composed of small nanosized domains of NiOOH\textsuperscript{16}, a much larger fraction of nickel centers are surface exposed in Ni–B\textsubscript{i} relative to its extended solid congeners, suggesting that its OER activity may be far more sensitive to changes in average structure and nickel valency than extended NiOOH materials.

We report in situ X-ray absorption spectroscopy (XAS) studies which track changes in nickel oxidation state and catalyst structure that accompany a greater than two orders of magnitude increase in OER activity during catalyst anodization. Correlation of coulometric measurements to in situ XANES spectra reveal that anodization increases the average oxidation state of Ni–B\textsubscript{i} films during catalysis, with fully activated films possessing a mean resting state nickel oxidation state of +3.6, in contrast to a mean resting state nickel oxidation state of about +3.16 for non-activated films maintained at the same potential. Based on the structural parameters extracted from fitting EXAFS data of anodized Ni–B\textsubscript{i} films, we propose that the in operando catalyst attains a Ni(IV) oxidation state within sheets of edge-sharing NiO\textsubscript{6} octahedra with ordered domain sizes no smaller than 2 nm. Elemental analysis reveals that iron is incorporated into these Ni–B\textsubscript{i} films upon anodization in reagent grade electrolyte, which contains sub-ppm levels of Fe. We find that the attainment of formal Ni(IV) character is highly sensitive to the amount of iron incorporated, and oxygen K-edge spectroscopy of Ni model compounds reveals significant covalency in Ni–O bonding in these formally Ni(IV)-containing compounds. The changes in oxidation state and short-range structure that accompany Ni–B\textsubscript{i} anodization are evocative of the transformation of η-NiOOH to γ-NiOOH, challenging the long-held view\textsuperscript{18,19} that the purely Ni(III) β-NiOOH phase effects more efficient OER catalysis. Our data reveals that the resting state required for active catalysis is one that possesses formal Ni(IV) centers, with Fe incorporation playing a key role in the attainment of this state.
2.2 Results

2.2.1 Catalyst Electrodeposition, Anodization and Electrochemistry.

Catalyst films were prepared by controlled potential electrolysis of 0.1 M KB\textsubscript{i} (all buffer solutions were prepared with ACS grade electrolyte unless noted otherwise), pH 9.2, electrolyte (0.1-B\textsubscript{i}) containing 0.40 mM Ni\textsubscript{(aq)}\textsuperscript{2+}. In our initial communication\textsuperscript{1} we reported that catalyst films were prepared by subjecting stirred 1 mM Ni\textsubscript{(aq)}\textsuperscript{2+} solutions in 0.1-B\textsubscript{i} to bulk electrolysis at 1.3 V with the passage of 0.3–10 C/cm\textsuperscript{2}. Similarly, the ex situ XAS study of Ni–B\textsuperscript{16} followed the same basic procedure to prepare the catalyst. Whereas

![Figure 2.1. Change in oxygen evolution current density as a function of anodization duration for a 1 mC/cm\textsuperscript{2} Ni–B\textsubscript{i} film on an FTO substrate, operated at (a) 1.1 V in 1.0 M KB\textsubscript{i} pH 9.2 electrolyte, (b) 3.5 mA/cm\textsuperscript{2} in 1.0 KB\textsubscript{i} pH 9.2 electrolyte, and (c) 1.1 V in 0.1 M KB\textsubscript{i} pH 9.2 electrolyte.](image)
catalyst films deposit rapidly under these conditions, such films suffer from poor adhesion to the substrate and heterogeneity in thickness over the electrode surface, in part due to the non-uniform rate of mass transport to different parts of the electrode under these conditions. For the purpose of the studies reported here, much thinner and more uniform films were desired. Films were prepared therefore from less concentrated Ni(aq)$^{2+}$ solutions and at an applied potential of 1.15 V without stirring. The passage of 1.0 mC/cm$^2$ during deposition required a period of 60–80 s. Because oxygen evolution is coincident with film formation at these potentials, the charge passed is not expected to be strictly representative of the number of nickel centers in the film. But this value does allow for an initial upper-limit estimate of catalyst loading for these brief deposition times. Such films therefore contain <10 nmol/cm$^2$ and are <7 nm thick (see section 3.5).

Following electrodeposition, films were anodized in stirred 1.0 M KB$_i$, pH 9.2, electrolyte (1.0-B$_i$) by application of 1.1 V (with correction for ohmic potential losses) for 2.5 h. Over the course of anodization, the current density increased by greater than two orders of magnitude (Figure 2.1a). Alternatively, films could be anodized by passing 3.5 mA/cm$^2$ over a similar duration, resulting in a decrease of about 300 mV in measured potential (Figure 2.1b). Operation of the catalyst at 1.1 V in 0.1-B$_i$, with compensation for ohmic losses, results in a very gradual increase in the current density over time (Figure 2.1c), with no plateau in activity observed after 3 h. These results demonstrate that the rate of anodization is dependent on total buffer concentration.

Figure 2.2a displays cyclic voltammograms (CVs) for independently prepared films (1.0 mC/cm$^2$) subject to anodization for varying times. For freshly-deposited non-anodized films, the initial sweep from 1.0 V to more negative potentials results in a broad and asymmetric cathodic wave with a shoulder at 0.87 V and a peak at $E_{p,c} = 0.81$ V, corresponding to reduction of the surface-adsorbed film. The return scan to more positive potentials displays an anodically shifted oxidation wave centered at $E_{p,o} = 1.05$ V; onset of
a catalytic wave is not observed until ~1.13 V. With anodization, the cathodic and anodic waves of the surface-adsorbed species become sharper and more symmetric, and the catalytic wave shifts to lower potential and becomes more pronounced. There is no difference in the voltammetric features of films anodized after 2 h; both 2-h and 4-h anodized films display cathodic and anodic waves centered at \( E_{p,c} = 0.87 \text{ V} \) and \( E_{p,a} = 1.025 \text{ V} \), respectively. The inset of Figure 2.2a shows the ratio of the integrated charge under the cathodic wave observed in the first scan to lower potentials in the case of each film relative to that of the 4-h-anodized film. (b) Coulometric analysis of a fully anodized 1 mC/cm\(^2\) Ni–B\(_i\) catalyst film.

Quantitative determination of the average oxidation state of nickel in anodized Ni–B\(_i\) catalyst films at 1.0 V was obtained by determining the charge required to discharge such films to the reduced Ni(II) state. Following anodization, films were held at 1.0 V for 300 s to allow the current density to attain a steady-state value (~1 \( \mu \text{A/cm}^2 \)). At 300 s, the potential was swept at 100 mV/s without pause to 0.2 V and back to 1.2 V. A background subtraction was employed to eliminate any excess charge caused by miscellaneous faradaic
processes occurring at the FTO substrate alone. Such charges accounted for less than 2% of the total charge passed. Determination of the cumulative charge passed during each sweep segment (Figure 2.2b), permits calculation of the mean number of electrons consumed per nickel center, provided the amount of nickel on the electrode can be accurately determined. Catalyst loading was quantified by digestion of films in a known volume of dilute acid immediately after the electrochemical experiment. CVs of the FTO substrates in 1.0-B\textsubscript{i} electrolyte after film dissolution were indistinguishable from background CVs collected before electrodeposition, indicating that dissolution was quantitative. Digests were analyzed for nickel concentration by inductively-coupled plasma mass spectrometry (ICP-MS). The results of such measurements on three independent films and the computed number of electrons discharged per nickel center (about 1.6 in each case) are listed in Table 2.1. These coulometric experiments establish an average nickel oxidation state of +3.61(7) for anodized Ni–B\textsubscript{i} films biased at 1.0 V.

This coulometric measurement also allows us to determine the average oxidation state of nickel centers in non-anodized films. As shown in the inset of Figure 2, the electrochemical reduction of non-anodized films to their Ni(II) state consumes 72% of the charge required to reduce anodized films. This implies an average number of electrons discharged per nickel center of about 1.16, and defines an average oxidation state of +3.16(5) for films prior to anodization.

<table>
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<tr>
<th>Charge / mC\textsuperscript{a}</th>
<th>Ni loading / nmol\textsuperscript{b}</th>
<th>No. e\textsuperscript{–} consumed per Ni</th>
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<td>1.14</td>
<td>7.5 (2)</td>
<td>1.63 (4)</td>
</tr>
<tr>
<td>1.13</td>
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<td>1.62 (4)</td>
</tr>
<tr>
<td>1.08</td>
<td>7.1 (2)</td>
<td>1.58 (4)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Total charge passed upon reduction of anodized Ni–B\textsubscript{i} catalyst films at 0.2 V.

\textsuperscript{b} Determined by quadrupole ICP-MS (see Section 2.5).
2.2.2 In situ X-Ray Absorption Spectroscopy

Nickel K-edge X-ray absorption spectra (XAS) were collected on Ni–Bi films deposited on an ITO electrode. The precise deposition sequence for the non-anodized and anodized films is described in section 2.5. In both cases, XAS spectra were collected 5 min after applying a potential to ensure that the system had reached steady state.

![XANES spectra](image)

**Figure 2.3.** (a) XANES spectra of model compounds: Ni(OH)$_2$ (blue ••), β-NiOOH (green - - - -), γ-NiOOH (red ***), NiPPI (black - - - -) and anodized Ni–Bi films at 0.4 (orange —) and 1.0 V (dark blue —). (b) XANES spectra of a non-anodized Ni–Bi film poised at 1.0 V (purple ••••), an anodized Ni–Bi film poised at 1.0 V (dark blue —), and β-NiOOH (green - - - -). The inset shows the edge energy at half jump height as a function of applied potential for anodized (dark blue •) and non-anodized (blue ▼) Ni–Bi.

Figure 2.3a presents the XANES spectra of an anodized Ni–Bi film poised at 1.0 and 0.4 V, together with model compounds Ni(OH)$_2$, β-NiOOH, γ-NiOOH and K$_2$Ni(H$_2$IO$_6$)$_2$ (potassium nickel(IV) paraperiodate, NiPPI) possessing formal nickel oxidation states of +2, +3, +3.6 and +4 respectively. The edge position of each model
compound shifts to higher energies with increasing formal oxidation state. The edge position of the crystalline $\gamma$-NiOOH compound used in this study, which is an off-stoichiometric compound with a formal nickel oxidation state of about +3.6, is approximately halfway (8345.0 eV, measured at half height $F/I_0 = 0.5$) between the stoichiometric Ni(III) compound $\beta$-NiOOH (8343.7 eV) and stoichiometric Ni(IV) compound NiPPI (8346.4 eV). The edge shape and position of the anodized film in its fully oxidized state (poised at 1.0 V) (8345.8 eV) is similar to that of $\gamma$-NiOOH (8345.0 eV) whereas, in its fully reduced state (poised at 0.4 V), the edge shape and position of the anodized film (8342.5 eV) matches that of Ni(OH)$_2$ (8342.4 eV), indicating a mean oxidation state of +2. Although the edge position of a XANES spectrum is not a straightforward indicator of the oxidation state of metals owing to the several parameters that contribute to the XANES spectra (i.e. charge density, ligand symmetry, and spin density), the trend observed here indicates that anodized Ni–Bi films poised at 1.0 V possess significant Ni(IV) content, with a mean oxidation state of nickel centers near +3.6, consistent with the coulometric measurements. For anodized Ni–Bi films poised at potentials of 1.15, 1.10, 1.05 and 1.00 V (Figure 2.3b inset), there was essentially no shift in the XANES edge energy. We therefore surmise that over this potential range anodized Ni–Bi films do not display any changes in average nickel oxidation state despite the three orders of magnitude change in the rate of catalytic turnover.

XANES spectra were also collected on a non-anodized Ni–Bi film under 1.0 V applied potential in 0.1-Bi. Because anodization is not pronounced under these conditions (Figure 2.1c), XAS spectra of such films are expected to be mostly representative of films prior to anodization with low catalytic activity. As shown in Figure 2.3b, the XANES spectrum of a non-anodized Ni–Bi film poised at 1.0 V displays an edge energy of 8344.5 eV (at $F/I_0 = 0.5$), which lies 0.8 eV positive of that of the stoichiometric Ni(III) compound $\beta$-NiOOH (8343.7 eV) and 1.3 eV below the edge position of anodized films held at the
same potential (8345.8 eV). This edge position suggests a formal nickel oxidation state for the non-anodized films between +3 and +3.6.

EXAFS data collected on anodized Ni–B$_i$ films in operando were found to be comparable to that of $\gamma$-NiOOH. The crystal structure$^{21,60}$ of $\gamma$-NiOOH is shown in Figure 2.4a, and a fragment of the edge-sharing NiO$_6$ octahedra that comprise the layered material is presented in Figure 2.4b. Figure 2.4c presents the $k^3$-weighted EXAFS spectra of $\gamma$-NiOOH along with that of an anodized Ni–B$_i$ catalyst film poised at 1.05 V. The corresponding Fourier transform (FT) EXAFS spectra are shown in Figure 2.4d. The
abscissa in the FT spectra is the apparent distance \( (R') \), which is shorter than the actual distance between the absorber-backscatterer atom pairs due to a phase shift.

The EXAFS spectra display two main peaks: peak I reflects the presence of Ni–O interactions (path a–b in Figure 2.4b), and peak II manifests Ni–Ni interactions (path a–c), as demonstrated by the EXAFS fits (vide infra). The positions of peaks in the FT EXAFS spectra of anodized Ni–B\textsubscript{i} films are similar to those of \( \gamma \)-NiOOH but there are differences in peak intensity. In particular, peak IV, corresponding to longer range interactions (path a–e) is suppressed significantly in the FT EXAFS spectrum of the catalyst film as compared to what is found in the case of the crystalline \( \gamma \)-NiOOH. Spectra of the anodized catalyst films held at 1.05 and 1.15 V displayed marginal differences, with slightly higher overall EXAFS intensities observed when the film is polarized at higher potential (Figure 2.5a). When an anodized catalyst film is reduced to Ni(II) by maintaining the potential at 0.4 V, the EXAFS spectrum becomes similar to that of the Ni(OH)\textsubscript{2} with longer Ni–O and Ni–Ni distances (Figure 2.5b).

The EXAFS curve fitting was first carried out for \( \gamma \)-NiOOH based on its known crystal structure, by including absorber-backscatterer vectors \( \leq 5.8 \) Å in length and fixing

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**Figure 2.5.** FT EXAFS spectra and \( k^3 \)-weighted EXAFS spectra (inset) of (a) an anodized Ni–B\textsubscript{i} catalyst film maintained at 1.05 V (dark blue) and 1.15 V (red) along with (b) Ni(OH)\textsubscript{2} (blue) and an anodized Ni–B\textsubscript{i} catalyst film held at 0.4 V (lime).
the number of neighbors in each shell (N values) to values determined from the crystal structure (6.0 in each case). Figure 2.6 shows the k-space and FT spectra of the best fit, and Table 2.2 summarizes the fitting parameters. The actual distances (R) of the EXAFS fits are in good correspondence with the crystallographic distances of γ-NiOOH. With these results in hand for the model compound, the fit of the experimental spectrum of anodized Ni–Bi was produced (Figure 2.7).

In order to estimate a lower-limit domain size, the Debye-Waller factors (σ²), were fixed to the values obtained from γ-NiOOH EXAFS curve fitting (Table 2.2), and the N values.

![Image](image.png)

Figure 2.6. Fit (black ——) to EXAFS spectrum of γ-NiOOH (red —). The inset shows the corresponding k³-weighted oscillations. Fit parameters are indicated in Table 2.2.

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<td>6.0</td>
<td>0.006 (1)</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

a Fitting region 1 ≤ R / Å ≤ 6, 2.9 ≤ k / Å⁻¹ ≤ 11.9. Values in parentheses indicate uncertainties. b Fixed values. c Multiple scattering path (a–e; Ni–Ni–Ni)
values were optimized for the best fit. We consider these $\tilde{\sigma}^2$ values to be a reasonable lower-limit because static disorder is expected to be lower in the crystalline $\gamma$-NiOOH compound relative to Ni–Bi. The resulting fit, which is displayed in Figure 2.7, returns an N value for the Ni–Ni vector (with $R = 2.82$ Å) of ~5. Much weaker peaks arising from interactions at distances >3 Å (peaks III and IV) also suggests a less-ordered structure or smaller cluster size in the Ni–Bi film compared to the crystalline $\gamma$-NiOOH compound. A lower-limit domain size consisting of ~40 Ni ions for the seemingly amorphous catalyst film is estimated from this Ni–Ni N value.

**Figure 2.7.** Fit (black ——) to EXAFS spectrum of anodized Ni–Bi at 1.05 V (blue —). The inset shows the corresponding $k^2$-weighted oscillations. Fit parameters are indicated in Table 2.3.

### Table 2.3. Anodized Ni–Bi Catalyst EXAFS Fitting Parameters

<table>
<thead>
<tr>
<th>Path</th>
<th>$R$ / Å</th>
<th>$N$</th>
<th>$\sigma^2$ / Å$^{-2}$</th>
<th>$\Delta E^0$ / eV</th>
<th>$R_\tilde{\sigma}$ / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni–O</td>
<td>1.89 (0.01)</td>
<td>5.9 (1)</td>
<td>0.007</td>
<td>3.3</td>
<td>3.1</td>
</tr>
<tr>
<td>Ni–Ni</td>
<td>2.82 (0.01)</td>
<td>5.1 (3)</td>
<td>0.006</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni–Ni</td>
<td>4.86 (0.07)</td>
<td>4 (3)</td>
<td>0.012</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni–Ni$^c$</td>
<td>5.70 (0.03)</td>
<td>3 (1)</td>
<td>0.004</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Fitting region $1 \leq R / \text{Å} \leq 6$, $2.8 \leq k / \text{Å}^{-1} \leq 11.8$. Values in parentheses indicate uncertainties. See Supporting Information for details.  

$^b$ The $\tilde{\sigma}^2$ values were set to the values obtained from $\gamma$-NiOOH curve fitting. 

$^c$ Multiple scattering path (a–e; Ni–Ni–Ni).
EXAFS data were collected on a non-anodized Ni–Bi film poised at 1.0 V to provide insight into the local structure of the catalyst film in its initially-deposited, less catalytically active state (Figure 2.8). β-NiOOH was considered a preliminary model compound for such films, since it displayed the closest mean Ni oxidation state (Figures 2.2 and 2.3b).

![Figure 2.8](image)

**Figure 2.8.** EXAFS FT spectra for non-anodized Ni–Bi poised at 1.0 V (blue), anodized Ni–Bi poised at 1.05 V (dark blue), and β-NiOOH (green). The inset shows the corresponding k²-weighted oscillations.

<table>
<thead>
<tr>
<th>Fit No.</th>
<th>Path</th>
<th>R / Å</th>
<th>N</th>
<th>σ² / Å²</th>
<th>ΔE⁰ / eV</th>
<th>Rᵣ / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni–O</td>
<td>1.90</td>
<td>6.0ᵇ</td>
<td>0.015</td>
<td>1.8</td>
<td>6.6</td>
</tr>
<tr>
<td></td>
<td>Ni–Ni</td>
<td>2.87</td>
<td>6.0ᵇ</td>
<td>0.013</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Ni–O</td>
<td>1.92</td>
<td>4.0 (4)ᶜ</td>
<td>0.008 (2)ᶜ</td>
<td>6.1</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>Ni–O</td>
<td>2.19</td>
<td>2.0 (4)ᶜ</td>
<td>0.008 (2)ᶜ</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni–Ni</td>
<td>2.90</td>
<td>4.4 (4)ᵈ</td>
<td>0.008 (1)ᶠ</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni–Ni</td>
<td>3.15</td>
<td>1.6 (4)ᵈ</td>
<td>0.008 (1)ᶠ</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ᵃ Fitting region 1.2 ≤ R / Å ≤ 3.2, 2.69 ≤ k / Å⁻¹ ≤ 12.60. Values in parentheses indicate uncertainties.ᵇ fixed values.ᶜᵈ Sum of the N values for the short and long interactions were fixed to 6.ᶜᶠ σ² values were set to be equal for the short and long interactions.
Figure 2.8 compares the EXAFS spectrum of a non-anodized Ni–B\textsubscript{i} film to that of its anodized congener and \(\beta\)-NiOOH. The EXAFS FT of a non-anodized Ni–B\textsubscript{i} film presents peaks at distances similar to those of anodized films; yet with much lower intensities. The peak intensities for \(\beta\)-NiOOH are lower than those of either Ni–B\textsubscript{i} film. For both NaNiO\textsubscript{2} and \(\beta\)-NiOOH, the best fits (Tables 2.4 and 2.5) were obtained by considering two distinct sets of distances for the first and second shell vectors that reflect a Jahn–Teller distortion (Figure 2.9).\textsuperscript{22,23}

Table 2.5. \(\beta\)-NiOOH EXAFS Curve Fitting Parameters$^a$

<table>
<thead>
<tr>
<th>Fit</th>
<th>Path</th>
<th>$R$ / Å</th>
<th>$N$</th>
<th>$\sigma^2$ /Å$^{-2}$</th>
<th>$\Delta E^0$ / eV</th>
<th>$R_l$ / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni–O</td>
<td>1.92 (3)</td>
<td>6.0$^b$</td>
<td>0.013 (2)</td>
<td>-0.3</td>
<td>17.7</td>
</tr>
<tr>
<td></td>
<td>Ni–Ni</td>
<td>2.82 (4)</td>
<td>6.0$^b$</td>
<td>0.017 (3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Ni–O</td>
<td>1.92 (5)</td>
<td>3.9 (0.5)$^c$</td>
<td>0.007 (2)$^d$</td>
<td>5.1</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>Ni–O</td>
<td>2.12 (5)</td>
<td>2.1 (0.5)$^c$</td>
<td>0.007 (2)$^d$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni–Ni</td>
<td>2.86 (2)</td>
<td>3.3 (0.2)$^c$</td>
<td>0.006 (1)$^d$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni–Ni</td>
<td>3.09 (2)</td>
<td>2.7 (0.2)$^c$</td>
<td>0.006 (1)$^d$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Fitting region 1.0 $\leq R$ / Å $\leq$ 3.6, 2.55 $\leq k$ / Å$^{-1}$ $\leq$ 12.52. Values in parentheses indicate uncertainties. $^b$ fixed values. $^c$ Sum of the $N$ values for the short and long interactions were fixed to 6. $^d$ $\sigma^2$ values were set to be equal for the short and long interactions.

Figure 2.8 compares the EXAFS spectrum of a non-anodized Ni–B\textsubscript{i} film to that of its anodized congener and \(\beta\)-NiOOH. The EXAFS FT of a non-anodized Ni–B\textsubscript{i} film presents peaks at distances similar to those of anodized films; yet with much lower intensities. The peak intensities for \(\beta\)-NiOOH are lower than those of either Ni–B\textsubscript{i} film. For both NaNiO\textsubscript{2} and \(\beta\)-NiOOH, the best fits (Tables 2.4 and 2.5) were obtained by considering two distinct sets of distances for the first and second shell vectors that reflect a Jahn–Teller distortion (Figure 2.9).\textsuperscript{22,23}

![Figure 2.9](image.png)

Figure 2.9. Models of the first and second shell scattering paths in (a) a structure where all Ni–O (lime green) and Ni–Ni (black) paths are equivalent, such as that found in \(\gamma\)-NiOOH and (b) a Jahn-Teller distorted structure where there exists two sets of non-equivalent Ni–O (lime green) and Ni–Ni (black) distances, such as that found in \(\beta\)-NiOOH or NaNiO\textsubscript{2}.
With β-NiOOH, the best fit to the EXAFS spectrum yields a ratio of long and short Ni–O interaction numbers of 3.9 to 2.1, which is similar to the 4:2 ratio expected from the Jahn-Teller distortion. An excellent fit was obtained for the non-anodized film (Figure 2.10) with a ratio of long and short Jahn–Teller distorted vectors of about 4:2 (Table 2.6: Fit 1). Importantly, the fit quality suffers appreciably ($R_f = 7.1$ vs. $2.0\%$) when only a single path is considered for the first and second shell vectors (Table 2.6: Fit 2). These fitting

![Figure 2.10](image-url)

**Figure 2.10.** Fit (black ——) to EXAFS spectrum of non-anodized Ni–Bi poised at 1.0 V (blue —). The inset shows the corresponding $k^3$-weighted oscillations. Fit parameters are indicated in Table 2.6.

<table>
<thead>
<tr>
<th>Fit</th>
<th>Path</th>
<th>$R$ / Å</th>
<th>N</th>
<th>$\sigma^2$ / Å$^{-2}$</th>
<th>$\Delta E_0$ / eV</th>
<th>$R_f$ / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni–O</td>
<td>1.90 (1)</td>
<td>4.0 (4)$^c$</td>
<td>0.003 (1)$^d$</td>
<td>5.7</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>Ni–O</td>
<td>2.10 (3)</td>
<td>2.0 (4)$^c$</td>
<td>0.003 (1)$^d$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni–Ni</td>
<td>2.83 (1)</td>
<td>4.60 (35)$^c$</td>
<td>0.005 (1)$^d$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni–Nid</td>
<td>3.05 (3)</td>
<td>1.40 (35)$^c$</td>
<td>0.005 (1)$^d$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Ni–O</td>
<td>1.92 (1)</td>
<td>6.0$^b$</td>
<td>0.001 (1)</td>
<td>2.5</td>
<td>7.1</td>
</tr>
<tr>
<td></td>
<td>Ni–Ni</td>
<td>2.81 (1)</td>
<td>6.0$^b$</td>
<td>0.008 (1)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$a$ Fitting region $1.0 \leq R / \text{Å} \leq 3.6$, $2.55 \leq k / \text{Å}^{-1} \leq 12.52$. Values in parentheses indicate uncertainties (see page S2). $^b$ Fixed values. $^c$ Sum of the N values for the short and long interactions were fixed to 6. $^d$ $\sigma^2$ values were set to be equal for the short and long interactions.
results point to a distortion in the local coordination geometry about Ni centers in non-anodized Ni–Bi films, as found in β-NiOOH and NaNiO₂.

### 2.2.3. X-ray PDF Analysis of Ni–Bi Catalyst Films

Catalyst samples were prepared for X-ray PDF analysis by controlled-potential electrolysis of an aqueous solution of 0.5 mM Ni(NO₃)₂ and 0.5 M potassium borate (KBi) electrolyte, pH 9.2 at an applied potential of 1.1 V vs. NHE. In order to isolate sufficient material for PDF analysis, fluorine-doped tin oxide (FTO)-coated glass plates (8 Ω/□, Hartford Glass) measuring 12 in × 9 in were used as substrate. For as-deposited samples, immediately following a 20 h deposition, the coated plates were rinsed with 18 MΩ deionized water and dried with compressed air. Catalyst samples were then mechanically isolated and packed into polyimide (kapton) capillary tubes (ca. 1 mm ID) for X-ray analysis. In the case of anodized samples, after deposition the plates were rinsed with deionized water and transferred, without drying, into 1 M KBi pH 9.2 electrolyte (reagent grade). The film was then anodized by chronopotentiometry at a current density of ~0.5 mA/cm² for 3 h, prior to isolation as described above. 30–40 mg of sample was typically isolated per deposition.

Synchrotron X-ray total scattering experiments were conducted on these samples at a temperature of 100 K. The rapid acquisition pair distribution function (RaPDF) technique was used with an X-ray energy of 78.396 keV (λ = 0.15815 Å). The measured Q[S(Q) – 1] (structure function) plots of the catalyst samples are in Figure 2.11a, and the resultant G(r) plots are displayed in Figure 2.11b. The structure function data show that these samples exhibit primarily diffuse scattering. Yet these samples are clearly nanocrystalline, since they exhibit well-defined local structural orders as manifested by the sharp peaks at low r in Figure 2.11a. It is also evident that the anodized catalyst (blue traces) has a larger structural coherence than the as-deposited sample (red traces) because the PDFs show a larger range of r with pronounced structural correlations. As suggested
by the sharp peaks in the difference curve (Figure 2.11b, green), the peak positions of each PDF are significantly mismatched. This reveals a substantial degree of structural modulation upon anodization of these materials.

Based upon the aforementioned EXAFS results, we adopted both $\beta$-NiOOH and $\gamma$-NiOOH structures as the starting models for PDF investigation. The PDF fits were carried out using the complex modeling framework SrFit. The PDFs of the nanocrystalline samples were calculated theoretically from atomic models by multiplying the bulk $G_{\text{bulk}}(r)$ by a spherical characteristic function $\gamma(r)$:

$$G_{\text{nano}}(r) = \gamma(r)G_{\text{bulk}}(r).$$

$G_{\text{bulk}}(r)$ was a PDF calculated using periodic boundary conditions while the characteristic function $\gamma(r)$ is the autocorrelation of the shape function of the sample. It has value unity inside the (average) nanoparticle and value zero outside. Both structural models from $\beta$-NiOOH and $\gamma$-NiOOH were applied to the nickel catalyst samples. Fit results are shown in Figure 2.12.

Preliminary inspection of the data presented in Figure 2.12 reveals that both models were capable of replicating the general features of the catalysts. This confirms the general assignment of the catalyst as comprised of nanocrystalline NiOOH-like phases. However,
between single-phase β-NiOOH and γ-NiOOH, the as-deposited material (Figure 2.12a) fits better to the former (top) with a lower agreement factor, $R_w$. The converse is true of the anodized catalyst (Figure 2.12b), which is better fit using the truncated γ-NiOOH structure (middle). However, close inspection of the fits in Figures 2.12a and 2.12b indicates that both structural models fit well to some specific PDF peaks in both cases. For example, the peaks at 3.3 Å and 4.3 Å in PDF of the anodized sample (Figure 2.12b) agree better with a β-NiOOH model (top) although the overall fit using the same model over the whole range is considerably worse. This suggested that samples likely contained a mixture of both phases. Indeed, a two phase model affords the best fit as shown in Figure 2.12 (bottom) and Table 2.7.

**Figure 2.12.** Fits to PDFs of (a) as-deposited Ni–B$_4$ and (b) anodized Ni–B$_4$ films. In each case, PDFs were fit to nanocrystalline models using top: only β-NiOOH with space group C2/m, middle: only γ-NiOOH with space group $R\overline{3}m$, and bottom: a two-phase fit comprising structures in both β-NiOOH and γ-NiOOH. In all cases the circles represent the experimental PDFs, black curves are the calculated PDFs of the best-fit structural model and the green curves offset below are the difference curves. Agreement factor ($R_w$) values are as follows: (a) from top to bottom 0.39, 0.32 and 0.28; and (b) from top to bottom 0.38, 0.42, and 0.31. Fitting results of the two phase fit are summarized in Table 2.7.
The structural data measured here can be used to estimate the average Ni valency for comparison to XANES and coulometric data using the bond valence sum (BVS) method. The valence of any Ni ion (\( V_{ij} \)) with a bond length \( R_{ij} \) in the as-deposited and anodized samples can be analyzed from the determined structures by:

\[
V_{ij} = \sum \exp\left(\left( R_0 - R_{ij} \right)/B \right)
\]

where \( R_0 \) is the tabulated bond length of unit valence and \( B \) is an empirical parameter.\(^{31}\)

For \( \gamma \)-NiOOH, empirical \( B \) and \( R_0 \) are found to be 0.35 Å and 1.78 Å, respectively, while for \( \beta \)-NiOOH, values of 0.37 Å and 1.75 Å are used. The BVS result is then weighted by the phase fraction. We calculate that the average valence of Ni ions in the as-deposited material is +3.1, and this increases to +3.8 upon anodization. These structure-based results are in good agreement with the electrochemical and spectroscopic studies.

### 2.2.4. Oxygen K-edge Spectroscopy of Ni model compounds

Having established the catalyst as comprised of Ni–O motifs in the NiOOH family, we deemed it important to investigate the extent of covalency in Ni–O bonding in such oxidic materials. Ligand K-edge spectroscopy is a powerful tool for probing metal–ligand covalency. We used electron energy loss spectroscopy (EELS) to measure the oxygen K-edge spectra of a series of model compounds in order to identify trends in nickel oxides that could be applicable to our catalyst films. EELS exploits the inelastic scattering of electrons by ions in a sample offers a means to measure electronic (as well as phononic,
and plasmonic) excitations.\textsuperscript{32,33} The energy loss near edge structure (ELNES) provides similar inner shell ionization information as X-ray absorption near edge structure (XANES). However, the higher spatial resolution of transmission electron microscopes makes ELNES a particularly powerful tool for the analysis of thin-film materials; selected areas may be interrogated, allowing the extraction of spectra that may be associated with different phases or compositions in a material.

EELS spectra were measured on NiO, Ni(OH)\textsubscript{2}, LiNi\textsuperscript{III}O\textsubscript{2}, and γ-Ni\textsuperscript{III/IV}OOH using a Zeiss Libra 200 aberration-corrected TEM fitted with an in-column energy filter, and operated at an accelerating voltage of 80 kV. O K edge spectra generally arise due to transitions between O 1s and unoccupied O 2p orbitals (which are filled in a purely ionic model of such materials, but due to covalency in bonding between O and Ni remain accessible). These spectra typically feature a “pre-peak” centered around 530 eV and a broader set of overlapping peaks stretching across the 535–550 eV range. The first peak arises as a result of transitions to states of O 2p character that are mixed with metal 3d orbitals, while the second set of peaks is associated with transitions to O 2p orbitals.

![Figure 2.13. Oxygen K-edge ELNES of nickel oxide model compounds. From top to bottom: Ni\textsuperscript{II}O, Ni\textsuperscript{II}(OH)\textsubscript{2}, LiNi\textsuperscript{III}O\textsubscript{2}, and γ-Ni\textsuperscript{III/IV}OOH. Spectra were normalized to the edge jump and offset for clarity.](image)
hybridized with metal 4s and 4p orbitals. The intensity of the first peak in particular has been shown to be a powerful indicator of the degree of covalency in metal-oxygen bonding.\textsuperscript{34–38} Our measured O K-edge spectra are presented in Figure 2.13. Most notably, the intensity of the pre-peak grows as the formal oxidation state of the nickel oxide increases. This pre-peak is particularly prominent in the case of the Ni(IV)-containing $\gamma$-NiOOH, indicating a pronounced degree of covalency in Ni–O bonds for this highly oxidized compound.

\subsection*{2.2.5. Elemental analysis and coulometric studies of Fe incorporation}

We sought to interrogate the potential role of incidental iron incorporation over the course of the anodization process, given the established disposition for Fe in electrolytes to be absorbed by nickel oxide electrodes.\textsuperscript{39–42} We surmised that it would be particularly revealing to identify the formal valency of Ni centers in films that had been anodized in rigorously Fe-free electrolyte. Reagent grade electrolyte typically contains ppm concentrations of Fe, which may be scrubbed from the solution by treatment with solid Ni(OH)\textsubscript{2} as described in the literature.\textsuperscript{41,42}

Ni–Bi films were electrodeposited from pH 9.2 aqueous solutions of 0.1 M KB\textsubscript{i} electrolyte containing 0.4 mM Ni\textsuperscript{2+} by constant potential electrolysis (CPE) at 1.05 V, as described above. Deposition was terminated upon the passage of 1.0 mC/cm\textsuperscript{2}. Immediately following deposition, films were rinsed in type I water and immersed in rigorously Fe-free 1.0 M KOH electrolyte (see Section 2.5). These films were anodized with stirring in this Fe-free electrolyte by CPE at 0.75 V for 3 h. A comparison of CPE traces obtained for Ni–Bi films anodized in reagent-grade KOH and those anodized in purified Fe-free KOH is shown in Figure 2.14. It is evident that the increase in activity during anodization is severely attenuated upon scrubbing Fe from solution.
After anodization films were poised at 0.6 V for 45 s in order to attain a low steady state current density (ca. 1 µA/cm²). At 45 s the voltage was swept at 100 mV/s without pause to −0.2 V and then back to 0.8 V (Figure 2.15a, top). Films were subsequently rinsed

**Figure 2.14.** Controlled-potential electrolysis at 0.75 V of a freshly-deposited Ni–Bᵢ film in reagent grade 1 M KOH (blue) and Fe-free 1 M KOH (red).

**Figure 2.15.** (a) Cyclic voltammetry in 1 M KOH of a Ni–Bᵢ film deposited onto an FTO-coated glass slide and anodized for 3 h in Fe-free 1.0 M KOH. Scan rate: 0.1 V/s. Current (top, ---) and total charge (bottom, —) data are offset for clarity. (b) Comparison of coulometric titration results for Ni–Bᵢ films. Results for as-deposited films and films anodized in reagent-grade 1 M KBᵢ pH 9.2 (far left and far right) are compared with those doped with varying amounts of Fe by incubation in 1 M KBᵢ at open-circuit for the designated amount of time. Fe percentage (relative to total Ni and Fe content determined by ICP) is shown above each category bar.
in type I water, dissolved in ultrapure nitric acid (doubly-distilled) and analyzed for Ni and Fe content by ICP-MS. The amount of Fe detected in such films that were anodized in scrubbed electrolyte amounted to 1.7% of the Ni content, representing a minimal increase in Fe content over films in their as-deposited state (1.2%) as compared to those anodized in unpurified reagent-grade KOH electrolyte, which we find to contain 8% Fe relative to total metal content (%Fe values as high as ~15% have been reported in the literature \cite{41, 42}. The total charge passed during each sweep segment was determined from the voltammetry data as described in Section 2.2.1 (Figure 2.15a, bottom). We observe that 1.2(1) electrons are consumed per Ni upon reduction to Ni(II). These results reveal that a Ni valency of +3.2(1) is sustained upon anodization in Fe-free solution.

Since iron incorporation is a chemisorption (acid–base reaction) process that occurs at the surface of the NiOOH layers, incubating films in reagent-grade (i.e. trace Fe-containing) 1 M KB\textsubscript{i} pH 9.2 at open-circuit for varying times, prior to anodization in Fe-free KOH may be used to “dope” the film with Fe to varying degrees. Incubating freshly deposited films in this manner for 5 or 30 minutes followed by anodization in Fe-free 1 M KOH and subsequent coulometric titration reveals that the increased Fe content of 2.1% and 3.4% correlates with formal Ni valency values of +3.3 and +3.6. As shown in Figure 2.15b, by comparison to data of as-deposited films (1.16(5) e\textsuperscript{-}/Ni) and those anodized in reagent-grade electrolyte (1.61(7) e\textsuperscript{-}/Ni) (vide supra), these results reveal that the removal of iron from solution clearly inhibits the formation of a more oxidized resting state during anodization.

2.3. Discussion

A Ni–B\textsubscript{i} catalyst film requires a pre-electrolysis regimen following electrodeposition to obtain high OER activities. Over the course of this anodization, the efficiency of Ni–B\textsubscript{i} films in mediating the OER is enhanced by greater than 2 orders of magnitude as indicated by Figure 2.1. This drastic improvement in catalytic activity is
reflected in the prominence of the catalytic wave in CVs of anodized films compared to the diminished catalytic wave at identical potentials in non-anodized films (Figure 2.2). Narrower and more symmetric voltammetric peak shapes for CVs of anodized catalyst films indicate that the anodization process results in greater homogeneity in the nickel equilibrium potentials. The rate of anodization is sensitive to the electrolyte concentration (Figure 2.1a vs. Figure 2.1c). By using low electrolyte concentrations, we have been able to retard anodization to the extent that over the time course of XAS data collection, we are able to monitor, in situ, the structural and oxidation state changes that accompany anodization and the attendant increase in catalytic activity.

2.3.1. Nickel Oxidation State Changes in Ni–Bi

Coulometric and XANES studies corroborate the average oxidation state of nickel in Ni–Bi for anodized and non-anodized films subjected to various potentials. For both anodized and non-anodized films, polarization at potentials well below the onset potential for water oxidation catalysis (0.4 V) induces complete reduction of the nickel centers to the +2 oxidation state (Figure 2.2). Conversely, anodized films polarized at 1.0 V, a potential at which oxygen evolution catalysis occurs, exhibit a mean oxidation state of +3.6 (Figures 2.2 and 2.3a, Table 2.1), whereas non-anodized films, held at the same potential, exhibit a mean oxidation state of +3.16 (Figures 2.2 and 2.3b). Thus the process of anodization increases the fraction of Ni(IV) centers in the film by at least a factor of 3 (from 20% to 60%) over the course of 4 h (Figure 2.2). Coulometric studies establish that the vast majority of this oxidation state change occurs within the first hour of anodization (Figure 2.2). This time window corresponds qualitatively to the time scale over which the vast majority of increase in OER activity is observed (Figure 2.1a). The similar time course observed for activity and oxidation state increases points to a strong correlation between the two properties. BVS analysis of X-ray PDF data also reveals an increase in the average Ni valency from +3.1 to +3.8, in accordance with the spectroscopic and coulometric data.
The increase in nickel oxidation state from ca. +3 to approximately +3.7 is concordant with the oxidation state change observed for phase conversion of β-NiOOH to γ-NiOOH. Importantly, polarization of the anodized Ni–Bi films beyond 1.0 V, up to a potential of 1.15 V, does not engender any further increase in the average formal oxidation state of nickel centers despite the fact that this same increase in potential corresponds to a three order of magnitude increase in the rate of OER catalysis. Together, these results establish that an increase in the Ni(IV) population in the catalyst resting state is correlated with an increase in overall activity.

2.3.2. Anodization-Induced Structural Changes in Ni–Bi.

The similarities between crystalline γ-NiOOH and anodized Ni–Bi catalyst films in terms of XANES edge position, formal nickel oxidation state and EXAFS spectra indicate that γ-NiOOH is an appropriate model compound for the structure of anodized Ni–Bi catalyst films. In γ-NiOOH, edge-sharing NiO$_6$ octahedra are arranged into higher-order layers, which are interstratified with alkali cations and water molecules (Figure 2.4a). EXAFS spectra of anodized Ni–Bi catalyst films exhibit a first shell Ni–O vector at 1.89 Å and a nearest-neighbor Ni–Ni vector at 2.82 Å associated with the presence of Ni-oxo/hydroxo structural units similar to those found in γ-NiOOH (Figure 2.4b–d). The γ-NiOOH structure is differentiated from β-NiOOH (and NaNiO$_2$) by a Jahn–Teller distortion of the low-spin d$^7$ Ni(III) centers of the latter, which gives rise to an axial elongation and equatorial contraction of the oxygen ion ligand field producing a 2:1 ratio of Ni–O scattering vectors of 1.87 and 2.03 Å, respectively (Figure 2.9, Table 2.5). This Jahn–Teller distortion in β-NiOOH results in two effects that distinguish its EXAFS spectrum from γ-NiOOH (and anodized Ni–Bi): (i) a drastic diminution in the intensity and (ii) broadening of the first and second shell scattering peaks arising from their poorly resolved splitting into two separate sets of peaks corresponding to a ~4:2 ratio of short equatorial and long axial vectors respectively about each Ni(III) center. The sharp peaks
observed for the first and second shell of Ni–Ni and Ni–O scattering vectors in the experimental spectrum of anodized Ni–B\textsubscript{i} are similar to the peak profiles of \(\gamma\)-NiOOH, and thus the local coordination geometry of anodized Ni–B\textsubscript{i} is akin to \(\gamma\)-NiOOH and not a Jahn–Teller distorted Ni(III) phase, such as \(\beta\)-NiOOH or NaNiO\textsubscript{2}.

Whereas anodized Ni–B\textsubscript{i} is structurally analogous to \(\gamma\)-NiOOH, non-anodized Ni–B\textsubscript{i} has an EXAFS spectrum that is more similar to a Jahn–Teller distorted Ni(III) phase. A good fit to the non-anodized Ni–B\textsubscript{i} spectrum (Figure 2.10) is obtained with a long to short axis ratio of 4.0 to 2.0 for the Ni–O vectors (Table 2.6), the ratio we expect for a Ni(III) compound. A slightly greater formal nickel oxidation state (+3.16) was determined from coulometric measurements, and correspondingly the XANES edge position is 0.8 eV higher relative to that of \(\beta\)-NiOOH (Figure 2.3b). These EXAFS results point to a local structural change upon anodization of Ni–B\textsubscript{i} that resembles phase conversion of \(\beta\)-NiOOH to \(\gamma\)-NiOOH.

While the nickelate layers of \(\beta\)-NiOOH and \(\gamma\)-NiOOH stack preferentially, we were unable to identify any EXAFS interactions due to interlayer backscattering in either model compound or catalyst film. However, given the large intersheet distance (~7 Å) in \(\gamma\)-NiOOH\textsuperscript{60} such interactions are expected to be too weak to resolve in EXAFS spectra, and would be anticipated to be even weaker in the case of the more disordered catalyst material. Despite the inability to detect any interlayer scattering interactions by EXAFS some degree of stacking of the sheet-like domains of Ni–B\textsubscript{i} is evident. The electrolyte concentration dependence of the rate of anodization (Figure 2.1a vs. 2.1c) provides experimental evidence in support of this contention. Cation intercalation is a critical requirement for the formation of \(\gamma\)-NiOOH from the alkali cation-free \(\beta\)-NiOOH.\textsuperscript{43} The intercalation of K\textsuperscript{+} ions between the NiO\textsubscript{2} sheets in Ni–B\textsubscript{i} films during anodization, may explain the observed electrolyte-dependence. Thus, increasing the buffer strength, and correspondingly the K\textsuperscript{+} ion activity, would be expected to enhance the rate of activation, provided that the domains of Ni–B\textsubscript{i}
are stacked to some degree. Alternatively, it is also plausible that the electrolyte concentration dependence is related to the adsorption of Fe ions from the solution; a lower concentration of the reagent grade electrolyte will mean a lower Fe concentration and consequently a slower rate of activation.

PDF data confirms the nickelate-based structure of Ni–B\textsubscript{i} films, but showed that samples comprised a mixture of phases (Figure 2.12). Phase heterogeneity is to be expected since deposition for the duration required to generate enough material for X-ray scattering (~20 h, vide supra) should unavoidably lead to generation of a small fraction of activated catalyst in the as-deposited material. In addition, anodization on the scale required for such large substrate plates, is unlikely to be exhaustive, leaving some non-anodized Ni–B\textsubscript{i} in the ostensibly “anodized” film. Indeed a two-phase fit results in improvement in fidelity to the experimental PDF as shown in the bottom plots of Figure 2.12. Fit residuals remain approximately 0.3 which is not uncommon for a PDF fit of ultra-small nanoparticles with domain sizes less than 2 nm\textsuperscript{29,30,44} Fit results (summarized in Table 2.7) show that the structural coherence of anodized catalyst is ~5 Å larger than the as-deposited analog. This result indicates some degree of electrochemical sintering during activation. As expected from the initial single-phase fits, a substantial increase (doubling) in the phase fraction of γ-NiOOH is observed upon anodization.

The size of the ordered domains in anodized Ni–B\textsubscript{i} may be estimated from the N values obtained from curve fitting (Figure 2.7, Table 2.3) of EXAFS spectra. The diminished longer-range interactions (at distances >3 Å) in FT EXAFS spectra, compared to an extended solid (Figure 2.4d, \textcolor{red}{\cdots} vs. \textcolor{black}{\cdots}), suggests a nanocrystallite model as does the inability to detect crystallites by X-ray diffraction methods. From the N-value for the Ni–Ni vector of ~5.1 (Table 2.3), we estimate that the smallest ordered domains in catalyst films are 2–3 nm in diameter. Thus, a simplified hexagonal cluster model is constructed with ordered domains of ~40 Ni centers (Figure 2.16) as a reasonable lower-limit average
structural model for Ni–B_i catalyst films. This domain size is also in agreement with X-ray PDF data that show structural correlations up to ~2 nm (Figure 2.12, Table 2.7). We, therefore, rationalize that our Ni–B_i electrosynthesis method is giving us access to such nanocrystalline oxides as uniform ultrathin films at intermediate pH.

2.3.3 Ni(IV) valency: Ligand covalency and influence of iron doping.

The discovery of these catalysts as comprising nanosized domains of Ni–O clusters raises key questions regarding the participation of oxygen ions in the redox chemistry and catalytic performance of active sites. The aforementioned results reveal that anodization increases the average oxidation state of nickel centers in the resting state of the catalyst such that formal Ni(IV) valency is attained. Moreover, because there is no detectable change in the XANES edge shift of anodized films (Figure 2.3b inset) between 1.0 and 1.15 V, the mechanism of action of catalytically active sites in the anodized film likely involves a further minor-equilibrium, possibly from these Ni(III/IV) resting states to Ni(IV/V) catalytic intermediates. While precise details on the electronic structure of these catalysts remain unclear. It is evident from oxygen K-edge spectroscopy (Figure 2.11) that

Figure 2.16. Lower-limit structural model for the average domain size of Ni–B_i. The Ni ions are shown in green, bridging oxo/hydroxo ligands are shown in red, and non-bridging oxygen ligands, which may include water, hydroxide, phosphate, or borate, are shown in pale green.
the oxidation of such oxidic materials entails the removal of electrons from orbitals with significant O character. Growth in the characteristic pre-peak feature at 530 eV from NiO and Ni(OH)$_2$ to LiNiO$_2$ and γ-NiOOH shows that the Ni-O bond covalency in nickel oxides increases as the compounds are increasingly oxidized. In light of these data it is reasonable to expect that in the Ni(III/IV) mixed-valence resting state and yet more so in the case of any catalytic intermediates that are generated in small populations in minor equilibrium, there exists a significant proportion of unpaired spin density on oxygen ions (O’ character). The exacerbation of unpaired spin density on oxygen centers and the formation of oxyl radicals has been proposed as an important pathway in O-O bond formation in the case of our cobalt thin-film catalysts.\textsuperscript{45–47} These preliminary results emphasize the importance of further computational and synthetic efforts aimed at uncovering more details of redox participation by oxygen ions in the OER.

In recent studies, Boettcher and co-workers demonstrated that reagent grade potassium borate (KB$_4$) pH 9.2 electrolytes contain ppm-level concentrations of Fe, which may be incidentally incorporated into such nickel oxido films over the course of anodization.\textsuperscript{42} Importantly their data revealed that (i) scrubbing Fe from a solution and anodization in the resultant “Fe-free electrolyte” leads to no appreciable activity enhancement over the course of several hours, and (ii) films prepared by intentional co-deposition of Fe with Ni still required anodization in order to achieve maximal activity. These insights led us to embark on a series of studies to definitively identify the roles of Fe inclusion and Ni valency changes in defining the activity of Ni oxide thin film OECs. To conclusively probe the influence of iron incorporation on the general electronic structure and redox properties of the catalyst, we studied the composition and electrochemical behavior of ultrathin catalyst films by coulometric titration.

Evaluating the elemental composition of the catalyst films upon anodization confirms the incorporation of iron into films from reagent-grade electrolyte. Scrubbing the
electrolyte of trace iron leads to a diminished activity of the films towards catalysis of the OER (Figure 2.11). Importantly, coulometric titration of films after anodization in Fe-free electrolyte definitively reveals that the absence of iron precludes the formation of Ni(IV) character upon anodization (Figure 2.12). Incrementally doping films with Fe by brief exposure to reagent-grade electrolyte at open circuit leads to gradual increases in the mean oxidation state of Ni upon anodization (Figure 2.12b). 3.4% Fe content appears sufficient to facilitate the complete phase change upon application of a potential bias. It is evident, however, that the incorporation of Fe is not the sole promoter of catalytic activity. Fe incorporation occurs by adsorption at open-circuit, but the phase change is driven by polarization at potentials in the region of the OER, for which the presence of iron is a crucial factor. Our data lead us to conclude that one key role played by iron is to allow the catalyst to achieve the highly oxidized Ni$^{3.6+}$ ($\gamma$–NiOOH-like) resting state that has been identified by XAS.

Some insight into the likely physicochemical basis for this effect of iron may be gleaned by considering the point of zero charge ($\text{pH}_{z}$) of nickel and iron oxides. The $\text{pH}_{z}$ provides a measure of the mean pK$_{a}$ of a surface-bound aquo and surface-bound hydroxo groups—a measure of the acidity of the oxide surface. In general, Fe oxides and oxyhydroxides display lower $\text{pH}_{z}$ values (7–7.5) than those of Ni (ca. 10).$^{48,49}$ We propose that the incorporation of Fe in the catalyst films increases the acidity of the metal–oxido moieties that comprise the catalyst. This increased acidity favors the oxidation of the nickel oxyhydroxide clusters to a greater degree. Additional studies to probe the acidity of the catalyst materials themselves are required to shed light on the role of Fe in giving access to highly oxidized Ni oxido clusters. Evaluating the influence of other Lewis acidic cations like Al$^{3+}$, Ce$^{3+}$, and Sc$^{3+}$ could prove helpful in identifying the underlying mechanism of activation. It is possible that the $\gamma$–NiOOH phase thus formed may in turn modulate the energetics of OER intermediate formation at Fe sites as suggested by the theoretical work
of Bell, Nørskov and co-workers. Such synergistic interactions between Fe dopants and γ-NiOOH may underlie the high activity of these films.

### 2.4 Conclusion

Anodization of electrodeposited films, which results in an almost three orders of magnitude improvement in catalyst activity, is accompanied by an increase in average nickel oxidation state to Ni(IV) and alteration of the structure of the nickel centers of electrodeposited ultrathin Ni–B_i catalyst films. A significant positive shift in the XANES edge to a position indicative of substantial formal Ni(IV) valency is observed, and EXAFS spectra indicate the presence of μ-oxo/hydroxo nickel centers organized into higher-order domains of edge sharing NiO_6 octahedra. O K-edge spectra of nickel oxides reveal substantial Ni–O covalency in such highly oxidized Ni-oxido systems. As-deposited Ni–B_i films display evidence for a Jahn–Teller distorted coordination geometry about the predominantly Ni(III) centers, reminiscent of the short-range structure of β-NiOOH. In contrast, anodized films possess short-range structural parameters akin to the mixed-valent γ-NiOOH phase. Thus, XAS spectra reveal that the short-range structure of anodized Ni–B_i is similar to γ-NiOOH and that of non-anodized Ni–B_i is similar to β-NiOOH. Electrochemical, XANES, and EXAFS data point to a conversion of local structure and nickel oxidation state in Ni–B_i films upon anodization that correlate to a dramatic enhancement in catalytic activity for O_2 evolution. By analogy of Ni–B_i to NiOOH, the results for Ni–B_i suggest that active sites of γ-NiOOH may be intrinsically more active towards the OER than those of β-NiOOH. In particular, the vast majority of studies of alkaline water oxidation mediated by nickel oxides have been conducted using nickel metal anodes upon which an oxide coating is formed via electrochemical polarization. Since the surface oxide coating may grow substantially (up to 1.4 µm) during OER, the charge transport properties of the compact oxide layer are invariably convoluted with the kinetics of the OER at surface exposed active sites. Indeed, gradual deactivation of
nickel anodes over time during alkaline OER, particularly when held at high overpotentials ($\eta \sim 600$ mV), has long been assigned to the formation of catalytically inert Ni(IV) centers within the surface oxide, leading to the contention that the all Ni(III) phase, $\beta$-NiOOH, is the most catalytically active nickel anode material for mediating the OER. In line with our observation for Ni–Bi, we propose the converse: that a predominantly Ni(IV) population, such as that found in the more highly oxidized $\gamma$-NiOOH-like structure is paramount to high OER activity. In our systems, Ni–Bi films are formed from solution precursors onto electrically conductive, oxidatively robust substrates, excluding interference from electron transport limitations, thus permitting isolation of the requirements for intrinsically efficient active site turnover. To this end, the results reported herein stand at odds with prevailing dogma concerning nickel oxide based OER in alkaline media. We have also found that the incorporation of iron into these films from reagent grade electrolytes plays a crucial role in facilitating the phase conversion during anodization. Without iron, Ni centers do not attain the Ni(IV) ($\gamma$-NiOOH) state during anodization and accordingly films are not activated. The precise role of iron remains unclear. Exploring the interfacial properties of these nickel and nickel-iron oxides as well as the possible substitution of iron for other elements will help to shed light on the basis for this effect.

### 2.5 Experimental Methods

**Catalyst Electrodeposition, Anodization and Electrochemistry.** Ni–Bi films were prepared on fluorine tin oxide (FTO) coated glass slides (Hartford Glass) by controlled potential electrolysis at 1.15 V (vs. NHE; all potentials are given vs. the normal hydrogen electrode) of a quiescent 0.1 M potassium borate electrolyte, pH 9.2, (0.1-Bi) containing 0.40 mM Ni$^{2+}$. A total charge of 1.0 mC/cm$^2$ was passed during deposition. An Ag/AgCl reference electrode and Pt mesh counter electrode were used for all electrochemical experiments. Following deposition, films were anodized in stirred 1.0 M
KB$_i$ electrolyte, pH 9.2 (1.0-B$_i$), by application of 1.1 V to catalyst films (with correction for ohmic potential losses) for 2.5 h. This preconditioning was also performed in 0.1-B$_i$ on an independently deposited film. Non-anodized films were electrodeposited under identical conditions.

Cyclic voltammograms (CVs) were performed on electrodeposited films that were anodized in 1.0-B$_i$ for times between 0 (non-anodized) and 4 h. The films were transferred immediately, without drying, to fresh 1.0-B$_i$. The electrode potential was maintained at 1.0 V for 30 s before scanning the CV from 1.0 V to lower potentials at a scan rate of 100 mV/s.

Film valency was determined coulometrically. Following electrodeposition and anodization, films were poised at 1.0 V for 300 s after which the potential was immediately swept from 1.0 V to 0.2 V and back to 1.2 V at 100 mV/s with compensation for ohmic potential losses. The cumulative charge passed during the scan was recorded; the amount of charge consumed in the reduction of nickel centers in the film was determined by subtracting the background charge passed by a 1 cm$^2$ FTO electrode (no catalyst coating) under identical conditions. Films were immediately removed from the electrolyte, allowed to dry in air, and subsequently dissolved in 5.00 mL of 2% aqueous nitric acid (Fluka Analytical, TraceSelect). Samples were analyzed for nickel content by Quadrupole Inductively Coupled Plasma Mass Spectrometry (Elemental Analysis, Inc., Lexington, KY).

Fe-free KOH electrolyte was prepared as described previously. Ni(NO$_3$)$_2$.6H$_2$O (99.9985% trace metals basis) was dissolved in water and treated with an aqueous solution of reagent grade KOH to precipitate Ni(OH)$_2$ as a suspension. Solid Ni(OH)$_2$ was isolated by decanting the remaining aqueous solution after allowing the suspension to settle overnight. The reagent-grade KOH solution to be purified was then used to re-suspend the Ni(OH)$_2$ and the mixture allowed to settle. After decanting, the electrolyte was treated
twice more with the solid Ni(OH)$_2$ (re-suspension and decantation) to rigorously scrub any trace Fe from the electrolyte.

**Model Ni Compounds.** NaNiO$_2$ was prepared by annealing NiO and Na$_2$O$_2$ (Aldrich) in a flow of O$_2$ according to a previously published procedure.$^{60}$ γ-NiOOH was prepared by treating NaNiO$_2$ with 5 mole equivalents of Br$_2$ in acetonitrile. β-NiOOH was prepared by treating a suspension of Ni(OH)$_2$ in 3 M aqueous KOH with 0.7 mole equivalents of Br$_2$. The identity and purity of each compound were verified by powder X-ray diffraction. Ni(OH)$_2$, Br$_2$, and K$_2$Ni(H$_2$IO$_6$)$_2$ were purchased from Aldrich.

**Catalyst Preparation for in situ XAS.** A glass electrochemical cell consisting of two compartments separated by a porous frit was employed for in situ spectroscopic experiments. The working compartment possessed flat walls (~2.5 cm wide) with a single circular hole, 1.5 cm in diameter. A 3 cm × 2 cm slip of ITO-coated polyethylene terephthalate (Kintec Company) was affixed with epoxy glue to the exterior of the wall of the cell, over the 1.5-cm hole, with the ITO layer (~0.15 μm thick) facing inwards. This ITO surface served as the substrate for electrodeposition of Ni–Bi films. The cell was connected to the potentiostat by making electrical contact to a portion of the ITO slip that protruded from the side of the working compartment. A Teflon cap containing a hole for the reference electrode was used to cover the working compartment and to ensure a fixed distance between working and reference electrodes between experiments.

Electrodeposition of catalyst for XAS experiments was terminated after passing 1.0 mC/cm$^2$. The cell was emptied of electrolyte and rinsed twice with water (18 MΩ resistivity, EMD Millipore). For anodized films, the electrochemical cell was charged with 1.0-Bi, and anodization was carried out at 1.3 V with stirring and without compensation for ohmic potential losses over a period of 3 h, after which spectra were collected over a range of applied potentials between 1.0 and 1.15 V. For non-anodized films, the electrochemical cell was refilled with 0.1-Bi after deposition and spectra were acquired at 1.0 V.
**XAS Data Collection and Analysis.** XAS spectra were collected at the Stanford Synchrotron Radiation Lightsource (SSRL) on beamline 7–3 at an electron energy of 3.0 GeV with an average current of 300 mA and at the Advanced Light Source (ALS) on beamline 10.3.2 at an electron energy of 1.9 GeV with an average current of 500 mA. At beamline 7–3 (SSRL), the radiation was monochromatized by a Si(220) double-crystal monochromator. The intensity of the incident X-ray was monitored by an N$_2$-filled ion chamber ($I_0$) in front of the sample. Model compound solid samples were diluted in boron nitride (1% w/w) and placed in an aluminum sample holder sealed with kapton tape. Data were collected as fluorescence excitation spectra with a Ge 30 element detector (Canberra). For model compounds, energy was calibrated by the first peak maximum of the first derivative of a nickel foil (8333.0 eV). The standard was placed between two N$_2$-filled ionization chambers ($I_1$ and $I_2$) after the sample. At beamline 10.3.2 (ALS), the radiation was monochromatized by a Si(111) double-crystal monochromator. Intensity of the incident X-ray was monitored by an N$_2$-filled ion chamber ($I_0$) in front of the sample. Fluorescence spectra were recorded by using a seven-element Ge detector array (Canberra). For electrochemical experiments, no transmission data could be collected. The energy was therefore calibrated using a glitch in the $I_0$ intensity. All data were collected at room temperature.

Data reduction of the EXAFS spectra was performed using EXAFSPAK (Drs. Graham George and Ingrid Pickering, SSRL). Pre-edge and post-edge backgrounds were subtracted from the XAS spectra, and the results were normalized with respect to edge height. Background removal in k-space was achieved through a five-domain cubic spline. Curve fitting was performed with Artemis and IFEFFIT software using ab initio-calculated phases and amplitudes from the program FEFF 8.2. These ab initio phases and amplitudes were used in the EXAFS equation:
The neighboring atoms to the central atom(s) are divided into j shells, with all atoms with the same atomic number and distance from the central atom grouped into a single shell. Within each shell, the coordination number \( N_j \) denotes the number of neighboring atoms in shell \( j \) at a distance of \( R_j \) from the central atom. \( f_{\text{eff}, j}(\pi, k, R_j) \) is the ab initio amplitude function for shell \( j \), and the Debye-Waller term \( e^{-2\sigma^2 j^2 k^2} \) accounts for damping due to static and thermal disorder in absorber-backscatterer distances. The mean free path term \( e^{-2R_j / \lambda_j(k)} \) reflects losses due to inelastic scattering, where \( \lambda_j(k) \) is the electron mean free path. The oscillations in the EXAFS spectrum are reflected in the sinusoidal term, \( \sin(2kR_j + \phi_j(k)) \) where \( \phi_j(k) \) is the ab initio phase function for shell \( j \). \( S_0^2 \) is an amplitude reduction factor due to shake-up/shake-off processes at the central atom(s). The EXAFS equation was used to fit the experimental data using \( N, R, \) and the EXAFS Debye-Waller factor \( (\sigma^2) \) as variable parameters. For the energy (eV) to wave vector (k, Å\(^{-1}\)) axis conversion, \( E_0 = 8340 \) eV and the \( S_0^2 \) value was fixed to 0.83.\(^63\)

**EXAFS Curve Fitting.** The goodness of the fit was evaluated by the EXAFS R-factor (\( R_f \)) that represents the absolute difference (least-square fit) between theory and data.\(^64,65\) For evaluation among different models, the reduced \( \chi^2 \) (\( \chi^2_v \)) was used:

\[
\chi^2_v = \chi^2 / (N_{\text{idp}} - N_{\text{var}})
\]

where \( N_{\text{idp}} \) is the number of independent points in the measurement, and \( N_{\text{var}} \) is the number of variable parameters in the fit. \( \chi^2 \) is defined by the following equation:

\[
\chi^2 = \frac{N_{\text{idp}}}{N_{\text{pts}}} \sum_{i}^{N_{\text{pts}}} \left[ \chi_i^{\text{data}} - \chi_i^{\text{calc}} \right]^2
\]

where \( \sigma_k \) is the measurement uncertainty in k-space, and \( N_{\text{pts}} \) is the number of points in the fitting range of the data. The measurement uncertainty was estimated by the root-mean-
square (rms) average of $\chi(R)$ between 15 and 25 Å as described in the literature. The uncertainty in the variables, scaled by the square root of $\chi^2$, are estimated by fitting parameters using a Fourier-filtered spectrum of a relevant R’ range of absorber-backscatter distances.

**X-ray Scattering and PDF analysis.** Synchrotron X-ray total scattering experiments were conducted at beamline ID11 at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The samples were measured at a temperature of 100 K using a flowing nitrogen cryocooler (Oxford Cryosystems). The rapid acquisition pair distribution function (RaPDF) technique was used with an X-ray energy of 78.396 keV ($\lambda = 0.15815$ Å). A 2-D CCD (FreLoN) camera (2084 × 2084 μm pixels size) was mounted orthogonal to the beam path with a sample-to-detector distance of 85.156 mm. For each sample the image plate was exposed for 15 minutes. The raw 2D data were azimuthally integrated and converted to 1D intensity versus $2\theta$ using FIT2D. PDFgetX3 was used to correct and normalize the diffraction data and then Fourier transform them to obtain the PDF, $G(r)$, according to

$$G(r) = 2/\pi \int_{Q_{\text{min}}}^{Q_{\text{max}}} Q[(S(Q) - 1)] \sin rQ \, dQ$$

Here $Q$ is the magnitude of the momentum transfer on scattering and $S(Q)$ is the properly corrected and normalized powder diffraction intensity measured from $Q_{\text{min}}$ to $Q_{\text{max}}$. $G(r)$ gives the probability of finding a pair of atoms separated by a distance of $r$. Finely powdered LaB$_6$ was also measured as a standard material to calibrate the sample-to-detector distance and to determine the $Q_{\text{damp}}$ and $Q_{\text{broad}}$ which are the parameters that correct the PDF envelope function for the instrument resolution effects. The refined values of $Q_{\text{damp}} = 0.0493$ Å$^{-1}$ and $Q_{\text{broad}} = 0.0157$ Å$^{-1}$ are then fixed in subsequent model fits to PDF data.
**Estimation of film thickness.** We estimate the thickness of these films by noting that a Ni–O distance of ~1.9 Å has been identified in the EXAFS studies described here, and we therefore approximate that the primary coordination sphere of each Ni center occupies a cube of volume ~125 Å³. With this consideration, a monolayer of catalyst would constitute ~0.7 nmol of nickel centers per cm² of surface area, corresponding to a charge of ~65 µC/cm². The ITO-coated substrates are not atomically smooth, and these films are expected to grow by nucleation. Therefore, the term “monolayer” in this case more aptly approximates a monolayer’s worth of material, and for such thin films, large regions of the ITO would be exposed. Bearing these qualifications in mind, we estimate a film thickness of 8 nm for a 1.0 mC/cm² film. A significant amount of O₂ evolution is coincident with film deposition and, as such, the amount of Ni centers should be less than that expected for the passage of 1.0 mC/cm² with 100% faradaic efficiency for deposition. Indeed, we find that the amount of Ni is ~63% of the charge passed in deposition (Table 2.1). This analysis only accounts for a Ni–Ni interlayer distance of ~5 Å, even though the interlayer distance in γ-NiO(OH) is ~7.2 Å. Thus, 8 nm is a reasonable upper limit for the thickness of these films.

**O K edge EELS.** The energy loss was calibrated post hoc using the established peak energy of the Ni L₃ edge (854 eV) and energy of the first O K edge peak (532 eV) of NiO[^4](purchased as powder from Sigma Aldrich). Backgrounds were fit to an exponential function in the pre-edge region and subsequently subtracted from the measured data. Spectra were normalized by the intensity of the edge jump 10–20 eV after the rising edge. In addition to NiO, stoichiometric Ni(OH)₂ and LiNiO₂ powders were also used as models, together with γ-NiOOH (prepared by treatment of NaNiO₂ with Br₂ in acetonitrile as described above).
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Chapter 3 — Mechanistic Studies into Oxygen Evolution Mediated by Nickel–Borate Electro catalyst Films

Portions of this chapter have been published:


3.1 Introduction

In Chapter 2 we discussed *in situ* extended X-ray absorption fine structure (EXAFS) and X-ray total scattering and pair distribution function (PDF) analysis work that shed light on the structural connectivity of nickel and oxygen ions in the nickel-borate (Ni–Bi) oxygen evolving catalyst. Together with *in situ* X-ray absorption near edge structure (XANES) spectra of Ni–Bi films, cyclic voltammetry and coulometric titrations were helpful in uncovering the resting state nickel valency in these materials. These studies also revealed key aspects of the anodization-induced structural transformations that are correlated with drastic improvements in catalytic activity (*ca.* 3 orders of magnitude).\(^1\)

We now report the OER kinetic profile of Ni–Bi films over a wide pH range (8.5–14) and divulge mechanistic insights into the origin of the considerable activity enhancement that is attendant to anodization. The electrosynthesis of ultrathin OEC films (≤ 15 monolayers) enable us to avoid internal electronic or ionic transport barriers. Our studies have enabled us to uncover a unique OER mechanism that stands in contrast to previously invoked OER mechanisms of nickel oxide anodes\(^2\)–\(^10\). Furthermore, we find that the apparent intrinsic/specific activity of Ni–Bi films is significantly greater than that found in Co–Bi systems of comparable catalyst loading for pH > 7. However pH-dependent profiles cause Co–Bi to supersede Ni–Bi in activity for pH ≤ 7. By defining the nature of the proton–coupled electron transfer (PCET) and buffer coordination pre–equilibria that occur during turnover, we find that trends in catalyst activity may be completely reversed at intermediate pH as compared to those at pH extremes. The results presented herein highlight the need for a detailed mechanistic understanding of OER for the construction of direct solar-to-fuels devices that operate at high efficiencies.
3.2. Results

3.2.1. Catalyst electrodeposition and anodization

Catalyst films were prepared by controlled potential electrolysis of 100 mM KB(OH)$_4$/H$_3$BO$_3$ (B$_i$) electrolyte, pH 9.2 containing 0.4 mM Ni$^{2+}$ at an applied potential of 1.15 V (vs. NHE) without stirring. Unless otherwise noted, a total charge of 1.0 mC/cm$^2$ was passed during deposition over a period of 60–80 s using fluorine–tin–oxide (FTO) coated glass slides as substrate. Following deposition, films were preconditioned with an anodization protocol that involved passage of 3.5 mA/cm$^2$ for 1–2 h in stirred solutions of 1.0 M B$_i$ electrolyte, pH 9.2.

3.2.2. Tafel slope determination.

The steady-state current density ($j$) for oxygen evolution from anodized films was evaluated as a function of the overpotential ($\eta$) in stirred Ni–free solutions of 0.5 M B$_i$ pH 9.2 electrolyte (Figure 3.1). To avoid diffuse double-layer effects,$^{11}$ a high ionic strength was maintained with 1.75 M KNO$_3$ supporting electrolyte. The applied voltage ($E_{appl}$) was varied in 7–20 mV increments in the region of water oxidation and maintained until $j$ attained a steady–state value. Compensation of $E_{appl}$ for Ohmic potential losses yielded the corrected potential ($E$), which was then converted to $\eta$ by subtraction of the thermodynamic potential for water oxidation ($E^\circ$) under the experimental conditions. Steady–state polarization data were acquired following anodization of films deposited by passage of 1.0, 0.40 and 0.083 mC/cm$^2$.

The amount of charge passed in oxidation or reduction of Ni–B$_i$ films involves a net transfer of ca. 1.6 electrons per nickel center.$^1$ With this knowledge, the charge consumed upon reduction of films by cyclic voltammetry permits a reliable estimation of the number of nickel centers in catalyst films (see Section 3.5) and thickness of the films.$^1$ Film thicknesses of approximately 5, 3 and 1 nm correspond to 15, 9 and 3 monolayer’s
worth of catalyst, respectively. Although the overall activity of these catalyst films at a specified overpotential increases with thickness, plots of $\eta$ (or $E$) as a function of $\log j$ (Tafel plots) display similar slopes, $b$, of 30 mV/decade ($2.3 \times RT/2F$), irrespective of loading.

These Tafel slopes are indicative of a net two–electron transfer in minor equilibrium prior to a chemical turnover–limiting step (TLS), resulting in a transfer coefficient, $\alpha$ ($\alpha = 2.3RT/bF$) of $2^{3/2}$. Tafel plots of films deposited onto a Pt rotating disk electrode (RDE) are identical irrespective of the rotation rates, $\omega = 2000$ rpm or 600 rpm, or whether stirring is the sole source of convection (Figure 3.2a). These observations confirm that the Tafel slope is representative of activation-controlled OER over the potential range explored. Tafel slopes are also reproducible for sequential runs, and do not depend on the direction of potential change (Figure 3.2b), indicating that the films are not significantly altered over the course of data collection.

Although only a fraction of the nickel centers may be involved in catalysis, a lower-limit value for the oxygen evolution turnover frequency ($\text{TOF}_{\text{min}}$) of Ni–Bi catalyst films at a specified overpotential can be estimated by determining the rate of turnover per nickel center in the film at that overpotential. At $\eta = 400$ mV in 0.5 M Bi pH 9.2 electrolyte, the

**Figure 3.1.** Tafel plots, $E = (E_{\text{appl}} - iR)$, $\eta = (E - E^0)$, for anodized catalyst films deposited onto FTO by passage of 1.0 (■), 0.40 (○), and 0.083 (▲) mC cm$^{-2}$ and operated in 0.5 M KBi 1.75 M KNO$_3$ pH 9.2 electrolyte. Tafel slopes are 31, 32 and 29 mV/decade, respectively.
TOF_{\text{min}} was determined to be 0.9, 0.5 and 0.5 mol O_2 (mol Ni)^{-1} s^{-1} for films prepared by passage of 1.0, 0.40 and 0.083 mC cm^{-2}, respectively (see section 3.6).

Tafel slopes were also extracted from open circuit potential ($E_{\text{OC}}$) decay transients, following the interruption of a potential pulse. Catalyst films were poised at 1.1 V in 0.5 M B_2 pH 9.2 electrolyte for 5 s. Upon switching to open circuit, the decay in $E_{\text{OC}}$ was
monitored as a function of time, \( t \) (Figure 3.3). The decrease in \( E_{OC} \) arises due to the discharge of the capacitance of the electrode, through the Faradaic resistance, mediated by the catalyst film (i.e. Ni centers in the film are reduced by water via the OER). Thus the characteristics of the overpotential of the electrode at open circuit (\( \eta_{OC} = E_{OC} - E^\circ \)) vs. time depends on the mechanism of \( O_2 \) evolution and therefore the Tafel slope, \( b \).

\[
\eta_{OC} = a - b \log(t + \tau)
\]  

(3.1)

with \( a = b \log(bC/j_0) \) and \( \tau = 10^{(\eta'/b)} bC/j_0 \). \( C \) is the capacitance of the electrode, \( j_0 \) is the exchange current density, and \( \eta' \) is the initial overpotential at \( t = 0 \). This open-circuit decay method assumes that any change in \( C \) during the experiment is negligible.

\( E_{OC} - t \) curves recorded for anodized and non-anodized films are shown in Figure 3.3. Owing to their considerably higher catalytic activity, the \( E_{OC} \) of anodized films decreases by almost 100 mV within the first 0.1 s after the potential is interrupted. In

**Figure 3.3.** Open circuit potential, \( E_{OC} \), and overpotential, \( \eta_{OC} = (E_{OC} - E^\circ) \), transients for non-anodized (green) and anodized (dark blue) 1.0 mC cm\(^{-2}\) NiB\(_i\) films immediately following a 10 s bias at 1.1 V in 0.5 M KB\(_i\) 1.75 M KNO\(_3\) pH 9.2 electrolyte. The red lines represent fits to eq. 3.1. Tafel slopes are 100 before anodization and 33 mV/decade after anodization. The inset shows the corresponding Tafel plots determined from the \( E_{OC} \) transients by calculating \( \log j \) at each time point using eq 3.2.
contrast, over the same duration a minimal decrease (< 10 mV) is observed in \( E_{\text{OC}} \) for non-anodized films. Fitting the decay trace of an anodized film to eq. 3.1 yields a Tafel slope of 33 mV/decade, which is in excellent agreement with the steady-state Tafel plot measurements of Figure 3.1. In contrast, a much higher Tafel slope of 100 mV/decade is extracted from the open circuit decay trace of non-anodized films. These transients permit the construction of Tafel plots of anodized and non-anodized films by recognizing that the instantaneous OER current density across the catalyst-electrolyte interface (log \( j_t \)) can be expressed as a function of the time elapsed during the OCP decay, \( t \):

\[
\log j_t = \log j_{t=0} - \log(1 + t/\tau)
\]

where \( \log j_{t=0} \) is the initial current density before open circuit conditions. The resulting Tafel plots (Figure 3.3 inset) illustrate the significant difference in the activity of anodized versus non-anodized films. We note that the Tafel plot of the anodized film is concordant with that obtained by steady state polarization measurements of Figure 3.1.

**Figure 3.4.** \( B_i \) concentration dependence of steady state catalytic current density at constant potential (\( E = 1.04 \) V (●), 1.05 V (●), 1.06 V (■)) for an anodized catalyst film deposited onto a Pt RDE by passage of 1.0 mC cm\(^{-2}\) and operated in \( B_i \) electrolyte, pH 9.2. Sufficient KNO\(_3\) was added to maintain a constant total ionic strength of 2 M in all electrolytes. Koutecký–Levich analysis was used to extract activation-controlled current densities in weakly-buffered electrolyte, where the measured current was dependent on rotation rate. The experimental reaction orders (slopes of the linear fits) in \( B_i \) are (from top to bottom) –0.95, –1.04 and –0.95.
3.2.3. Determination of reaction order in $B_i$.

The dependence of reaction rate on buffer strength was interrogated by controlled potential electrolysis of anodized catalyst films at 1.04, 1.05 and 1.06 V in Ni–free electrolyte, pH 9.2 with varying $B_i$ concentrations $[B_i]$ from 630–6.3 mM (Figure 3.4). Sufficient KNO$_3$ was added to each solution to preserve a constant high ionic strength of 2 M. Diffuse double layer effects, which lead to spuriously elevated Tafel slopes and distorted reaction orders (Figure 3.5a) can be eliminated by operating at constant ionic

![Diagram](image-url)

**Figure 3.5.** (a) Tafel plots, $E = (E_{applied} - iR)$, $\eta = (E - E^\circ)$, for a 1.0 mC cm$^{-2}$ anodized catalyst film deposited onto FTO and operated in 1.0 (■), 0.5 (■), 0.2 (▲), and 0.1 (◆) M KB$_i$ without any added supporting electrolyte. Tafel Slopes are 34, 35, 38, and 41 mV/decade, respectively. (b) Dependence of steady state electrode potential, $E = (E_{applied} - iR)$ and overpotential, $\eta = (E - E^\circ)$ for a 1.0 mC cm$^{-2}$ catalyst film operated at 0.4 mA cm$^{-2}$ in 0.1 M KB$_i$ electrolyte with varying concentrations of KNO$_3$ as supporting electrolyte.
strength as well as maintaining a low concentration of buffering species relative to an inert supporting electrolyte (Figure 3.5b).\textsuperscript{15}

Catalyst films were deposited onto a Pt RDE that had been pre–treated to render any current due to Pt oxide formation negligible (see section 3.5). For each electrolyte examined, the RDE was operated until a steady–state current value was attained at various $\omega$. In instances where the $[B_i]$ was less than 100 mM, the observed currents were subject to mass transport limitations, as evidenced by the dependence of $i$ on $\omega$. In these cases, Koutecký–Levich (K–L) plots of $i^{-1/2}$ as a function of $\omega^{-1/2}$ were constructed (Figure 3.6) to extract the activation–controlled current values by linear extrapolation to the limit of infinitely high rotation rates (i.e. $\omega^{-1/2} \rightarrow 0$).\textsuperscript{16,17} In all cases, Ohmic potential losses amounted to less than 1 mV and therefore they were neglected. Figure 3.4 shows the logarithm of the activation-controlled current density plotted as a function of log$[B_i]$. For $[B_i] \geq 40$ mM, the slope of the plot establishes an inverse first order dependence of current density on $B_i$ activity. In electrolytes of very low buffer strength ($[B_i] < 40$ mM), film activity deviates from this reaction order, and an ostensibly zeroth order regime is observed.

**Figure 3.6.** Steady state Koutecký–Levich plots of a 1.0 mC cm$^{-2}$ catalyst film prepared onto a Pt RDE and operated at $E = 1.04$ V at 2500, 1600, 900, and 625 rpm in 40 (●), 25 (■), 16 (▲), 10 (▼), and 6.3 (◆) mM KB$_i$ electrolyte, with added KNO$_3$ to preserve an ionic strength of 2 M.
3.2.4. Determination of reaction order in H$^+$ activity.

Given the explicit reaction order in B$\text{}_i$, any measurements of reaction rate dependence on pH will inevitably alter the activity of boric acid, borate anion, or both. To evaluate the reaction order in H$^+$ activity, anodized films were deposited onto a Pt RDE and steady-state data were collected as a function of pH. Initially, a galvanostatic titration at 10 $\mu$A cm$^{-2}$ in an electrolyte with a constant [B$\text{}_i$]$_{\text{total}} = 100$ mM was undertaken in the presence of 2 M KNO$_3$. The titration was commenced at pH 8.5 and the potential required to sustain constant current density was measured as the pH of the solution was raised incrementally. At low current density, no local pH gradients arise, even when the pH is adjusted outside of the ideal B$\text{}_i$ buffering regime. Additionally, Ohmic potential losses were less than 0.5 mV and they can be neglected. The plot of potential as a function of pH (Figure 3.7) shows two limiting slopes of $-64$ mV/pH unit and $-96$ mV/pH unit for pH ranges 8.5–9.8 and 10–12, respectively. The bifurcation observed at pH 10 indicates that either:

1. There is a change in mechanism (such as a change in Tafel slope) at pH 10 or
2. There exists an inverse first order dependence of reaction rate on only one of the two buffering species, borate, B(OH)$_4^-$ or boric acid, B(OH)$_3$.

**Figure 3.7.** pH dependence of steady-state electrode potential at constant current density ($j_{\text{anodic}} = 10$ $\mu$A cm$^{-2}$) for an anodized 1.0 mC cm$^{-2}$ catalyst film on FTO operated in 0.1 M B$\text{}_i$ 2 M KNO$_3$ electrolyte. Slopes equal $-64$ (---) and $-96$ (----) mV/pH unit.
A separate experiment was conducted to distinguish between scenarios (1) and (2). Films were deposited onto a Pt RDE, and Tafel data were collected using Bi solutions at pH 8.5, 9.2, 10.2, 11.2 and 12.0 (Figure 3.8a). In each electrolyte, the total buffer concentration [Bi] was varied such that the concentration of borate anion, \([B(OH)_4^-]\), was maintained at 100 mM; 0.9 M KNO₃ was added to each solution to preserve a constant ionic strength of about 1 M. Where necessary, the activation-controlled current densities were obtained from K–L analysis. There is no mechanistic change over the pH range explored; all Tafel slopes lie between 28 and 32 mV/decade. This suggests that scenario (2) is at the root of the change observed for pH > 10. Interpolation of each Tafel plot at 2.5 mA cm⁻² (+), 0.25 mA cm⁻² (*), and 0.025 mA cm⁻² (×). Slopes are −90, −89, and −88 mV/pH unit respectively.

Figure 3.8. (a) Tafel plots, \(E = (E_{appl} - iR)\) for anodized Ni–Bi catalyst films deposited on a Pt rotating disk electrode by passing 1.0 mC cm⁻², and operated in 0.60 M Bi pH 8.5 (●), 0.20 M Bi pH 9.2 (▲), 0.11 M Bi pH 10.2 (■), 0.10 M Bi pH 11.2 (●), and 0.10 M Bi pH 12.0 (▼). Each electrolyte contained an additional 0.9 M KNO₃ as supporting electrolyte to maintain an ionic strength of about 1 M. Koutecký–Levich plots were constructed to extract activation-controlled current densities where necessary. (b) Interpolation of Tafel plots at 2.5 mA cm⁻² (+), 0.25 mA cm⁻² (*), and 0.025 mA cm⁻² (×). Slopes are −90, −89, and −88 mV/pH unit respectively.

A separate experiment was conducted to distinguish between scenarios (1) and (2). Films were deposited onto a Pt RDE, and Tafel data were collected using Bi solutions at pH 8.5, 9.2, 10.2, 11.2 and 12.0 (Figure 3.8a). In each electrolyte, the total buffer concentration [Bi] was varied such that the concentration of borate anion, \([B(OH)_4^-]\), was maintained at 100 mM; 0.9 M KNO₃ was added to each solution to preserve a constant ionic strength of 1 M. Where necessary, the activation-controlled current densities were obtained from K–L analysis. There is no mechanistic change over the pH range explored; all Tafel slopes lie between 28 and 32 mV/decade. This suggests that scenario (2) is at the root of the change observed for pH > 10. Interpolation of each Tafel plot at 2.5, 0.25 and 0.025 mA cm⁻² yields the potential dependence on pH (Figure 3.8b). The single observed slope \((\partial E/\partial \text{pH})_j = -90 \text{ mV/pH}\) over the pH range 8.5–12.0 is a convolution of the pH dependence of the current density \((\partial \log j/\partial \text{pH})_E\) and the potential dependence of the current density \((\partial E/\partial \log j)_{pH}\). That is:

\[
\frac{\partial E}{\partial \text{pH}}_j = -\left(\frac{\partial \log j}{\partial \text{pH}}\right)_E \left(\frac{\partial E}{\partial \log j}\right)_{pH}
\]  

(3.3)
Substituting \((\partial E/\partial pH)_j = -90 \text{ mV}/\text{pH}\) (from Figure 3.8b) and \((\partial E/\partial \log j)_{\text{pH}} = 30 \text{ mV/decade}\) (the Tafel slope) into eq. 3.3 gives \((\partial \log j/\partial pH)_E = +3\). The reaction order in H\(^+\) activity \((\partial \log j/\partial \log a_{H^+})_E\) may thus be determined as:

\[
\left( \frac{\partial \log j}{\partial \log a_{H^+}} \right)_E = - \left( \frac{\partial \log j}{\partial \text{pH}} \right)_E
\]  

This yields an apparent reaction order in proton activity \(a_{H^+}\) of \(-3\). This data only informs us of the loss of three acid equivalents before the turnover-limiting step during catalytic turnover. Importantly, these data are not sufficient to distinguish between (i) an inverse first order dependence on B(OH)\(_4^-\) plus an inverse third order dependence on H\(^+\) and (ii) an inverse first order dependence on B(OH)\(_3^-\) plus an inverse second order dependence on H\(^+\).

A galvanostatic titration in 100 mM B\(_i\) from pH 11–13 was used to investigate a change in the pH dependence under alkaline conditions, which might be expected to arise when the pH is elevated beyond the \(pK_a\) of an active site species. As shown in Figure 3.9, a plateau in the plot of \(\eta\) vs. pH is observed at pH ~ 12.2. However, since Tafel data acquired in 0.1 and 1.0 M KOH (Figure 3.9 inset) continue to exhibit slopes close to 29 mV/decade,

![Figure 3.9](image_url)

**Figure 3.9.** Plot of the pH dependence of steady-state electrode overpotential (\(\eta\)), at constant current density \((j_{\text{anodic}} = 10 > \mu\text{A cm}^{-2}\)) for an anodized 1.0 mC cm\(^{-2}\) catalyst film deposited onto FTO and operated in 0.1 M B\(_i\) 2 M KNO\(_3\) electrolyte. The inset shows Tafel plots, \(\eta = (E - iR - E^\circ)\), for anodized catalyst films deposited onto a Pt RDE by passage of 1.0 mC cm\(^{-2}\) and operated at 2000 rpm in 0.1 M KOH 1.9 M KNO\(_3\) pH 12.9 (\(\bigcirc\)) and 1.0 M KOH 1.0 M KNO\(_3\) pH 13.8 (\(\Delta\)) electrolyte. Tafel slopes are 28 and 30 mV/decade, respectively.
the mechanistic change that results in this plateau in the $\eta$ vs. pH plot does not arise from changes in Tafel slope. Instead, this behavior must arise exclusively from changes in the measured H$^+$ reaction order.

According to Figure 3.9, for pH > 12.2 there is no dependence of the current density on pH at constant overpotential. This parameter, $(\partial \log j / \partial \text{pH})_\eta$, is related to the pH dependence of the current density at constant potential, $(\partial \log j / \partial \text{pH})_E$ through the transfer coefficient, $a (a = 2.3RT/bF$, where $b$ is the Tafel slope$^{18}$)

$$\left( \frac{\partial \log j}{\partial \text{pH}} \right)_E = \left( \frac{\partial \log j}{\partial \text{pH}} \right)_\eta + \alpha \quad (3.5)$$

Both Tafel slopes are close to 29 mV/decade, and therefore $a = 2.3RT/0.029F = 2$. By substituting $(\partial \log j / \partial \text{pH})_\eta = 0$ and $a = 2$ into eq. 3.5 we find $(\partial \log j / \partial \text{pH})_E = 2$, indicating a reaction order in H$^+$ activity of $-2$ (eq. 3.4). The exact interpretation of the change in pH dependence relies on which species is assumed to dissociate from active sites: borate acid or boric acid. If borate dissociates (together with an inverse 3rd order H$^+$), then these results would be consistent with the conclusion that one of the three kinetically relevant protic centers of Ni–B$_i$ active sites possesses a pK$_a$ of 12.2. In strongly alkaline electrolytes, this species is deprotonated in the resting state of the catalyst and ceases to contribute to the electrochemical rate law. On the other hand, if it is boric acid that dissociates (together with an inverse 2nd order dependence on H$^+$), then the observed plateau at pH 12.2 would be consistent with a boric acid dissociation constant, $K_d$, on the order of $10^{-4}$ M (the concentration of boric acid at pH 12.2, based on a pK$_a$ of 9.1 at an ionic strength of ~ 2 M).

3.2.5. Tafel data in B$_i$-free electrolyte.

To explore OER kinetics in the absence of a weak base, steady state polarization data were collected in 1 M NaClO$_4$ pH 8.5 solution. Films were deposited onto a Pt RDE by passage of 1.0 mC cm$^{-2}$ and anodized in B$_i$ buffered solutions. Tafel data were obtained in NaClO$_4$ electrolyte by extrapolation of K–L plots at each potential considered with the
goal of eliminating mass transport limitations through the bulk electrolyte. Over the course of the experiment, small aliquots (1–5 μL) of 1 M NaOH were added periodically to preserve the bulk pH at 8.50(1). Tafel data (Figure 3.10) are the average of three runs.

The resulting Tafel plot displays a greatly elevated slope compared to Tafel data acquired in Bi electrolyte, pH 8.5 (Figure 3.10a). The kinetic profile of catalyst films in Bi buffered media following operation in Bi–free electrolyte was comparable to the activity

![Figure 3.10.](image)

**Figure 3.10.** (a) Tafel plots, $E = (E_{\text{appl}} - iR)$, $\eta = (E - E^\circ)$, for anodized catalyst films deposited onto a Pt RDE by passage of 1.0 mC cm$^{-2}$ and operated in 1 M NaClO$_4$ pH 8.5 electrolyte (●). Koutecký–Levich analysis of steady state current densities at various rotation rates was used to eliminate mass transport limitations through solution. The data shown is the average of three consecutive runs. A Tafel plot of an identical catalyst film in 0.6 M KBi 0.9 M KNO$_3$ pH 8.5 (0.1 M Bi$^{3+}$, total ionic strength = 1 M) electrolyte (▲), displaying a 32 mV/decade Tafel slope (---), is shown for comparison. (b) Activity profile of a 1.0 mC cm$^{-2}$ catalyst film deposited onto a Pt RDE and operated in 0.5 M KBi 1.75 M KNO$_3$ pH 9.2 electrolyte after operation in 1.0 M NaClO$_4$, pH 8.5 electrolyte (▲), compared to the activity profile of a freshly prepared catalyst film (■).
of a freshly prepared film (Figure 3.10b), indicating that the Tafel behavior obtained in the absence of B_i cannot be attributed to the corrosion of catalyst films in buffer–free electrolyte.

3.3. Discussion

3.3.1. Steady-state Tafel data.

Tafel behavior describing the effect of potential, E, or overpotential, $\eta$, on steady-state current density, along with experimentally determined reaction orders form the basis of the mechanistic analysis of oxygen evolution by Ni–B_i catalyst films. Steady-state current densities are proportional to the activation-controlled velocity of the OER if the reaction is not subject to mass-transport limitations. This requirement is true of the electrokinetic studies described herein, since in well-buffered electrolytes Tafel data collected using a RDE is identical irrespective of rotation rate or whether stirring was the sole means of mass transport with the electrode stationary (Figure 3.2a), resulting in Tafel slopes, b, (where $b = \partial E/\partial \log j$) of 28 mV/decade in each case. In cases where mass transport limitations were encountered (poorly-buffered media, or electrolytes completely lacking a weak base electrolyte), Koutecký–Levich analysis was employed to extract activation-controlled current densities. Furthermore, the Tafel plots are the same for sequential runs and independent of the direction of potential change during data acquisition (Figure 3.2b), verifying that catalyst films are not altered appreciably over the course of experiments. Precise control of catalyst film thickness was accomplished by managing the total charge passed during deposition. Although the resultant film thicknesses ranged from 1 to 5 nm (equivalent to 3–15 monolayer’s of catalyst), Tafel plots collected for each film gave similar slopes, close to 30 mV/decade (Figure 3.1). Since activated transport through the film can impose additional potential barriers to electronic/ionic conductivity,\textsuperscript{19–21} consistent slopes over a range of film thicknesses (particularly at almost monolayer
coverage) demonstrates the absence of non–Ohmic potential losses between the potential applied at the electrode and that experienced by active sites. For anodized catalyst films, Tafel plots (Figure 3.1) yield 30 mV/decade slopes that are consistent with a mechanism involving a chemical turnover-limiting step (TLS) that follows a two–electron pre–equilibrium. The reciprocal of the Tafel slope in dimensionless form is known as the transfer coefficient, \( \alpha = \frac{2.3RT}{\beta F} = 2 \) for \( \beta = 29.5 \text{ mV/decade} \) at 25 °C. Although the Tafel slopes are independent of film thickness, the apparent exchange current densities and hence the overall activity of films does increase with loading. This would be expected to occur, as anodes with thicker catalyst layers should possess more active sites per unit geometric area in these porous films. Lower–limit TOFs of 0.9 mol O\(_2\) (mol Ni)\(^{-1}\) s\(^{-1}\) are observed at \( \eta = 400 \text{ V} \) in pH 9.2 electrolyte and 1.7 mol O\(_2\) (mol Ni)\(^{-1}\) s\(^{-1}\) at \( \eta = 325 \text{ mV} \) in 1 M KOH. Lower-limit TOF for these catalysts may be calculated at any \( \eta \) by recognizing that the TOF decreases by an order of magnitude per 30 mV increment. Thus, these catalyst films rival the most active OER anodes reported to-date.

### 3.3.2. OER of non-anodized Ni–Bi

Monitoring the decay in open circuit potential after interrupting an applied potential bias offers a complementary means of determining the Tafel slope of an electrokinetic reaction. This method is the most appropriate means of extracting electrokinetic information on the OER at the less catalytically active non-anodized films, since polarization of the electrode for an extended period of time leads to anodization. The higher activity of anodized films is immediately evident in the very rapid decay at early times due to more efficient O\(_2\) evolution as compared to the less catalytically active non-anodized films (Figure 3.3). Indeed, since the Tafel slope for anodized films is found to be 33 mV/decade (in agreement with Figure 3.1), the corresponding OCP-decay transient indicates that the surface concentration of catalytic intermediates in anodized Ni–Bi decreases by over three orders of magnitude in the first 100 ms after the potential is...
removed. In contrast, the Tafel slope of non-anodized films is considerably higher, approaching 100 mV/decade. Tafel slopes of 120 (± 20) mV/decade are generally expected for mechanisms involving turnover-limiting electron transfer (ET) from the resting state:

$$A^{\text{TLS}} \rightarrow B + e^-$$  \hspace{1cm} (3.6)

The turnover velocity for such a reaction will be given by:

$$v = k_{ET} \theta_A$$  \hspace{1cm} (3.7)

where $k_{ET}$ is the rate constant for the turnover limiting electron transfer, and $\theta_A$ is the surface coverage of the resting state species, $A$:  \hspace{1cm} (3.8)

$\Gamma_A$ is the surface concentration of active sites that exist in state A (expressed in mol/cm$^2$), and $\Gamma_{\text{max}}$ is the total surface concentration of active sites. It is important to note that $\Gamma_{\text{max}}$ need not equal the surface concentration of solvent–exposed metal centers, or even the concentration of electroactive Ni centers, since the number of active sites may actually represent a very small proportion of these centers. Under Langmuir conditions, since A is the resting state, $\theta_A$ may be assumed to be a constant equal to 1.  \hspace{1cm} (3.9)

The rate constant $k_{ET}$ is given by:

$$k_{ET} = k^0_{ET} \exp \left( \frac{\beta \eta F}{RT} \right)$$  \hspace{1cm} (3.10)

The parameter $k^0_{ET}$ is the ET rate constant at $\eta = 0$, and $\beta$ is the symmetry factor for the microscopic (irreversible) ET step, which determines the amount of the total driving force due to $\eta$ (i.e. $\Delta G = -\eta F$), that causes a decrease in the activation energy barrier (i.e. $\Delta(\Delta G^\text{i}) = -\beta \eta F$)  \hspace{1cm} (3.11)

Thus the electrochemical rate law for a reaction that proceeds by eq. 3.6 will be:

$$j = 4Fk^0_{ET} \exp \left( \frac{\beta \eta F}{RT} \right)$$  \hspace{1cm} (3.10)

This will lead to a Tafel slope ($\partial \eta / \partial \log j$) of $2.3 \times RT / \beta F$. $\beta$ is usually close to 0.5 (± 0.1)  \hspace{1cm} (3.12)

resulting in a Tafel slope of around 120 mV/decade at 298 K. Importantly, in this case, the symmetry factor, $\beta$, and the transfer coefficient for the overall OER, $\alpha$, are numerically identical, since the kinetics of the overall multi-electron reaction are governed entirely by
the microscopic rate-limiting ET step. In cases where one or more electron transfers exist in equilibrium, β and α are distinct.

It is unclear whether the suppression of the Tafel slope of non–anodized films from 120 mV/decade to 100 mV/decade arises due to the existence of a marginally altered β value of 0.6, or is a result of the unavoidable partial anodization of the film during deposition. However, the existence of a turnover–limiting electron transfer in non–anodized films is reasonable. The resting state nickel valency in non-anodized films is predominantly +3, and the local coordination environment of Ni centers in such films exhibits the Jahn–Teller (J–T) distortion that is expected for low-spin d^7 ions. Thus the first oxidation process during turnover should be kinetically sluggish, as it would incur a large reorganizational energy penalty associated with a low-spin d^7 → d^6 transformation. We propose therefore that this high reorganizational energy associated with Ni^{3+} oxidation contributes to very low catalytic activity of non–anodized Ni–B_i films.

3.3.3. OER of anodized Ni–B_i.

XAS shows that anodization of Ni–B_i films leads to a gradual phase change (involving changes in both local structure and resting state nickel valency) that eliminates the J–T distortion present in non-anodized films. In the absence of structural distortion in local geometry, the oxidation of Ni centers in anodized films should be more facile. Indeed, the 30 mV/decade Tafel slope obtained by steady state Tafel plots (Figures 3.1 and 3.2) and open-circuit decay transients (Figure 3.3) indicates that the turnover–limiting step is a chemical in nature and does not involve ET.

Before evaluating the dependence of activity on pH and therefore the existence of proton–transfer (PT) equilibria prior to the TLS, it was necessary to establish the dependence of reaction rate on buffer strength, since any [B_i] dependence might have to be considered in the interpretation of any pH dependence. The resulting inverse first order dependence of current density on [B_i] over almost 1.5 decades (Figure 3.4) is consistent
with the reversible dissociation of a Bi species from an active site over this range in buffer strength. Boric acid and borate species are known to adsorb to oxide surfaces in aqueous media by coordination to the metal centers. The −1 reaction order in Bi (Figure 3.4) establishes that the ligation of the buffer species is governed by the Langmuir isotherm with a high surface coverage of the adsorbate. Accordingly, the Bi-free active sites necessarily exist in minor equilibrium with a Bi-bound resting state. Decreasing the concentration of Bi in the electrolyte gives rise to an increase in activation-controlled current density until a point where there appears to be no dependence of reaction velocity on Bi (< 40 mM Bi).

While demonstrating an association between buffering species and active sites, Bi dependence studies alone cannot distinguish which Bi species (boric acid, borate anion (B(OH)$_4^-$), or polyborates) must dissociate from active sites during turnover for oxygen to be evolved. The result of modeling the speciation of Bi over the relevant pH range is shown in Figure 3.11. The pH dependence of the steady-state electrode potential at a constant high ionic strength changes from about −60 mV/pH over the Bi buffering range to about −90 mV/pH for pH > 10 (Figure 3.7). In contrast, Tafel data collected between pH 8.5 and pH 12 at a constant concentration of borate anion exhibit Tafel slopes of approximately 30 mV/decade (Figure 3.8a). The pH dependence of the steady-state electrode potential at constant [B(OH)$_4^-$] was determined to be about −90 mV/pH by interpolating the Tafel plots at constant current density (Figure 3.8b). These results show that depending on the exact identity of the buffer species that is liberated into bulk solution, either a two- or three-proton pre-equilibrium occurs prior to the TLS. Were both species to be liberated from active sites, the combined concentration of boric acid and borate in solution should appreciably modulate OER kinetics on Ni–Bi films, and an experiment in which the total Bi (boric acid + borate) concentration is held constant as the pH is varied (Figure 3.7) should yield a single slope and the genuine reaction order in H$^+$ activity. However, if the desorption equilibrium applies to only one species of the conjugate pair,
the pH dependence of reaction rate will inevitably be convoluted with the reaction order in that species unless the total B\textsubscript{i} concentration is adjusted to maintain a constant activity in the coordinated species alone, or the pH regime is such that B\textsubscript{i} speciation does not change appreciably with pH. Considering that boric acid behaves as a Lewis acid \((\text{B(OH)}_3 + \text{H}_2\text{O} \rightleftharpoons \text{B(OH)}_4^- + \text{H}^+)\) it seems reasonable to expect that coordination between B(OH\textsubscript{3}) and the oxide surface will emulate the acid-base behavior of this buffer. Thus, we presently favor the reversible binding and dissociation of boric acid and a two-proton minor equilibrium as the mechanistic origin of the pH and buffer dependence results observed here.

It is imperative that electrokinetic data be acquired in an excess of supporting electrolyte. If not, the potential dependence of anion migration and the effects on local pH and specific adsorption of B\textsubscript{i} will skew Tafel data and lead to slopes that are dependent on B\textsubscript{i} concentration, and apparent fractional reaction orders (Figure 3.5a). These effects are eliminated by maintaining a constant, high ionic strength \((I \geq 1 \text{ M})\) using an anodically inert supporting electrolyte such as KNO\textsubscript{3}, which when present at an appreciable
concentration, serves to reduce the transference number of borate anion (the fraction of the total ionic current that is carried by borate anions) (Figure 3.5b).

Taken together, the results of Figures 3.1–3.8 reveal the electrochemical rate law for oxygen evolution in moderate to high borate ion concentrations (20–300 mM) at anodized Ni–B films to be:

\[
j = k_0 (a_{B(OH)_3})^{-1} (a_{H^+})^{-2} \exp \left( \frac{2EF}{RT} \right)
\]  

(3.11)

where \(k_0\) is proportional to the exchange current density and independent of potential. This rate expression contains the inverse first order dependence on borate activity as shown in Figure 3.4, the inverse third order dependence on proton activity (Figures 3.7 and 3.8), as well as the factor of 2 (transfer coefficient) in the exponential term in the applied potential, \(E\). At constant borate activity, pH and \(T = 25 °C\), the partial derivative of \(E\) with respect to \(\log j\), \((\partial E/\partial \log j)\) yields a Tafel slope of 30 mV/decade, consistent with Figure 3.1. The experimental rate law in eq. 3.11 is consistent with the mechanistic sequence:

\[
\begin{align*}
\text{A} &\rightleftharpoons \text{B} + \text{B(OH)}_3 + 2e^- + 2H^+ & K_1 \\
\text{B} &\rightarrow \text{C} & k_2
\end{align*}
\]  

(3.12)

(3.13)

This mechanism involves reversible, net boric acid dissociation from the resting state, and a two–electron, two–proton equilibrium followed by a chemical TLS. \(K_1\) is the equilibrium constant at \(E_{appl} = 0\), and \(k_2\) is the rate constant for the chemical TLS. Eq. 3.12 is likely to proceed in a number of discrete steps, however these would all exist as quasi-equilibria and such a sequence is kinetically indistinguishable from a single step. In addition, there may be any number of distinct chemical equilibrium steps prior to the TLS, but these cannot be resolved kinetically.

According to eq. 3.13, the steady state velocity of oxygen evolution can be expressed as,

\[
\nu = k_2 \theta_B
\]  

(3.14)

\(\theta_B\) represents the partial surface coverage of intermediate B. \(\theta_B\) can be defined in terms of the surface coverage of the resting state A (\(\theta_A\)) as follows:
which involves the application of the Nernst equation to eq. 3.12. Substituting for $\theta_B$ in eq. 3.14 gives:

$$v = k_2 K_1 \theta_A (a_{B(OH)\_3})^{-1} (a_{H^\+})^{-2} \exp \left( \frac{2EF}{RT} \right)$$  \hspace{1cm} (3.16)

If Langmuir conditions are assumed, the surface coverage of the resting state is high, $\theta_A$ would not be expected to change appreciably over the potential range, and may be considered a potential-independent constant equal to 1. In this case, eq. 3.16 approximates the experimental rate law (eq. 3.11) with

$$k_0 = 4FK_1 \theta_A$$  \hspace{1cm} (3.17)

In situ XAS studies of anodized Ni–B$_i$ films show that there is no systematic shift in the nickel K–edge position with applied potential over the potential range used for Tafel data acquisition. This result is consistent with the assumption that the speciation of the resting state, A, is invariant over the potential range explored and therefore permits $\theta_A$ to be taken as a constant (eq. 3.17 above). XANES spectra and coulometric studies also established that the average oxidation state of Ni in anodized catalyst films was +3.6 to +3.8, thereby indicating a substantial amount of formal Ni$^{IV}$ valency in the catalyst resting state. In fact, there appears to be even more formal +4 valency in Ni–B$_i$ compared to Co–OEC. Computational studies of Ni$^{IV}$–containing extended solid nickelates have demonstrated significant covalency in Ni–O bonding, and extensive delocalization of hole-density onto oxygen centers upon oxidation of the parent Ni$^{III}$ compounds. Our own O K-edge studies on nickel oxides corroborate these results (Chapter 2). In addition, EPR studies of a tetracobalt cubane model compound possessing one formally Co$^{IV}$ center as a molecular model of our cobalt-based catalyst revealed a radical distributed almost equally over all Co and O ions, effectively leading to a formal oxidation number of [Co$_4$]$^{3.125+}$O$_4$. Thus, it is reasonable to expect that this Ni$^{IV}$ valency in the catalyst resting state is
distributed extensively over multiple Ni and O centers in the nickel–oxido clusters that form the ordered domains.

Figure 3.9 is effectively a Pourbaix diagram of the catalyst active sites. As mentioned in section 3.3.3, the plateau observed at pH 12.2 may be taken as an indicator that one of the protic species possesses a pKₐ of about 12.2 in the borate-dissociation/3-proton framework, or as indicative of a dissociation constant of boric acid of \( \text{ca.} \ 10^{-4} \) M in the boric acid dissociation, 2-proton framework. Regardless, this pH dependence data is important in considering the likely protonation state of Ni–O moieties under the conditions of turnover. At the pH regimes considered in this study, a Ni^{III/IV}–OH₂ resting state is unlikely, given the Pourbaix diagram for nickel.\(^4^1\) In addition, the point of zero charge (pH₇) for nickel oxides, which defines the average of the pKₐ values of surface–bound water (M–OH₂) and surface-bound hydroxyl (M–OH) groups\(^4^2\) have been found to be about 8 and 9.75 for Ni(OH)₂ and NiO respectively.\(^4^3–4^5\) Thus we can anticipate the pKₐ of a Ni^{III/IV}–OH₂ intermediate would be less than 8. Taking these data into consideration we propose that the edges of clusters in the catalyst film are terminated with hydroxo (as opposed to aquo) groups. Proton loss from these centers upon oxidation affords highly reactive oxide species that initiate O–O bond formation. Previous EPR studies\(^4^0\) have pointed to the importance of proton loss in PCET steps for generating localized reactive intermediates. In the Co–OECs and Ni–OECs, the ensuing change in ligand field strength upon deprotonation could localize the unpaired spin density on specific centers leading to their subsequent reactivity towards O–O bond formation. This concept is validated by computational studies of cobalt oxido clusters as Co–OEC models.\(^4^6\) Hence while the resting state valency would be delocalized over the entire cluster, the catalytic intermediates are likely to possess spin density that is more localized due to proton loss.
A mechanistic scheme for oxygen evolution in B$_i$–buffered electrolyte that is consistent with the interfacial properties of the oxidic surface as well as the electrokinetic data presented herein is shown in Figure 3.12. We assign the two–electron minor equilibrium step to the double oxidation of a dinickel active site, which proceeds with the overall deprotonation of two terminal hydroxyl groups. These PCET processes are proposed to lead to a highly oxidized intermediate that may be tentatively described as [Ni$_2^{IV/V}$] or [Ni$_2^{4.6}$]. Since this intermediate exists in minor equilibrium at a very low surface coverage, its formal potential must lie well above the potential supplied at the electrode. Nevertheless, this formal [Ni$_2^{IV/V}$] designation is likely not an accurate description of the true electronic structure of the intermediate; we expect that the electron-transfer pre–equilibria arise from orbitals with predominantly O 2p character, resulting in oxyl radical character. The loss of protons must contribute significantly to the accessibility of such highly oxidized intermediates by virtue of the PCET potential leveling effect.$^{47-49}$ Since the turnover–limiting step is chemical in nature and unlikely to involve

**Figure 3.12.** Proposed pathway for O$_2$ evolution by NiB$_i$ in B$_i$ ([B(OH)$_4$]$^-$ > 20 mM) electrolyte, pH 8.5–14. The reversible dissociation of boric acid and an overall two-electron, two-proton equilibrium followed by a rate limiting chemical step, is consistent with the experimental electrochemical rate law. Oxidation state assignments are approximate; oxidizing equivalents are likely extracted from orbitals with predominantly O 2p character, particularly for the pre-TLS intermediate.
proton transfer to the electrolyte, we find it reasonable to propose that this step involves O–O bond formation and/or Ni–O bond scission. Computational studies on our Co–based system suggests that direct coupling of two terminal Co\textsuperscript{IV}(O) groups to form an O–O bond is thermodynamically favorable and proceeds with a low kinetic barrier\cite{46} signifying that it may in fact be the breaking of the metal–oxygen bond that is the turnover-limiting step in these late transition metal oxide catalysts. Spectroscopic studies as well as extensive synthetic and computational modeling will be employed to shed light on the electronic structure of catalytic intermediates and the details of the turnover-limiting process. Further electrochemical studies, particularly on molecular models are also needed to shed light on the details of the coupled multi-proton, multi-electron sequences. A recent report\cite{50} based largely on computational studies proposes a mechanism in Ni-Fe oxides involving O–O bond formation at Fe sites within a Ni-oxido framework. Given the established absorption of Fe from reagent grade electrolytes into these Ni–Bi films during anodization (Chapter 2), we recognize that the participation of Fe directly in catalysis remains a distinct possibility that cannot be ruled out. At present, given the correlation between activity and Ni(IV) character—a valence state the realization of which is facilitated by Fe content (Chapter 2)—we propose a mechanism that entails mainly Ni centers.

3.3.4 OER in Bi-free electrolyte.

Certainly, one important role of Bi is to preserve the local and bulk pH during O\textsubscript{2} evolution. However, the inverse first order dependence of reaction velocity on Bi activity in eq. 3.15 implicates a deleterious role of the buffer on OER kinetics. Despite this ostensibly “inhibitory” effect, the crucial importance of borate to the kinetics of water oxidation on Ni–Bi films is evident in Tafel plots acquired in Bi–free electrolyte (Figure 3.10a). In the absence of Bi, very high Tafel slopes are observed and high current densities cannot be achieved. Following operation in Bi–free electrolyte, films display no loss in activity in Bi electrolyte (Figure 3.10b), excluding the possibility of catalyst corrosion over
the period of polarization in B₃-free electrolyte. We have observed a similar result in the Tafel data of Co–P₃ films in phosphate–free electrolytes (see Chapter 5). These preliminary electrokinetic data suggest that proton transfer processes may become turnover–limiting in the absence of a good proton acceptor, at low hydroxide ion concentrations. In Chapter 5 additional studies are discussed that shed light on the origin of the change in Tafel slopes observed for these materials in buffer-free electrolytes. Nevertheless these results underscore the critical importance of borate to facilitating proton transfers, thereby expediting the PCET sequences necessary for rapid O₂ evolution.

3.3.5 Differences in mechanism and activity of Co– and Ni–OECs.

Differences in activity between oxido Co–OECs and Ni–OECs are governed to a large extent by the characteristics of the PCET pre–equilibrium. A two–electron oxidation is required before the chemical turnover–limiting step in anodized Ni–B₃ OEC films (30 mV/decade Tafel slope), whereas turnover at Co–OEC films involves a one-electron pre-equilibrium (60 mV/decade Tafel slope).

We propose that this difference arises because O–O bond formation in both systems proceeds by radical coupling of two active site oxygen centers. In Co–OEC, this oxygen–centered unpaired spin density arises upon generation of somewhat localized, low-spin formally d⁵ Co⁺⁺⁺ centers. Realization of a similar electronic structure would require more substantial oxidation for a nickel catalyst than for a cobalt–based system. As such, it would be expected to lead to a lower exchange current density, but also a lower Tafel slope, provided the ET steps remain kinetically facile. This is indeed what is observed when one compares Co–B₃ with Ni–B₃ at comparable catalyst loadings at pH 9.2 (Figure 3.13a). Additionally, the more extensive oxidation would also demand greater accompanying H⁺ loss.
Because of the differences in pH and buffer dependence for the two catalysts, Ni–B\textsubscript{i} increasingly outperforms Co–P/B\textsubscript{i} as elevated pH (Figure 3.13b). However, at neutral pH and slightly acidic conditions, Co–P/B\textsubscript{i} surpasses Ni–B\textsubscript{i} in activity. The majority of studies on the OER have been conducted in highly alkaline media\textsuperscript{52–54} and these have led to useful trends in correlating specific thermodynamic parameters (such as M–O bond strengths, enthalpies of formation of the metal(III) hydroxide compound, and adsorption enthalpies of proposed intermediates) with catalytic activity, resulting in the general consensus that for first row transition metal oxides, OER activity increases in the order: MnO\textsubscript{x} < FeO\textsubscript{x} < CoO\textsubscript{x} < NiO\textsubscript{x}\textsuperscript{55–58} However, as evident from Figure 3.12b, activity trends

Figure 3.13. Comparison of ultrathin Co–B\textsubscript{i} and Ni–B\textsubscript{i} OEC films with identical catalyst loadings of 6 nmol metal ions/cm\textsuperscript{2}. (a) Tafel plots of Co–B\textsubscript{i} (●) and Ni–B\textsubscript{i} (▲) in 0.5 M KB\textsubscript{i} 1.75 M KNO\textsubscript{3} pH 9.2 electrolyte. Tafel slopes equal 55 and 31 mV/decade, respectively (b) Schematic of the pH dependence of the current density and lower-limit turnover frequency of Co–B\textsubscript{i} at a constant overpotential of 400 mV (blue —) and 300 mV (light blue —) compared to that of Ni–B\textsubscript{i} at 400 mV (light green —) and 300 mV (green —) overpotential. Curves were calculated using the appropriate experimentally-determined electrochemical rate laws. Ni-based films display a much higher apparent specific activity (since the true number of active sites cannot be known) than Co-based films above pH 8. However, due to their disparate electrochemical rate laws, a crossover is expected to occur around neutral pH, at which point Co-based films would yield higher activity anodes. The precise pH at which crossover occurs depends on the overpotential applied due to the different Tafel slopes.
in concentrated base may not hold in intermediate pH electrolytes because of disparate PCET and buffer association pre-equilibria involved in the mechanism of the OER at different catalysts.

3.4 Conclusion

Electrodeposited ultrathin anodized Ni–B\textsubscript{i} catalyst films exhibit a Tafel slope of 30 mV/decade in well-buffered electrolytes between pH 8.5 and 14. Electrokinetic studies demonstrate that oxygen evolution in B\textsubscript{i}-buffered electrolyte entails the reversible dissociation of boric acid from the resting state and a two-electron, two-proton (or alternatively borate dissociation and a two-electron, three-proton) equilibrium followed by a chemical turnover-limiting step. Under highly alkaline conditions, a change in reaction order in proton activity is observed that is attributed to the full dissociation ($K_d = 10^{-4}$ M) of boric acid from the active site (or the full deprotonation of a protic center with a $pK_a$ of 12.2). On the basis of previous in situ XAS, a mixed valence Ni\textsuperscript{III/IV} resting state is invoked, although radical character on oxygen ions in this resting state as well as the subsequent catalytic intermediate states is anticipated. These studies highlight the contradicting roles of the buffer as both an inhibiting adsorbate and a proton acceptor for PCET at intermediate pH. The much lower catalytic activity of non-anodized films appears to arise, in part, from the large reorganizational energy involved in electron transfer from the Jahn–Teller distorted Ni\textsuperscript{III} resting state found in non-anodized films, which makes this electron transfer rate-limiting. The low Tafel slope of anodized Ni–B\textsubscript{i} films makes this catalyst ideal for integration with photovoltaic systems for solar water splitting.

3.5 Experimental Methods

**Materials.** Ni(NO\textsubscript{3})\textsubscript{2}•6H\textsubscript{2}O 99.9985% was used as received from Strem. KOH 88%, KNO\textsubscript{3} 99.0–100.5% and H\textsubscript{3}BO\textsubscript{3} 99.9% were reagent grade and used as received from
Macron. NaClO₄ hydrate (99.99% metals basis) was used as received from Aldrich. All electrolyte solutions were prepared with type I water (EMD Millipore, 18 MΩ cm resistivity). Fluorine–tin–oxide (FTO) coated glass (TEC-7) was purchased as pre–cut 1 cm × 2.5 cm glass pieces from Hartford Glass. Unless stated otherwise, all experiments used FTO with 7 Ω/sq surface resistivity.

**General Electrochemical Methods.** Potentiometric and voltammetric measurements were undertaken with a CH Instruments 760C or 760D bipotentiostat, a BASi Ag/AgCl reference electrode, and a Pt-mesh counter electrode. Rotating disk electrode (RDE) measurements were conducted using a Pine Instruments MSR rotator and a 5 mm diameter Pt–disk rotating electrode. All electrochemical experiments were performed at 23 ± 1 °C using a three–electrode compartment cell with a porous glass frit separating the working and auxiliary compartments. Electrode potentials were converted to the NHE scale using \( E_{\text{NHE}} = E_{\text{Ag/AgCl}} + 0.197 \) V. Overpotentials were computed using \( \eta = E_{\text{NHE}} - 0.68 \) V at pH 9.2. Unless stated otherwise, the electrolyte comprised 0.5 M potassium borate (KB₃), 1.75 M potassium nitrate, pH 9.2 (henceforth referred to as KB₃/KNO₃ electrolyte).

**Film Preparation.** Catalyst films were prepared via controlled–potential electrolysis of 0.1 M KB₃, pH 9.2 electrolyte solutions containing 0.4 mM Ni²⁺. To minimize precipitation of Ni(OH)₂ from these solutions, 25 mL of 0.2 M KB₃ was added to 25 mL of 0.8 mM Ni²⁺ solution. The deposition solutions were subsequently filtered through a 0.2 μm syringe filter (Pall) to remove any Ni(OH)₂ that formed. The solutions thus prepared remained clear over the course of deposition, which was carried out onto an FTO–coated glass piece. These FTO working electrodes were rinsed with acetone and water prior to use. A ~0.6 cm wide strip of Scotch tape was applied to the FTO coated side such that a 1 cm² area was exposed to solution. Unless stated otherwise, deposition by controlled potential electrolysis was carried out on quiescent solutions at 1.15 V without \( iR \) compensation and with passage of 1 mC cm⁻². A typical deposition lasted 70 s.
Following deposition, films were rinsed by dipping briefly in 0.1 M KB\textsubscript{i}, pH 9.2 solution to remove any adventitious Ni\textsuperscript{2+}. For anodization, films were subsequently electrochemically treated in 1 M KB\textsubscript{i}, pH 9.2 electrolyte by passing an anodic current of 3.5 mA cm\textsuperscript{−2} with stirring. A steady potential was obtained after about 30 min of anodization. Unless stated otherwise, anodized films were anodized for 1 h.

**Potentiostatic Tafel Data Collection.** Current–potential data were obtained by conducting controlled potential electrolysis in KB\textsubscript{i}/KNO\textsubscript{3} electrolyte pH 9.2 at a variety of applied potentials (\( E_{\text{app}} \)). Prior to film deposition and anodization, the solution resistance of the electrolyte to be used for Tafel data collection was measured using the \( iR \) test function. The electrolysis solution was exchanged for Ni\textsuperscript{2+}–containing KB\textsubscript{i} electrolyte, without disturbing the relative positions of the working and reference electrodes and films were deposited. Following film preparation, the working electrode was rinsed in fresh Ni-free KB\textsubscript{i} electrolyte and transferred, without drying, to the same electrolysis bath in which the solution resistance was measured. The electrode was allowed to equilibrate with the electrolyte solution for 5 min while being held at the open circuit potential. The solution was stirred and steady–state currents were then measured at applied potentials that descended from 1.13 V to 1.00 V in 7–20 mV steps. For currents greater than 10 \( \mu \)A cm\textsuperscript{−2}, a steady state was reached at a particular potential in less than 400 s. For currents lower than 10 \( \mu \)A cm\textsuperscript{−2}, longer electrolysis times (15–20 min) were utilized to ensure that steady state had been achieved. The solution resistance measured prior to the data collection was used to correct the Tafel plot for Ohmic potential losses.

**Cyclic Voltammetry.** CVs of anodized catalyst films were recorded in KB\textsubscript{i}/KNO\textsubscript{3}, pH 9.2 electrolyte. After 2 min at open circuit, catalyst films were held at 1.0 V for 60 s, immediately after which CV scans were initiated from 1.0 V. The potential was decreased at a scan rate of 100 mV s\textsuperscript{−1} with stirring, and with correction for Ohmic potential losses (measured prior to film deposition). At a switching potential of 0.2 V, the direction of scan was reversed, and CVs were terminated at 1.1 V.
Dependence of Tafel data on film thickness and calculation of lower-limit TOF.

Steady–state polarization data were acquired following anodization of films deposited by passage of 1.0, 0.4 and 0.083 mC cm$^{-2}$. Deposition durations were about 67, 25 and 11 s, respectively. We note that the charge passed cannot be used as a simple measure of the Ni loading because: (1) non–Faradaic double–layer charging currents for short deposition times (and particularly for the thinnest of these films) accounts for a non–trivial proportion of the total charge passed; and (2) oxygen evolution accompanies deposition, and so a fraction of the charge passed is consumed for OER and not solely for film deposition. Thus, in order to evaluate film loadings, CVs of each film were acquired as described above and the charge consumed upon film reduction was determined by integration of the cathodic surface wave. Charges of 0.91, 0.53 and 0.21 mC cm$^{-2}$ were obtained from analysis of the CVs. We have established that the charge passed upon film oxidation or reduction involves the net transfer of 1.6 electrons per nickel center for films of comparable thickness. Thus, the charges correspond to loadings of about 5.9, 3.4 and 1.4 nmol/cm$^2$ of Ni centers, corresponding to films of approximate thicknesses of 5, 3 and 1.0 nm.

Knowing the amount of nickel on each electrode, and by interpolating Tafel data for each film at $\eta = 400$ mV, respective currents at this overpotential can be converted into turnover frequency per nickel center, given that each turnover requires the removal of four electrons. Since the number of active sites is expected to be only a fraction of the number of nickel centers, this calculation returns a lower–limit for the TOF of each active site. The calculated lower-limit on the TOFs at $\eta = 400$ mV in 0.5 M KB$_i$ 1.75 M KNO$_3$, pH 9.2 are 0.92, 0.51 and 0.49 mol O$_2$ (mol Ni)$^{-1}$ s$^{-1}$ for films deposited by passage of 1.0, 0.4 and 0.08 mC cm$^{-2}$ respectively. Similarly, in the case of a 1.0 mC cm$^{-2}$ catalyst film operated in 1 M KOH 1 M KNO$_3$ pH 13.85 electrolyte, we calculate a lower-limit on the TOF of 1.7 mol O$_2$ (mol Ni)$^{-1}$ s$^{-1}$ at $\eta = 325$ mV.

Mass transport dependence studies. To verify that Tafel data were not subject to mass transport limitations, a platinum rotating disk electrode (RDE) (Pine Instrument
Company) was used to collect steady state data. The Pt–disk (5 mm diameter) was polished to a mirror finish with 0.05 μm α–alumina (CH Instruments). Prior to film deposition, the Pt disk was electrolyzed at 1.4 V (vs NHE) in 1 M Kβi, pH 9.2 electrolyte for 30 min to anodize the Pt surface exhaustively as to minimize current arising from platinum oxide formation upon application of a potential step. Following this pre–treatment, catalyst films were deposited onto the Pt RDE in an otherwise identical manner to that described above. Tafel data were collected in Kβi/ KNO₃ electrolyte with E_{appl} stepped from 1.13 to 1.00 V in 7–20 mV increments. At each potential step, steady–state data were collected at rotation rates (ω) of 2000 and 600 rpm; data were also collected in the absence of disk rotation, but in a well-stirred solution. Background currents arising from the OER at the Pt RDE itself are insignificant compared to currents due to the OER mediated by Niβi. The excellent agreement among Tafel slopes (28 mV/decade) under these disparate conditions reveal that Tafel data are not limited by mass transport over the current/potential range explored. In addition, these experiments demonstrate that the kinetic profile of the catalyst does not depend on the nature of the underlying substrate.

**Tafel data in the absence of excess supporting electrolyte.** Tafel data were acquired as in subheading B, with the exception that electrolytes contained only Kβi and no KNO₃. Tafel data were collected in 0.1, 0.2, 0.5 and 1.0 M Kβi, pH 9.2 electrolyte. Apparent Tafel slopes decrease from 40 to 35 mV/decade as the borate concentration (and ionic strength of the electrolyte) increases.

**Supporting electrolyte effect.** The surface of a 0.2 cm² FTO-coated glass electrode was exposed by application a 1 cm wide piece of scotch tape to isolate a 2.0 mm × 1.0 cm strip. The solution resistances of six electrolytes, each containing 0.1 M Kβi at pH 9.2, with varying concentrations of KNO₃ from 0–2 M were measured using the iR test function. Without disturbing the relative positions of the working and reference electrodes, a 1.0 mC cm⁻² catalyst film was deposited and anodized. Following anodization, the catalyst film was operated in each solution at a fixed current density of 0.4 mA cm⁻². In
this galvanostatic experiment, the potential required to sustain this current density was recorded after at least 300 s had elapsed. Potential values were then corrected for \(iR\) drop using the measured solution resistances. Prior to operation in each electrolyte, the catalyst film was briefly rinsed in fresh electrolyte of identical composition, to avoid cross–contamination. \(\text{KNO}_3\) concentrations \(\geq 1\) M were found to be sufficient to eliminate any diffuse double layer effects and attendant complications arising from elevated local concentrations of borate anions.

**Open circuit decay transients.** NiB\(_i\) films were prepared as described above. Following deposition, the films were immersed in KB\(_i\)/\(\text{KNO}_3\) pH 9.2 electrolyte and held at 1.1 V (vs. NHE) for 10 s, after which \(E_{\text{appl}}\) was removed. This short duration was sufficient for the current to plateau without the onset of anodization. A second potentiostat, which was connected in parallel, was used to measure the voltage across the working and reference electrodes throughout the potential bias and for 2 min subsequent to the removal of \(E_{\text{appl}}\) (open circuit). The sampling interval was 5 ms. The open circuit potential (OCP) was plotted as a function of time. The electrode was then rinsed in water and anodized in 1 M KB\(_i\) pH 9.2 electrolyte. Following anodization, films were immersed in KB\(_i\)/\(\text{KNO}_3\) pH 9.2 electrolyte and the open circuit decay experiment was repeated, this time with a sampling interval of 2.5 ms. The open circuit potential was plotted as a function of time. These transients were fit to eq. 3.1 to extract the Tafel slopes for OER for anodized and non–anodized films. The OCP transients were also converted into Tafel plots using eq. 3.2.

**Borate Dependence Studies.** To determine the reaction order in borate, solutions were prepared with B\(_i\) concentrations in the range of 0.63–6.3 mM. An appropriate amount of \(\text{KNO}_3\) was added to ensure an ionic strength of 2 M. The solution resistance of each electrolyte was recorded without disturbing the relative positions of the working and reference electrodes, and then a 1.0 mC cm\(^{-2}\) catalyst film was deposited onto a Pt RDE. Following anodization, the catalyst film was operated at 1.05 V in each solution at \(\omega = 2500, 1600, 900\) and 625 rpm. At each rotation rate, the current was allowed to reach its
steady-state value before proceeding to the next rate. Prior to operation in each electrolyte, catalyst was rinsed in fresh electrolyte of identical composition to avoid cross-contamination. The experiment was then repeated at 1.04 V and 1.06 V. Ohmic losses due to solution resistance accounted for <1 mV and they were therefore neglected. Appreciable changes in current values with \( \omega \) were observed for electrolytes of low buffer strength ([B\(_i\)] < 40 mM), implying that the reaction was not purely activation controlled. As such, Koutecký–Levich (K–L) plots (\( i^{-1} \) as a function of \( \omega^{-1/2} \)) were constructed to allow for extraction of activation-controlled currents by linear extrapolation to the limit of an infinitely high rotation rate. \( \log j \) was plotted as a function of \( \log [B_i] \) over the \([B_i]\) range 0.63 M–40 mM. In electrolytes of very low buffer strength ([B\(_i\)] < 40 mM), a slope of ca. zero is observed.

**pH dependence studies in B\(_i\) electrolyte.** A 0.2 cm\(^2\) (1 cm × 2 mm) area of an FTO-coated glass electrode was isolated with scotch tape and a 1 mC cm\(^{-2}\) catalyst film was deposited. The electrode was operated at a current of 2 \( \mu \)A (equivalent to 10 \( \mu \)A cm\(^{-2}\)) in 100 mM KB\(_i\) 2 M KNO\(_3\), pH 8.5 electrolyte. The steady state electrode potential (measured after operation for ≥ 2 min at each pH) was recorded as the pH of the solution was raised up to pH 12.0 in increments of about 0.1 pH units using \( \mu \)L aliquots of 10% KOH solution. Ohmic potential losses amounted to <0.1 mV and they were ignored. Additionally, at these very low current densities, no local pH gradients arise even when the pH is adjusted outside of the ideal B\(_i\) buffering regime. The steady-state electrode potential was plotted as a function of pH.

A 1.0 mC cm\(^{-2}\) catalyst film was prepared onto a Pt RDE. Tafel data were collected in electrolytes with B\(_i\) concentrations equal to 0.601, 0.200, 0.110, 0.101, and 0.100 M at pH 8.5, 9.2, 10.2, 11.2 and 12.0, respectively, to ensure that each electrolyte contained ~0.1 M borate anion, assuming a \( pK_a \) of 9.2 for boric acid. Sufficient KNO\(_3\) was added to each solution to yield a concentration of 0.9 M, and therefore to maintain an ionic strength of 1 M. In each solution, steady state data were collected without \( iR \) compensation at 2500,
1600, 900, and 625 rpm, and where necessary, K–L analysis was used to extract activation–controlled current values. Although the measured current, and for that matter the \(iR\) drop, varied with rotation rate, the difference in these Ohmic losses due to solution resistance between different rotation rates at the same applied potential was negligible (<1 mV). The product of the previously measured solution resistance and the average current value over the rotation rate range analyzed was subtracted from the applied potential to yield the \(iR\)-corrected potential. The upper and lower limits for applied potentials were chosen such that current densities would fall between 3.5 mA cm\(^{-2}\) and 10 \(\mu\)A cm\(^{-2}\). Data were recorded at potential intervals of 10 mV to yield Tafel slopes. Tafel plots were interpolated at 2.5, 0.25 and 0.025 mA cm\(^{-2}\) to furnish the potential dependence on pH at constant current density.

**\(pK_a\) titrations.** A 1.0 mC cm\(^{-2}\) catalyst film was prepared onto an FTO–coated glass electrode (0.2 cm\(^2\)), and operated at a current of 2 \(\mu\)A (equivalent to 10 \(\mu\)A cm\(^{-2}\)) in 100 mM Kb, 2 M KNO\(_3\), pH 11.3 electrolyte. The steady–state electrode potential was recorded using a Hg/HgO (1 molal NaOH) reference electrode as the pH of the solution was raised in increments of 0.2–0.25 pH units up to pH 12, with \(\mu\)L aliquots of 50% KOH solution. The experiment was continued in separate electrolytes of identical composition (100 mM Kb, 2 M KNO\(_3\)) whose pH had been previously adjusted to pH 12.25, 12.5, 12.8 and 13.15, respectively. Ohmic potential losses amounted to <0.1 mV in each electrolyte and could be safely ignored. The measured potentials (vs Hg/HgO) were converted to the NHE scale using \(E(\text{NHE}) = E(\text{Hg/HgO, 1 molal NaOH}) + 0.108\).\(^{59}\) The corresponding overpotentials were calculated by subtracting the thermodynamic potential for the OER at each pH from the \(E(\text{NHE})\) values. The steady state electrode overpotential was plotted as a function of pH at 10 \(\mu\)A cm\(^{-2}\).

**Tafel data in B\(_{-}\)-free electrolyte, pH 12.9, 13.8.** A 1.0 mC cm\(^{-2}\) catalyst film was deposited onto a Pt RDE and Tafel data were acquired in 0.1 M KOH 1.9 M KNO\(_3\) and 1.0 M KOH 1.0 M KNO\(_3\) solutions (pH 12.9 and 13.8, respectively). For these solutions, no mass transport limitations were encountered over the accessible overpotential range (\(\eta = \))
220–330 mV), and activation-controlled steady state Tafel data were acquired at a single rotation rate of 2000 rpm.

**Tafel data in Bι-free electrolyte, pH 8.5.** A 1.0 mC cm\(^{-2}\) catalyst film was deposited onto a Pt RDE as described above. The activation-controlled steady state current density was measured with \(iR\) compensation as a function of applied potential by K–L analysis at 20 mV intervals in 1.0 M NaClO\(_4\), pH 8.50 electrolyte. 1–5 \(\mu\)L aliquots of 1 M NaOH were added periodically to ensure minimal drift (± 0.01 pH units) in bulk pH over the course of the experiment. Three consecutive runs were acquired and the Tafel data were averaged. The activity of films in Bι electrolyte (0.5 M KBι 1.75 M KNO\(_3\), pH 9.2 electrolyte) after operation in 1 M NaClO\(_4\) pH 8.5 were compared with Tafel data acquired using a fresh catalyst film. Since the activity of a catalyst film after operation in Bι–free electrolyte is comparable to that of a fresh film, the possibility of film corrosion causing the Tafel behavior observed in buffer-free electrolytes is excluded.

**Deposition and Tafel plots of CoBι films.** Co–Bι catalyst films were prepared via controlled–potential electrolysis of 0.1 M KBι, pH 9.2 electrolyte solutions containing 0.5 mM Co\(^{2+}\). Depositions were carried out using an FTO–coated glass piece as the working electrode. These FTO–coated glass electrodes were rinsed with acetone and water prior to use in all experiments and a ~0.6 cm wide strip of Scotch tape was applied to the FTO coated side such that a 1 cm\(^2\) area was exposed to solution. Deposition by controlled potential electrolysis was carried out on quiescent solutions at 0.9 V (vs. NHE) without \(iR\) compensation and with passage of 0.6 mC cm\(^{-2}\) (equivalent to 6 nmol cm\(^{-2}\) Co). A typical deposition lasted 12 s.

Current–potential data were obtained for this 0.6 mC cm\(^{-2}\) Co–Bι film by conducting controlled potential electrolysis in KBι/KNO\(_3\) pH 9.2 electrolyte at a variety of applied potentials. Prior to film deposition, the solution resistance of the electrolyte to be used for collection of Tafel data was measured using the \(iR\) test function. The electrolysis solution was exchanged for Co\(^{2+}\)–containing KBι electrolyte, without disturbing the
relative positions of the working and reference electrodes. The film was prepared by controlled-potential electrolysis. Following film preparation, the working electrode was rinsed in fresh Co-free KBi electrolyte and transferred, without drying, to the same electrolysis bath in which the solution resistance was measured. The electrode was allowed to equilibrate with the electrolysis solution for 5 min while being held at the open circuit potential. The solution was stirred and steady-state currents were then measured at applied potentials that descended from 1.13 V to 1.00 V in 10 mV steps. At each potential, 400 s to 600 s were allowed for the film to reach steady state. The solution resistance measured prior to the data collection was used to correct the Tafel plot for Ohmic potential losses.

3.6 References


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Chapter 4 — Interplay of oxygen evolution kinetics and photovoltaic power curves on the construction of artificial leaves

Portions of this chapter have been published:


4.1 Introduction

In the preceding chapters we have discussed spectroscopic and mechanistic studies of nickel-borate oxygen evolving catalyst films. These studies have elucidated the molecular basis for the activity changes that are observed upon anodization of the electrodeposited films, and we have rationalized their remarkably high activity at intermediate-to-alkaline pH conditions in terms of their mechanism of action. We now turn our attention to considering the integration of these catalysts with light-harvesting materials in photoelectrochemical (PEC) water splitting assemblies. As mentioned briefly in Chapter 1, numerous device configurations have been proposed for PEC water splitting and they can be broadly categorized into those devices wherein the photovoltaic material makes a rectifying junction with solution as opposed to those in which the rectifying junctions are protected from solution or “buried”. Figure 4.1 schematically depicts the latter with a double junction configuration of absorber materials with progressively larger band gaps.

**Figure 4.1.** Qualitative band diagram of a double junction PV–PEC water splitting cell depicting the thermodynamic potential separation of the OER and HER ( ), and the quasi–Fermi level ( ) and bend edge positions ( ) throughout the cell under illumination with sustained water splitting at current density, j. The potential at each solution interface is given by the OER, \( \eta_{OER} \), and HER, \( \eta_{HER} \), overpotentials required to sustain the operating current density, j. For clarity of representation, solution and contact resistance losses are
that are connected in series using thin–film ohmic contacts to generate open circuit voltages ($V_{oc}$) that are large enough to drive water splitting. Thin-film ohmic contacts are at the termini of this stack to both protect the semiconductor from the chemistries occurring in solution and to enable efficient charge transfer to catalyst overlayers, which execute the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER).

Whereas water splitting catalysis is combined with charge separation, current rectification, and photovoltage generation in a solution junction PEC device, in a buried junction device, catalysis is separated from the current rectification, charge separation, and photovoltage generation, which occur at the internal junction. In contrast to a solution junction, the photovoltages produced at buried junctions are free to float and are not fixed relative to a material-specific flatband potential. Therefore, for buried junction devices, there is no requirement that the flatband potentials of the semiconductors result in band edges that straddle the thermodynamic potentials of the OER and HER under the conditions of operation. This fact dramatically expands the number of light-absorbing materials available for buried junction PEC water splitting. Additionally, as the buried junction device represents a photovoltaic power source in series with an electrochemical load, the OER and HER catalysts may be optimized independently such that maximum power transfer occurs to drive water splitting. We elaborate here on this latter issue and show that the kinetic profile of the catalyst is a key determinant of the overall solar-to-fuels efficiency (SFE).

We interrogate here the interplay of OER catalysis and photovoltaic performance in defining SFE of the artificial leaves based on Ni–Bi and Co–Bi catalysts. Building on the theoretical work of Hanna and Nozik and adapting the engineering loss analysis model of Rocheleau and Miller, we use Ni–Bi and Co–Bi electrokinetic data as a basis for modeling the electrochemical load of water splitting in a PEC cell. We show that Ni–Bi and Co–Bi exhibit markedly different Tafel slopes pointing to different mechanisms of oxygen evolution, which translate into disparate electrochemical loads for water splitting. By
assembling the electrochemical profiles of Ni–B\textsubscript{i} and Co–B\textsubscript{i} systems with multi–junction PV components of similar power conversion efficiency but disparate open–circuit voltages, \( V_{oc} \), we show that OER catalyst kinetics is a key determinant of SFE when water splitting is performed near its thermodynamic limit (\textit{i.e.} low \( V_{oc} \)). This observation has not broadly been appreciated previously because most PEC cells have employed semiconducting materials with large bandgaps that provide high voltages that are energetically far removed from the thermodynamic limit of water splitting.

**4.2 Results**

**4.2.1 Catalyst Film Electrosynthesis**

Water splitting catalysts were deposited as thin films by controlled potential electrolysis of Co\textsuperscript{2+} and Ni\textsuperscript{2+} solutions in 0.1 M potassium borate electrolyte, pH 9.2 (B\textsubscript{i}) at a potential of 0.92 and 1.15 V (\textit{vs.} the normal hydrogen electrode, NHE), respectively.\textsuperscript{8–11} Following electrodeposition, Co films were rinsed and placed in electrolyte containing no additional Co to yield steady state current density values that are unchanged over time.
The log of the steady state current density of Co–B\textsubscript{i} films versus the applied overpotential exhibited good linearity over ~2.5 decade range in current density and yielded a Tafel slope of 52 mV/decade (Figure 4.2). This Tafel slope is similar to those previously observed for films grown from phosphate electrolyte at pH 7,\textsuperscript{12} and it is diagnostic of a mechanism involving an equilibrium of a one electron reaction that precedes a rate limiting chemical step for oxygen evolution.

In contrast to Co–B\textsubscript{i} films, which exhibit high initial OER activity that is sustained indefinitely, Ni–B\textsubscript{i} requires preconditioning by anodic polarization in order to obtain steady state current densities that are high and remain unchanged over time\textsuperscript{11} Over the course of this anodic preconditioning, Ni–B\textsubscript{i} films exhibit a dramatic rise in activity and undergo structural changes reminiscent of a β–NiOOH to γ–NiOOH phase conversion\textsuperscript{11} The logarithm of the steady state current density of preconditioned Ni–B\textsubscript{i} films \textit{versus} the applied overpotential exhibits good linearity over ~2.5 decade range in current density and yields a Tafel slope of 29 mV/decade (Figure 4.2), in contrast to the value observed for Co–B\textsubscript{i} under similar conditions. A thorough mechanistic investigation of thin Ni–B\textsubscript{i} films (Chapter 3) reveals that the low Tafel slope for Ni implies a mechanism involving a two electron equilibrium prior to the rate limiting step of oxygen evolution, as opposed to the one-electron pre-equilibrium observed for the Co–B\textsubscript{i} catalyst.\textsuperscript{13}

\subsection*{4.2.2 \textit{j–V} Modeling of Buried-Junction Semiconductor–Catalyst Assemblies}

The disparate Tafel behaviors of Ni and Co films are paramount to determining the anodic electrochemical load in an artificial leaf. As discussed in Chapter 1, the electrochemical load of water splitting is described by the following equation\textsuperscript{7}

\[ V_{op}(j) = E^0 + \eta_{OER}(j) + \eta_{HER}(j) + \eta_{\Omega}(j) \]  

(4.1)

where \( V_{op} \) is the overall operational voltage necessary for water splitting at a given current density \( j \), \( E^0 \) is the thermodynamic potential stored in water splitting, 1.23 V under standard
conditions, and $\eta_\Omega$ represents the voltage required to overcome resistive losses in the device including contact resistance between the components and ion transport resistance arising from the electrolyte solution. Typically these resistances are ohmic and therefore can be represented by the simple product of the net current and an aggregate cell resistance, $R$. The $\eta_{\text{OER}}$ and $\eta_{\text{HER}}$ terms represent the overpotential losses accompanying the oxygen evolution and proton reduction half reactions, respectively, and they are illustrated in Figure 4.1. Both overpotential terms are functions of the current density as given by the Tafel law,

$$\eta = b \log \left( \frac{j}{j_0} \right)$$

in which $b$ is the Tafel slope and $j_0$ is the exchange current density, representing the extrapolated rate at which the forward and back reactions occur under conditions of zero driving force, $\eta = 0$. Combining eqs. 4.1 and 4.2 with consideration of the ohmic nature of the cell resistance term engenders the following expression for the electrochemical load of water splitting,

$$V_{\text{op}}(j) = 1.23 + b_{\text{OER}} \log \left( \frac{j}{j_{0,\text{OER}}} \right) + b_{\text{HER}} \log \left( \frac{j}{j_{0,\text{HER}}} \right) + jR$$

In this expression, $b_{\text{OER}}, j_{0,\text{OER}}, b_{\text{HER}}$ and $j_{0,\text{HER}}$ represent the Tafel slopes and exchange current densities of the oxygen evolution and proton reduction catalysts, respectively. In order to isolate the impact of disparate OER catalyst kinetics, we chose to model the hydrogen evolution catalyst using values typical of the HER on high surface area Ni electrodes\textsuperscript{14,15} and similar to those used in the artificial leaf,\textsuperscript{16,17} $j_{0,\text{HER}} = 10 \ \mu\text{A cm}^{-2}$ and $b_{\text{HER}} = 30 \ \text{mV/decade}$\textsuperscript{14} and to assume a conservative value of $R = 10 \ \Omega$. Extrapolation of the Tafel data in Figure 4.2 yields exchange current densities for Co–B\textsubscript{i} and Ni–B\textsubscript{i} of $2.1 \times 10^{-12}$ and $5.0 \times 10^{-18}$ A cm\textsuperscript{-2}, respectively. These values, taken together with the Tafel slopes of the two catalysts yields the current density–voltage curves shown in Figure 4.3 for water splitting by Co–B\textsubscript{i} and Ni–B\textsubscript{i}. Consistent with the larger exchange current density for Co–B\textsubscript{i}, the onset of appreciable water splitting occurs at a lower potential relative to
However, the lower Tafel slope of Ni–Bi causes its $j$–$V$ curve to rise far more steeply, requiring a lower voltage at high current density. In this treatment, we assume that the Tafel behavior shown is Figure 4.2 is retained over the entire overpotential range and acknowledge that mass transport limitations and/or changes in OER mechanism at high overpotential may perturb the theoretical $j$–$V$ behavior in Figure 4.3.

As further points of comparison, published Tafel data for RuO$_2$ and LaMnO$_3$ in 1 M NaOH are also overlaid on the graph to model the electrochemical load of water splitting using these catalysts. The reported Tafel data for RuO$_2$ and LaMnO$_3$ correspond to materials prepared by high temperature calcination of metal salt precursors at $>350$ °C. As such, these materials may not be suitable for direct integration into PV–PEC architectures. We therefore include them in Figure 4.3 as exemplars of high and low performance OER catalysts and thus they provide a benchmark for the impact of catalyst performance on SFE.
4.3 Discussion

In the artificial leaf, the operating current density is given by the intersection of the $j-V$ curve for the PV and the $j-V$ curve representing the electrochemical load for water splitting. This operating current density multiplied by the thermodynamic potential of water splitting, 1.23 V, defines the power stored in water splitting and the ratio of this power to the incident power of the solar flux, 100 mW/cm$^2$, defines the SFE. For the purposes of illustration, we model in Figure 4.3 the idealized PV behavior of a triple junction amorphous Si(a–Si) | nanocrystalline Si(nc–Si) | nanocrystalline Si(nc–Si) triple junction cell stack exhibiting $V_{oc} = 1.94$ V and $j_{sc} = 8.96$ mA cm$^{-2}$, and a hypothetical multi-junction cell with a $V_{oc} = 2.13$ V and $j_{sc} = 8.15$ mA cm$^{-2}$. Idealized behavior of the PV is modeled by ignoring efficiency losses due to high series or low shunt resistances and assuming a diode ideality factor of 1 (details of PV modeling provided in the Section 4.5). Both idealized cells exhibit a power conversion efficiency of 16%, but display dramatically different SFEs when paired with the various OER catalysts.

For the cell possessing the lower $V_{oc}$, the electrochemical load curves for water splitting using Ni–Bi, and Co–Bi intersect the $j-V$ curve of the PV at 1.85 and 1.89 V (Figure 4.3), respectively, which is beyond the maximum power point ($V_{mp} = 1.83$ V) of the PV. As the PV current density declines sharply beyond $V_{mp}$, an artificial leaf utilizing Co–Bi is expected to exhibit a lower hydrogen production current density (7.6 mA cm$^{-2}$) than one utilizing Ni–Bi (8.7 mA cm$^{-2}$). Water splitting stores 1.23 V and, thus, these current densities translate to SFE = 9.3% and 10.7% for Co–Bi and Ni–Bi, respectively. The SFE declines further for the case of LaMnO$_3$, which displays an overall water splitting current density of 4.4 mA cm$^{-2}$ and a SFE = 5.4%. In contrast, RuO$_2$, despite displaying greater OER catalytic activity than thin film Co–Bi and Ni–Bi, exhibits only a marginally larger SFE = 11.1%. The artificial leaf becomes even more insensitive to OER catalytic activity if the $V_{oc}$ of the PV can be increased (Figure 3). For the higher $V_{oc}$ cell, all of the catalysts exhibit SFE = 10.0%, highlighting the fact that good catalyst performance and
high SFE is only mandated if a suitable PV with a $V_{mp}$ matched to the electrochemical load can be designed near the thermodynamic potential of water splitting.

The forgoing analysis assumes that the PV exhibits ideal diode behavior with minimal series and maximal shunt resistances. In practice, multi–junction Si devices suffer from poor fill factors symptomatic of non–ideal diode behavior and parasitic resistance losses. Thus, we stress that the trends observed here are purely theoretical and that a more rigorous analysis performed on a specific PV/catalyst pairing would be necessary for device optimization. We do note however, in a practical artificial leaf with minimized ohmic losses, an overall SFE = 5.2% has been observed for a PV cell of 7.7% efficiency.

4.4 Conclusion

In summary, we illustrate here that a key determinant of high SFE for artificial leaves, and more generally, photoelectrochemical cells, is the OER kinetic profile. In particular, thin Ni–Bi catalyst films exhibit a 29 mV/decade Tafel slope as compared to a 52 mV/decade slopes observed for Co–Bi under similar electrolyte conditions. The disparate kinetics of Co–Bi and Ni–Bi translate into improved SFE of an artificial leaf utilizing the latter, suggesting that Ni–Bi is particularly well-suited to direct solar-to-fuels generation.

We note that the critical role of catalysis in SFE has generally been under-appreciated because PEC cells to date have generally relied on semiconducting materials with large bandgaps (e.g., SrTiO$_3$, TiO$_2$, WO$_3$ display bandgaps, $E_g > 2.5$ V) which supply very high voltages to drive water splitting. These materials have typically been used as components of solution-junction PEC devices rather than buried junction devices complicating their analysis using the simple power matching model presented here. Notwithstanding, the extremely poor catalytic activity of semiconducting oxides such as SrTiO$_3$, TiO$_2$, and WO$_3$ can be masked by the large voltages they deliver to drive water splitting via high overpotential pathways (e.g. hydroxyl radical formation). As
illustrated in Figure 4.4, qualitatively, large band gap oxide PEC devices can be viewed to a first order as exaggerated cases of the high $V_{oc}$ PV we model in Figure 4.3, wherein, load curves for poor catalysts still intersect the $j$–$V$ curve of the semiconductor at or below the $V_{mp}$. The maximum SFE of such cells, however is intrinsically limited owing to inefficient utilization of the solar spectrum. High SFEs can only be achieved for PVs operating near the thermodynamic potential of water splitting so that the absorption of the solar spectrum can be maximized. In this case, as illustrated in Figures 4.3 and 4.4, the overall SFE becomes extremely sensitive to catalyst performance.

These results show that the construction of efficient PEC devices such as the artificial leaf reduces to a problem of catalyst design. To this end, Co–B and Ni–B are ideal water splitting catalysts when integrated to well-designed Si-junctions or other PV cells operating near the thermodynamic potential for water splitting. The results herein show that SFEs = 10% are easily within reach if Co–B and Ni–B catalysts are integrated.
with PV cells operating at 15% efficiency thus highlighting the promise of artificial leaves as a low cost method for direct solar–to–fuels production.

4.5 Experimental Methods

**Materials.** Ni(NO$_3$)$_2$•6H$_2$O 99.9985% was used as received from Strem. H$_3$BO$_3$ (99.5%), and KOH (85%) were used as received from Sigma–Aldrich. NaOH (99%) and KNO$_3$ (99%) were used as received from Mallinckrodt. All buffers were prepared with reagent grade water (Ricca Chemical, 18 MΩ–cm resistivity) or Millipore Type–I. Fluorine–tin–oxide (FTO) coated glass slides (TEC–7) were purchased as pre–cut pieces from Hartford Glass.

**Electrochemical methods.** All electrochemical experiments were performed at ambient temperature with a CH Instruments 760D potentiostat and a BASi Ag/AgCl reference electrode. All electrode potentials were converted to the NHE scale using $E_{\text{NHE}} = E_{\text{Ag/AgCl}} + 0.197$ V. Unless otherwise stated, the electrolyte was 0.1 M potassium borate at pH 9.2 (B$_i$).

**Co–B$_i$ catalyst film formation and Tafel data collection.** Bulk electrolyses were performed in a two–compartment electrochemical cell with a glass frit junction of fine porosity. For catalyst electrodeposition, the auxiliary compartment was charged with ~50 mL of 0.1 M B$_i$ electrolyte and the working compartment was charged with ~50 mL of solution comprising 25 mL of 0.2 M B$_i$ electrolyte and 25 mL of 1 mM Co$^{2+}$ solution. The working electrode was a 1 cm × 2.5 cm piece of FTO–coated glass. The FTO coated side was masked so as to expose a 1 cm$^2$ area of the electrode to the solution. Pt mesh was used as the auxiliary electrode. Electrolysis was carried out at 0.92 V on quiescent solutions without $iR$ compensation and with the reference electrode situated 2–3 mm from the ITO surface. Electrolysis was continued until 24 mC of charge were passed.

Tafel data were obtained by conducting controlled–potential electrolysis in 1 M B$_i$ electrolyte at a variety of applied potentials. Prior to film deposition, the solution resistance
of the 1 M KB₄ electrolyte to be used for Tafel data collection was measured using the \( iR \) test function. The electrolysis solution was exchanged with Co²⁺-containing 0.1 M B₄ electrolyte, without disturbing the relative positions of the working and reference electrodes. The film was prepared by controlled-potential electrolysis as described above. Following film preparation, the working electrode was rinsed in reagent grade water, and transferred without drying, to the same electrolysis bath in which the solution resistance was measured. The electrode was allowed to equilibrate with the electrolysis solution for 5 min while being held at the open circuit potential. The solution was stirred and steady-state currents were then measured at applied potentials that descended from 1.17 V to 0.96 V in 10–30 mV steps. For currents greater than 10 \( \mu \text{A cm}^{-2} \), a steady state was reached at a particular potential in 400–600 s. For currents lower than 10 \( \mu \text{A cm}^{-2} \), longer electrolysis times (15–20 min) were utilized to ensure that steady state conditions had been achieved. The solution resistance measured prior to the data collection was used to correct the Tafel plot for ohmic potential losses.

**Ni–B₄ catalyst film formation, anodization, and Tafel data collection.** Ni–B₄ catalyst films were prepared by controlled–potential electrolysis of 0.1 M B₄ electrolyte solutions containing 0.4 mM Ni²⁺. To minimize precipitation of Ni(OH)₂ from these solutions, 25 mL of 0.2 M B₄ was added to 25 mL of 0.8 mM Ni²⁺ solution. The deposition solutions were subsequently filtered through a 0.2 \( \mu \text{m} \) syringe filter (Pall Inc.) to remove any precipitated Ni(OH)₂ that formed. The solutions thus prepared remained clear over the course of all depositions, which were carried out using an FTO-coated glass piece as the working electrode. These FTO-coated glass electrodes were rinsed with acetone and water prior to use in all experiments and the FTO-coated side was masked so as to expose a 1 cm² area of the electrode to the solution. Deposition by controlled-potential electrolysis was carried out on quiescent solutions at 1.15 V without \( iR \) compensation and with passage of 1 mC cm⁻². A typical deposition lasted 70 s. Following deposition, films were rinsed
with 0.1 M B\textsubscript{i} and subsequently anodized in 1 M B\textsubscript{i} electrolyte by passage of 3.5 mA cm\textsuperscript{-2} for 1 h with stirring.

Current–potential data were obtained by conducting controlled potential electrolysis in 0.5 M B\textsubscript{i} 1.75 M KNO\textsubscript{3} electrolyte at a variety of applied potentials. Prior to film deposition and anodization, the solution resistance of the electrolyte to be used for Tafel data collection was measured using the $iR$ test function. The electrolysis solution was exchanged for Ni\textsuperscript{2+}–containing B\textsubscript{i} electrolyte, without disturbing the relative positions of the working and reference electrodes. The film was prepared by controlled-potential electrolysis and anodized as described above. Following film preparation, the working electrode was rinsed in fresh Ni–free B\textsubscript{i} electrolyte and transferred, without drying, to the same electrolysis bath in which the solution resistance was measured. The electrode was allowed to equilibrate with the electrolysis solution for 5 min while being held at the open circuit potential. The solution was stirred and steady–state currents were then measured at applied potentials that descended from 1.1 V to 1.00 V in 7–20 mV steps. For currents greater than 10 $\mu$A cm\textsuperscript{-2}, a steady state was reached at a particular potential in < 400 s. For currents lower than 10 $\mu$A cm\textsuperscript{-2}, longer electrolysis times (15–20 min) were utilized to ensure that steady state conditions had been achieved. The solution resistance measured prior to the data collection was used to correct the Tafel plot for ohmic potential losses.

$j$–$V$ curve modeling. The $j$–$V$ curve representing the electrochemical load of water splitting was calculated using equation 4.3 over a current density range from $10^{-5}$ A cm\textsuperscript{-2} to $10^{-1}$ A cm\textsuperscript{-2}. A 10 $\Omega$ cell resistance was assumed along with $j_{0,HER} = 10 \mu$A cm\textsuperscript{-2} and $b_{HER} = 30$ mV/decade. The Tafel slopes and exchange current density values for Co–B\textsubscript{i} and Ni–B\textsubscript{i} were taken from linear fits to the data in Figure 4.2 whereas Tafel slopes and exchange current density values were taken published data for RuO\textsubscript{2}\textsuperscript{18} and LaMnO\textsubscript{3}\textsuperscript{19}.

The $j$–$V$ curve representing idealized power output from a triple junction Si photovoltaic stack was modeled using reported data for a a–Si| nc–Si | nc–Si cell\textsuperscript{20} which exhibits $V_{oc} = 1.94$ V and $j_{sc} = 8.96$ mA cm\textsuperscript{-2} (Figure 4.3). These two experimental
parameters were used to calculate the dark saturation current of an idealized cell, $j_0$, using the following equation:

$$j_0 = \frac{j_{sc}}{\exp\left(\frac{qV_{oc}}{nk_BT}\right) - 1} \quad (4.4)$$

where $q$ is the fundamental charge of an electron, $k_B$ is the Boltzmann factor, $T$ is the temperature, taken as 300 K, and $n$ is the diode ideality factor, taken as 1. Using the calculated value of $j_0$, the ideal $j-V$ curve is calculated using

$$j = j_{sc} - j_0 \left(\exp\left(\frac{qV}{nk_BT}\right) - 1\right) \quad (4.5)$$

The same analysis was applied to a hypothetical idealized cell with a 10% increase in $V_{oc}$ and a concomitant 10% decrease in $j_{sc}$ so to preserve the same overall power conversion efficiency of 16%. We note that the above equations produce upper limit ideal behavior because they do not account for parasitic resistances that may exist within or between the individual p–n junction components of the triple junction stack.

### 4.6 References


Chapter 5 — Proton-Electron Transport and Transfer in Electro catalytic Films. Application to a Cobalt-Based O₂-Evolution Catalyst.

Portions of this chapter have been published:

5.1 Introduction

In Chapter 3 we discussed the use of steady state polarization measurements (Tafel data) to elucidate the factors that control active site turnover in Ni–Bi films. Disparate PCET and buffer adsorption kinetics make Ni–Bi films more active OER anodes than their analogous Co-based films under slightly alkaline to strongly basic (pH 8–14) conditions, whereas Co–Pi/Bi films display higher activity at neutral pH. In these comparisons, we endeavored to measure the properties of films prepared by deposition of similar amounts of material. As emphasized in the Chapter 1, besides the increasing the intrinsic activity of a catalyst (such as Ni–Bi vs Co–Pi at pH 9), lower overpotentials may be attained by exploiting thicker films with more active sites per geometric area. Thus, we might ask the question: for two thin-film catalysts A and B, where A is more active than B, will thicker films of A always necessarily offer lower overpotentials than B? Or could thick films of B actually surpass the activity of analogously thick films of A?

To answer this question, we must recognize that besides the catalytic reaction itself, two major controlling factors are (i) the transport of electrons from or to the electrode to regenerate the active form of the catalyst and (ii) the transport of the substrate from the bathing solution through the film toward the catalytic centers. In the above-listed reactions and in many others, protons are consumed or produced during catalysis. Proton-coupled electron transfers 1–8 thus play a key role in the catalytic cycle. The transport of protons and/or the acid and basic forms of the buffer often added to the solution may therefore influence the catalytic responses. In such systems, one should consider also that the transport of electrons through the film may be coupled with the transfer of protons. The purpose of the work reported herein was to investigate the interplay of these various, potentially governing factors in the framework of a reasonably general process. A completely general analysis would embark the reader in a taxonomic nightmare with no guarantee of actual generality. In contrast, a reasonably general reaction scheme should
retain most of the essential controlling factors, with some simplifying assumptions, allowing a tractable analysis of their interplay. Figure 5.1, with some accompanying simplifications and approximations, as detailed in the following study, represents such a reasonably general framework. It is represented for an oxidative process, but transposition to reduction is straightforward. One of the main simplifying assumptions is that the substrate is in large concentration in the solution and in the film, so large that it remains constant as it is the case when the solvent, e.g. water, is the substrate. This simplifying situation is considered here in order to focus on the other factors notably proton transfer and transport. Cases in which penetration and diffusion of the substrate through the film are rate-controlling factors may be treated when necessary by adaptation of the present and previous analyses.9–13

The kinetic responses expected for such processes will be discussed in the first part of this chapter, as the result of interplay between the various rate-controlling factors. The second part will be devoted to the application of this methodology to the electrocatalytic oxidation of water by Co–P$_i$ films.14–19 Spectroscopic studies 20,21 of these cobalt-based catalysts (Co–OECs) have established a mixed valence Co$_{III/IV}$ resting state, and

Figure 5.1. Electrocatalytic oxidation of the substrate A into the products B in the presence of an acid-base couple ZH$^+$/Z by means of an immobilized PH/Q + e$^-$ catalyst couple.
mechanistic studies\textsuperscript{22} suggest a rapid, one-electron, one-proton equilibrium between Co\textsuperscript{III}–OH and Co\textsuperscript{IV}–O (Co\textsuperscript{III}–O•) in which a phosphate species is the proton acceptor, followed by a chemical turnover-limiting process involving oxygen-oxygen bond coupling (Figure 5.2). Subsequently, lower valence intermediates are rapidly oxidized to regenerate the resting state species (a net 3e\textsuperscript{−}, 3H\textsuperscript{+} process), and thus the kinetics of these steps do not contribute to the overall rate law. As a consequence, the cobalt-based O\textsubscript{2}-evolution catalyst may be analyzed according to a simple scheme (Scheme 5.1) that involves the PH (Co\textsuperscript{IV}O-Co\textsuperscript{III}OH) and Q (Co\textsuperscript{IV}O-Co\textsuperscript{IV}O) forms of the catalyst merely considering that \( k_{\text{cat}} = 4k_{C} \) in equations (5.2) and (5.3). As porous materials, the accessibility of active sites distributed throughout the film is a key factor for activity.\textsuperscript{23,24}

5.2. Theoretical treatment of substrate oxidation by means of an immobilized proton–electron catalyst couple

Although any electrochemical non-destructive technique may be used to investigate the kinetic responses of systems like the one shown in Figure 5.1, rotating-disk electrode voltammetry (RDEV) is particularly convenient and holds transport characteristics that are similar to those prevailing under preparative-scale conditions. Transport of the reactants in
the solution to or from the film/solution may be controlled through the rotating rate, \( \omega \), which modulates the size, \( \delta \), of the diffusion-convection layer (Figure 5.1):

\[
\delta (cm) = 1.61 \times D (cm^2 s^{-1})^{1/3} \times \nu (cm^2 s^{-1})^{1/6} \times \omega (rad s^{-1})^{-1/2}
\]

(5.1)

\((D: \text{diffusion coefficient}, \nu: \text{kinematic viscosity})\)

The aim of the analysis herein is to predict the current–potential curves under the control of the various transport and reactivity factors sketched in Figure 5.1. A popular way of representing these relationships is the so-called “Tafel plot” relating the log of the current, \( i \), or current density, \( j \), to the electrode potential or to the overpotential, \( \eta \) (difference between the electrode potential, \( E \), and the equilibrium potential of the reaction being catalyzed, \( E_A^{eq} \)). In the following report we will use current densities rather than currents.

Historically, the Tafel equation is the irreversible version of the more general Butler–Volmer equation, which describes the relationship between the kinetics of an electrochemical charge transfer reaction, represented by the log of the current, or current density, and its thermodynamics, represented by the overpotential. The ensuing Tafel plots of such reactions are usually linear, in which case they are characterized by their slope and by the value of the exchange current density, \( i.e., \) the current density at overpotential zero. The Tafel slope is related to the electrochemical transfer coefficient, \( \alpha \), comprised between 0 and 1. This is often close to 0.5 for single-electron electrochemical reactions, which corresponds to Tafel slope (when plotted as log \( j \) versus potential) of \( F/2RT \ln 10 \). In fact the “Tafel” slope for electrocatalytic reactions in general, and in particular those depicted in Figure 5.1, have no reason to systematically have this value. The ensuing Tafel plots are not even necessarily linear. Strictly speaking, the current density–potential relationships characterizing electrocatalytic systems such as represented in Figure 5.1 are not conventional Tafel plots of electrochemical charge transfer reactions. To conform to usage, we nevertheless retain the appellation “Tafel plot” in the very broad sense of a log
current (or current density) vs. overpotential relationship that would result from the interplay of the various rate-controlling factors of an electrocatalytic reaction.

A methodology for describing the kinetics as a function of various controlling factors has been developed in the framework of rotating disk electrode voltammetry for electrocatalytic electrode coatings in the 1980s.\cite{13,28} It must however be extended in two directions to meet the requirements of the current study. The earlier approach was essentially focused on the catalytic plateau currents that are encountered with such systems at large overpotentials, whereas the study here is concerned with a description of the foot of the current–potential response, where the contribution of reactant transport in the solution is expected to be minimal, although not necessarily negligible. The other extension concerns the coupling between electron transfer and proton transfer in electrocatalytic films of the type shown in Figure 5.1.

Proton-coupled electron transfer (PCET) reactions have been the object of intense investigation during the last decade with particular emphasis on concerted proton–electron transfers (CPET) in which proton and electron are exchanged during a single step.\cite{1,29} In the electrocatalytic films under discussion, coupling between proton and electron transfers comes into play at two levels. One involves the proton-electron hopping through the film, which replaces the single electron hopping of previous studies. The other concerns the production of protons at the electrode from the oxidation of the reduced form of the catalyst (PH yielding Q + H\(^+\)) in the presence or absence of a buffer (ZH\(^+\)/Z).

Electrocatalytic films such as those that are object of the present analysis are porous structures where the solvent can penetrate, where the substrate, products, solvated protons and buffer components can diffuse freely in the pores. Proton–electron hopping conduction takes place in the solid sections of the structure where continuity is ensured even at the cost of dynamic percolation.\cite{30} On the whole, the various elements of the structure can be averaged so as it can be considered as equivalent to a homogeneously distributed set of
catalytic sites between which protons and electrons can hop in a coupled manner and through which substrate, products, solvated protons and buffer components may diffuse freely through an equivalent isotropic film as sketched in Figure 5.1. Thus these processes occur in a similar manner as already described for polymer electrode coatings.\(^3\)

Additional assumptions, approximations or restrictions are:

(i) The analysis is restricted here to the case where catalysis and proton-electron hopping are performed by the same centers. If necessary, it could be extended to cases where the catalytic centers and the conduction centers are not the same as previously illustrated with electron-hopping examples.\(^2\)

(ii) Proton-electron hopping through the film may follow a concerted pathway (CPET) that goes directly from PH to Q or two stepwise pathways, a PTET pathway (proton transfer first, from PH to P, followed by electron transfer between P and Q) or a ETPT pathway (electron transfer first, between PH and QH, followed by proton transfer, from QH to Q). We consider the case where the proton transfers involved in the stepwise pathways are fast and unconditionally at equilibrium.

(iii) The electron transfer electrode reaction regenerating Q from the oxidation of PH with production of a proton may likewise follow concerted or stepwise pathways. We consider the cases where the concerted reaction is fast and unconditionally at equilibrium and where the proton transfer and electron transfer reactions are all fast and unconditionally at equilibrium in the stepwise pathways.

(iv) The substrate, A, is assumed to be in large concentration in the solution and in the film, so large that it remains constant. This simplifying situation is considered here in order to focus on the other factors notably proton transfer and transport. Cases in which penetration and diffusion of the substrate through the film are rate-controlling factors may be treated when necessary by adaptation of the present and previous analyses.\(^2\)
(v) We further assume that the partition coefficients of $H^+$, $ZH^+$ and $Z$ between the solution in the pores and the solution outside the film are approximately equal to unity.

In the following analysis, each current density is defined as the current intensity divided by the projection of the real surface area on the geometrical electrode surface. It is convenient to represent the possible control by each of the factors by a characteristic current density as summarized in Table 5.1. The expressions of these characteristic current densities result from the following analysis.

<table>
<thead>
<tr>
<th>Rate-controlling phenomenon</th>
<th>Characteristic current density</th>
<th>Parameters, remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalytic reaction</td>
<td>$j_c = Fk_{cat}C_{cat}d_f$</td>
<td>$k_{cat} = k_{2nd}C_{subst}$: pseudo-first order rate constant of the catalytic reaction</td>
</tr>
<tr>
<td>Proton-electron hopping</td>
<td>$j_{H,e} = \frac{FD_{H,e}C_{cat}}{d_f}$</td>
<td>$D_{H,e}$: proton–electron hopping “diffusion” coefficient (see text)</td>
</tr>
<tr>
<td>Proton diffusion in the film</td>
<td>$j_{H,\text{in}} = \frac{FD_{H,\text{in}}C_{H^+}^0}{d_f}$</td>
<td>$D_{H,\text{in}}$: proton diffusion coefficient in the film. $D_{ZH,\text{in}}, D_{Z,\text{in}}$ : diffusion coefficients of $ZH^+$ and $Z$ in the film.</td>
</tr>
<tr>
<td>Diffusion of the buffer components in the film</td>
<td>$j_{ZH,\text{in}} = \frac{FD_{ZH,\text{in}}C_{ZH}^0}{d_f}$</td>
<td>$D_{ZH,\text{in}}, D_{Z,\text{in}}$ : diffusion coefficients of $ZH^+$ and $Z$ in the film.</td>
</tr>
<tr>
<td>Proton diffusion in the solution and fast equilibration at the film solution interface</td>
<td>$j_{H,\text{out}} = \frac{FD_{H,\text{out}}C_{H^+}^0}{\delta}$</td>
<td>$D_{H,\text{out}}$: proton diffusion coefficient in the solution.</td>
</tr>
<tr>
<td>Diffusion of the buffer components in the solution and fast equilibration at the film solution interface</td>
<td>$j_{ZH,\text{out}} = \frac{FD_{ZH,\text{out}}C_{ZH}^0}{\delta}$</td>
<td>$D_{ZH,\text{out}}, D_{Z,\text{out}}$ : diffusion coefficients of $ZH^+$ and $Z$ in the solution.</td>
</tr>
</tbody>
</table>

$^a d_f$: film thickness, $\delta$: diffusion layer thickness (equation 1). $C_{cat}$: total concentration of the catalyst in the film. $C_{subtr}$: concentration of substrate in the film. $C_{H^+}^0$, $C_{ZH}^0$, $C_{Z}^0$: concentrations of $H^+$, $ZH^+$ and $Z$ in the solution, respectively.
Proton–electron hopping through the film may be likened to a linear diffusion transport obeying Fick’s laws of diffusion as shown in Section 5.7, assuming that there is no electric field effect within the film because the hopping process does not involve net charge transport. Association with the catalytic reaction (Figure 5.1) leads to the following steady-state expressions of Fick’s law modified by a kinetic catalytic term:
\[ D_{H,e} \frac{d^2 C_{PH}}{dx^2} + k_{cat} C_Q = 0 \]  
\[ D_{H,e} \frac{d^2 C_Q}{dx^2} - k_{cat} C_Q = 0 \]  
Here \( x \) is the distance to the electrode and the “C”’s represent the concentrations of the subscript species.

Insofar the proton transfer steps are at equilibrium (condition ii above), equations (5.2) and (5.3) apply irrespective of the mechanism of proton-electron hopping, although \( D_{H,e} \) may have different expressions in each case (Section 5.7).

Condition (iii) above implies that the following equivalent expressions of the Nernst law apply at the electrode surface (\( x = 0 \)).

\[ \frac{(C_Q)_{x=0} \times (C_{H^+})_{x=0}}{(C_{PH})_{x=0} \times C^0} = \exp \left[ \frac{F}{RT} \left( E - E_{Q+H^+/PH}^0 \right) \right] \]
\[ \frac{(C_Q)_{x=0} \times (C_{ZH})_{x=0}}{(C_{PH})_{x=0} \times (C_Z)_{x=0}} = \exp \left[ \frac{F}{RT} \left( E - E_{Q+ZH/PH+Z}^0 \right) \right] \]

where the two standard potentials characterizing the catalyst PH/Q couple are related by:
\[ E_{Q+ZH/PH+Z}^0 = E_{Q+H^+/PH}^0 + \frac{RT}{F} \ln \left( \frac{K_a}{C^0} \right) \]

\( (K_a \) is the acidity constant of \( \text{ZH}^+ \), \( C^0 \) is a normalizing concentration that is conveniently taken as equal to 1 M.)

The above Nernst equations may also be expressed as a function of the overpotential \( \eta = E - E_A^{eq} \), where \( E_A^{eq} \) is the equilibrium potential of the reaction to be
catalyzed. It is not necessarily a standard potential and may contain reactant concentration terms, such as the pH, according to the reaction under consideration and to the most convenient definition of the overpotential in each particular case.

Integration of equations 5.2 and 5.3, taking into account the appropriate boundary conditions and noting that we are interested in what happens in the foot of the current responses, leads to (see Section 5.7):

$$\frac{(C_Q)_{x=0}}{C_{cat}} = \frac{j}{\sqrt{j_k j_{H,e}} \tanh \left( \sqrt{\frac{j_k}{j_{H,e}}} \right)}$$  \hspace{1cm} (5.5)

**5.2.1. High buffer concentrations (insignificant buffer consumption within the catalyst film)**

Joint control by catalytic reaction and proton–electron hopping is observed when the concentration of buffer is sufficiently large that the concentrations of its two components are constant throughout the film. The buffer serves to neutralize the protons generated by the PCET electrode reaction and to convert, at least partially, its diffusion toward the solution into a diffusion of ZH toward the solution and a diffusion of Z toward the electrode in addition to participating as reactants in the PCET reaction at the film–electrode interface. Then the Tafel plots are predicted to obey the following equation (see Section 5.7).

$$\log j = \log j_0 + \frac{F}{RT \ln 10}$$  \hspace{1cm} (5.6)

where $j_0$, the current density at zero overpotential can be considered as a nominal “exchange current density”. It can be expressed as:

$$\log j_0 = \log \left[ \frac{C_0}{C_{H^+}} \sqrt{j_k j_{H,e}} \tanh \left( \sqrt{\frac{j_k}{j_{H,e}}} \right) \right] + \frac{F(E_A^{eq} - E_{Q+H^+/PH}^0)}{RT \ln 10}$$  \hspace{1cm} (5.7a)
Where eq. 5.7a introduces a useful parameter, the “optimal” thickness:

\[
d_f^{opt} = \frac{D_{H,e}}{\sqrt{k_{cat}}}
\]  

(5.8)

The Tafel plots are thus predicted to have a slope of \(\frac{F}{RT} \ln 10\) and to depend on film thickness as pictured in Figure 5.3a. Below the “optimal” value, \(d_f^{opt}\), the current

**Figure 5.3.** Electrokinetic profile at large buffer concentrations. (a) Tafel plot trends predicted for a series of increasing thicknesses, from bottom to top. (b) Variation of the current density with the film thickness (relative to the optimal film thickness \((d_f^{opt})\), at \(\eta = 0\). \(j_0\) and \(j_{max}^{\infty}\) are defined in equations (5.7a & 5.7b) and (5.9a & 5.9b), respectively. For \(d_f\) see equation (5.8). (c) Concentration profile of oxidized catalyst form, \(Q\) (relative to the concentration of \(Q\) at the electrode–film interface), in the case of mixed control by the turnover-limiting reaction and the diffusion-like proton–electron hopping under pure kinetic conditions for a series of films with thicknesses equal to 0.5 \(d_f^{opt}\), 1 \(d_f^{opt}\), 2 \(d_f^{opt}\), and 3 \(d_f^{opt}\). (d) Concentration profile of \(Q\) (relative to total catalyst concentration in the film) as a function of increasing electrode potential (from bottom to top) for a film of thickness equal to \(d_f^{opt}\).
density response increases proportionally to film thickness, whereas beyond $d_f^{opt}$, the response plateaus off. This is best represented as a variation of the exchange current density with the film thickness as shown in Figure 5.3b where the maximal value reached by $j_0$, noted $j_0^{max}$, may be expressed by: 

$$j_0^{max} = F \frac{C^0}{C_{H^+}^{eq}} C_{cat} \sqrt{k_{cat} D_{H,e}} \exp \left( \frac{F (E_{A}^{eq} - E_{Q+H^+/PH}^0)}{RT} \right)$$

(5.9a)

$$= F \frac{C^0}{C_{H^+}^{eq}} C_{cat} k_{cat} d_f^{opt} \exp \left( \frac{F (E_{A}^{eq} - E_{Q+H^+/PH}^0)}{RT} \right)$$

Thus, equations (5.7a and 5.7b) may be recast as:

$$j_0 = j_0^{max} \tanh \left( \frac{d_f}{d_f^{opt}} \right)$$

(5.10)

More rigorously, the variation of the exchange current density with the film thickness (Figure 5.3b) shows two limiting behaviors:

1. When

$$d_f/d_f^{opt} \to 0 \quad j_0 \to j_0^{max} \left( \frac{d_f}{d_f^{opt}} \right) = F \frac{C^0}{C_{H^+}^{eq}} C_{cat} k_{cat} \exp \left( \frac{F (E_{A}^{eq} - E_{Q+H^+/PH}^0)}{RT} \right) d_f$$

The exchange current density is governed solely by the catalytic reaction, and is consequently directly proportional to film thickness.

2. Alternatively, when

$$d_f/d_f^{opt} \to \infty \quad j_0 \to j_0^{max} \quad (as \ given \ by \ eq. \ 5.10)$$

The exchange current density is then independent of film thickness, being under the mixed control of the catalytic reaction and the diffusion-like proton-electron hopping under “pure kinetic conditions”.

Under these conditions, the total amount of Q in the film (given by the integrated concentration profile of Q) (Figure 5.3c) ceases to be dependent of the film thickness as a result of mutual compensation of catalytic reaction and diffusion-like proton-electron hopping. Instead, the
electrogenerated Q sites are confined in a reaction-diffusion layer of thickness equal to $\sqrt{D_{H,e}/k_{cat}}$.

It follows that there is no significant advantage to continuing to increase the thickness much beyond $d_f^{opt}$, since $j_0$ reaches a value equal to $j_0^{max}$ within experimental uncertainty. As shown in Figure 5.3d, increasing the electrode potential merely shifts the position of the PH/Q+H$^+$ equilibrium at the electrode–film interface. This consequently leads to greater values of $C_Q$ throughout the film and consequently a greater current density (Figure 5.3a).

We note that the current response is independent of the rotation rate. In other words the “Koutecky–Levich” plots are horizontal. Koutecky–Levich plots in RDEV are plots of the inverse of current density against the inverse of the square root of the rotation rate.$^{35}$ In the present discussion they may be taken at any potential along the Tafel plot. When they are linear, the intercept is representative of phenomena occurring in the film whereas the slope reflects reactant transport in the solution. This approach is actually not general because Koutecky–Levich plots are not always linear. Examples of non-linear Koutecky–Levich plots have been given in the analysis of redox polymer film responses.$^{28}$ Observing a non-linear Koutecky–Levich plot does not mean that the events taking place in the film are inseparable from transport in solution, but that it requires a somewhat less straightforward procedure. Examples will be given in the following analysis.

5.2.2. Buffer free conditions

Non-linear Koutecky–Levich plots are observed when no buffer has been introduced in the solution, which represents the converse extreme of the case where the whole system was completely buffered as examined earlier. Then (see Section 5.7),

$$\frac{(C_{H^+})_{x=0}}{C_{H^+}^0} = j \left( \frac{1}{J_{H,\text{in}}} + \frac{1}{J_{H,\text{out}}} \right) + 1$$
An extreme of a non-buffered situation is when the production of protons at the electrode is much larger than the proton concentration in solution, i.e. when: \( (C_{H^+})_{x=0} \gg C_{H^+}^0 \). Then,

\[
\frac{(C_{H^+})_{x=0}}{C_{H^+}^0} = \frac{j}{j_{H,in}} + \frac{j_{H,\text{out}}}{1} + 1
\]

with \( j_{H,in} = \frac{F D_{H,in} C_{H^+}^0}{d_f} \) and \( j_{H,\text{out}} = \frac{F D_{H,\text{out}} C_{H^+}^0}{\delta} \).

In most cases the RDEV diffusion-convection layers, \( \delta \), are larger (typically on the order of \( 10^{-2} - 10^{-3} \) cm) than the catalytic film thickness, \( d_f \) (usually ca. \( 10^{-4} - 10^{-6} \) cm). Since the ratio of the diffusion coefficients (\( D_{H,in} \) and \( D_{H,\text{out}} \)) is not very different from 1, \( j_{H,in} \gg j_{H,\text{out}} \) and therefore:

\[
\frac{(C_{H^+})_{x=0}}{C_{H^+}^0} = \frac{j}{j_{H,\text{out}}}
\]

In this case there is joint control of the current density by proton-electron hopping and the diffusion of solvated protons outside the film. The Tafel plots are then expected to obey equation (5.11) as shown in Figure 5.4a (See Section 5.7 for full derivation).

\[
\log j = \frac{1}{2} \log(j_0 \times j_{H,\text{out}}) + \frac{F}{2RT \ln 10}
\]  

(5.11)

**Figure 5.4.** Tafel data in the absence of buffer. (a) Tafel plots predicted for a series of increasing thicknesses from bottom to top. (b) Variation of the current density at \( \eta = 0 \) with the film thickness (relative to the optimal film thickness). \( j_0 \) and \( j_0^{\text{max}} \) are defined in equations (5.7a, 5.7b) and (5.9a, 5.9b) respectively. \( j_{H,\text{out}} \) is defined in Table 5.1.
Interestingly, the Tafel slope is $F/2R \ln 10$ (a 120 mV slope in an $E$ (or $\eta$) vs. log $j$ plot. Conventionally this would be assigned to a reaction scheme involving rate-limiting electron transfer from the resting state. But here we show that such a slope may arise for very different reasons. In this case, there is a dependence of $j$ on catalyst thickness. A rate-limiting electron transfer mechanism would not display a dependence of $j$ on film thickness, since only the first layer of catalyst at the film–electrode interface will be active.

The current density upon extrapolation to zero overpotential, $j_0$, is given by equations 5.7a, 5.7b or 5.9a, 5.9b and equation 5.10. The parameter $j_{H,\text{out}}$ which characterizes proton transport in solution, is defined in Table 5.1. In the first term of equation 5.11, $j_0$ is inversely proportional to $c_{H^+}^0$ (equation 5.7b) whereas $j_{H,\text{out}}$ is directly proportional to $c_{H^+}^0$ (Table 5.1) making the first term of equation 5.11, independent of pH. The Tafel plot predicted by equation 5.11 may however be pH dependent if $E_A^{eq}$, which serves as reference in the definition of the overpotential, depends itself on pH.

Koutecky–Levich (K–L) plots are not linear, even if they may look linear within the necessarily limited range of accessible rotation rates. Figure 5.5 illustrates this

![Figure 5.5. Koutecky–Levich plots in absence of buffer: $j_0/j$ as function of diffusion layer thickness, $\delta$, for two different values of the overpotential: $\eta = 0.4$ (red squares) and $\eta = 0.5$ (blue dots) with $j_0 = 2 \times 10^{-10}$ A/cm$^2$, $D_{H,\text{out}} = 5 \times 10^{-5}$ cm$^2$/s, $c_{H^+}^0 = 10^{-6}$ M (pH 6). Dots correspond to typical rotation rates: 2500, 1600, 1225, 900 and 625 rpm (using equation (1) with $v = 10^{-2}$ cm$^2$/s). Dotted lines correspond to purposely forced linear fitting of the data corresponding to rotation rates between 625 and 2500 rpm.](image)
misleading state of affairs. It also shows that, in such a situation, the slope of the apparently linear K–L relationship varies with the electrode potential in contrast to what is expected with truly linear K–L relationships.

One might be tempted to define an exchange current density for this case, as being the current density at zero overpotential. The extrapolated current density thus obtained, $\sqrt{J_0 \times J_{H,\text{out}}}$ is however somewhat unusual as compared to conventional electrochemical reactions in the sense that it incorporates the rate of proton transport in the solution and therefore depends on the RDEV rotation rate (through $j_{H,\text{out}}$ and equation 5.1). This exchange current density varies with the film thickness as shown in Figure 5.4b, first proportionally for $d_f \ll d_f^{\text{opt}}$, then reaching saturation with a value $\sqrt{J_0^{\text{max}} \times J_{H,\text{out}}}$ in which the expression of $J_0^{\text{max}}$ is the same as in equations 5.9a and 5.9b introduced previously in the case of perfect buffering.

### 5.2.3. Intermediate buffer concentrations

At intermediate buffer concentrations, the same assumptions concerning proton transfer and transport leads to a general implicit expression of the Tafel plots given by equation 5.12 (see Section 5.7):

$$\frac{F}{RT \ln 10} \eta = \log \left( \frac{J}{J_0} \right)$$

$$+ \log \left[ \frac{J_{Z,\text{out}}}{J_0} \times \frac{J_0}{J_{H,\text{out}}} \left( \frac{J}{J_0} \times \frac{J_0}{J_{Z,\text{out}}} - 1 \right) + \frac{\left( \frac{J}{J_0} \times \frac{J_0}{J_{Z,\text{out}}} - 1 \right)^2}{4} \right]$$

$$= 4 \left( \frac{J}{J_0} \times \frac{J_0}{J_{Z,\text{out}}} + \frac{C_0^{Z}}{C_0^{Z}} \right) \frac{J_{Z,\text{out}}}{J_0} \times \frac{J_0}{J_{H,\text{out}}}$$

(5.12)

Once again the “exchange current density”, $j_0$, is defined by equations 5.7 or 5.9 and 5.10). The buffer base and proton solution transport characteristic currents, $j_{Z,\text{out}}$ and $j_{H,\text{out}}$, respectively, are defined in Table 5.1.
Equation 5.12 allows the construction of series of Tafel plots as shown in Figure 5.6. It is seen that, at a given value of the buffer concentration, the high-buffer behavior tends to be reached at low overpotentials, whereas the no-buffer behavior tends to be reached oppositely at high overpotentials. In between these two limits the Tafel plots plateaus off. The current density is then \( j = j_{z, \text{out}} \), obtained when the concentration of the buffer base at the electrode surface comes close to zero as a result of the reaction with the catalytically generated protons. The current response in then solely controlled by the transport of the buffer base from the solution toward the film.

One key result here is that the combination of the various controlling factors, catalytic reaction, proton–electron hopping conduction through the film as well as proton transfer and transport may result in quite different Tafel slopes (\( \log j \) vs. \( E \) or \( \eta \)), \( F/RT \ln 10 \), \( F/2RT \ln 10 \) or \( 0 \). Tafel plots possessing such varied slopes as those represented in Figure 5.6 are quite unusual relative to conventional electrochemical reactions. Illustrating experimental examples of such behaviors are given in the next sub-section, which is
5.3. Application of the methodology to a cobalt-based O₂-evolution catalyst

The electrokinetics of Co–Pᵢ, a cobalt oxide-based O₂-evolution catalyst may be analyzed according to the scheme described by Figures 5.1 & 5.2 using the methodology developed in Section 5.2 by simply considering that \( k_{\text{cat}} = 4k_C \) in equations 5.2 and 5.3. In this analysis, the overpotential is defined as:

\[
\eta = E - E_{\text{eq}}^{\text{O}_2/\text{H}_2\text{O}} \quad \text{where} \quad E_{\text{eq}}^{\text{O}_2/\text{H}_2\text{O}} = E_{\text{O}_2/\text{H}_2\text{O}}^0 - \frac{RT \ln 10 \cdot 10^{-9}}{4F} \log \left( \frac{P_\text{O}_2}{P_\text{H}_2\text{O}} \right) - \frac{RT \ln 10}{F} \ pH \tag{5.13}
\]

with \( E_{\text{O}_2/\text{H}_2\text{O}}^0 = 1.23 \text{ V vs. NHE} \).\(^{37}\)

A series of RDEV experiments was carried as a function of two main parameters, the concentration of the buffer (including the absence of buffer) and the film thickness. The steady state current density was measured point-by-point at a series of decreasing electrode potential values and at different rotation rates.

5.3.1. High buffer concentrations (≥ 100 mM Pᵢ)

In the presence of a large amount of buffer (0.1 M NaPᵢ, at pH 7), Tafel plots with a slope of \( F/RT \ln 10 \ (1/59 \text{ mV at } 297 \text{ K}) \) are obtained for a series of film thicknesses (Figure 5.7a). They were observed to be independent of rotation rates (from 625 rpm to 2500 rpm). The current density increases with film thickness before reaching saturation. These observations are what is anticipated for joint control by the catalytic reaction and by proton–electron hopping as discussed in the preceding section (Figure 5.3a). The variation of the Tafel plot intercept at \( \eta = 0 \) (“exchange current density”) is thus expected to follow the variation shown in Figure 5.3b and to obey equations 5.7, 5.8 and 5.9. This is indeed observed in Figure 5.7b whilst application of these equations (5.7–5.9) leads to:
5.3.2. Buffer-free conditions.

Tafel plots acquired at pH 6 in absence of buffer display a F/2RT ln10 slope at various rotation rates for various film thicknesses (Figure 5.8). In this case the overpotential is defined using the thermodynamic potential of 0.866 V vs. NHE (application of equation 13 with pH = 6). These data are distinct from the background currents associated with the RDE surface alone and are unaltered with changing the ionic strength, supporting electrolyte, or the elimination of CO₂, and therefore carbonate, from the electrolyte. It clearly appears that the response is dependent on film thickness thus ruling out a limitation by the PCET kinetics at the electrode surface. As detailed in the preceding section, the F/2RT ln10 slopes are coherent with a catalytic PCET process with water as proton acceptor.

\[
\frac{d}{d_{\text{opt}}} = \frac{D_\text{H}_2 \text{O}}{k_{\text{cat}}} = 1440 \text{ nm} \quad (5.14)
\]

\[
J_{0, \text{pH}7}^{\text{max}} = 1.75 \times 10^{-10} \text{ A/cm}^2 \quad (5.15)
\]

based on \(E_{\text{H}_2\text{O}_2/\text{H}_2\text{O}, \text{pH}7}^{\text{eq}} = 0.807 \text{ V vs. NHE} \) (eq. 5.13 with \(P_{\text{H}_2} / P_0 = 0.2\), and pH = 7).
The intercept, the logarithm of the current density at zero overpotential, is then \( \log(\sqrt{j_{H,\text{out}} \times j_0}) \). It allows access to the same intrinsic information on the system as in the high buffer concentration situation, yet taking into account the diffusion properties of the proton as required for the estimation of \( j_{H,\text{out}} \). Because it is partially controlled by proton diffusion toward the solution in the absence of buffer.

The intercept, the logarithm of the current density at zero overpotential, is then \( \log(\sqrt{j_{H,\text{out}} \times j_0}) \). It allows access to the same intrinsic information on the system as in the high buffer concentration situation, yet taking into account the diffusion properties of the proton as required for the estimation of \( j_{H,\text{out}} \). Because it is partially controlled by proton diffusion toward the solution in the absence of buffer.

**Figure 5.8.** Tafel plots of Co–P₃ films operated in 0.1 M NaClO₄ pH 6 electrolyte with no buffer present as a function of approximate film thickness (in nm) 48 (red ■), 200 (green ▲), 575 (blue ●) at two rotation rates. (a) 2500 rpm. (b) 625 rpm. The slope of the solid lines is \( F/2RT\ln10 \)

**Figure 5.9** (a) Plots of \( j_{H,\text{out}} \times j_0 \) as function of \( 1/\delta \) (using equation 5.1 with \( D = 5 \times 10^{-5} \) cm²/s and \( v = 10^{-2} \) cm²/s) for films of various estimated film thicknesses (in nm) 48 (red ■), 200 (green ▲), 575 (blue ●). (b) Slopes, \( \Sigma \), of the straight lines in (a) as a function of film thickness relative to optimal film thickness (\( \Sigma = D_{H,\text{out}}^0 \sigma_{H^+}^{\text{max}} j_0 \times \delta_f/d_f^{\text{opt}} \)).
diffusion toward the solution, the current response is sensitive to the rotation rate of the electrode. This dependence is reported quantitatively in Figure 5.9a where the variation of \( j_{\text{H, out}} \times j_0 \) with \( 1/\delta \) is displayed and indeed obeys the simple proportionality predicted from the application of equation 5.10 and the definition of \( j_{\text{H, out}} \) in Table 5.1:

\[
j_{\text{H, out}} \times j_0 = \frac{1}{\delta} F D_{\text{H, out}} C_{H^+}^0 j_{0, \text{pH6}}^{\text{max}} \frac{d_f}{d_f^{\text{opt}}} \tag{5.16}
\]

Since the three films examined in Figure 5.9 are much thinner than \( d_f^{\text{opt}} \) (1440 nm), \( d_f \ll d_f^{\text{opt}} \) and \( \tanh(d_f/d_f^{\text{opt}}) \to d_f/d_f^{\text{opt}} \). Therefore equation 5.16 becomes:

\[
j_{\text{H, out}} \times j_0 = \frac{1}{\delta} F D_{\text{H, out}} C_{H^+}^0 j_{0, \text{pH6}}^{\text{max}} \left( \frac{d_f}{d_f^{\text{opt}}} \right) \tag{5.17}
\]

A simple proportionality to film thickness is indeed observed as reported in Figure 5.9b, which plots the slopes of the straight lines in Figure 5.9a against the film thickness under the form of a \( D_{\text{H, out}} f_{0, \text{pH6}}^{\text{max}} d_f/d_f^{\text{opt}} \) vs. \( d_f/d_f^{\text{opt}} \) diagram, the slope of which, \( D_{\text{H, out}} f_{0, \text{pH6}}^{\text{max}} \), may be used to estimate \( D_{\text{H, out}} \) after taking \( f_{0, \text{pH7}}^{\text{max}} = 1.75 \times 10^{-10} \) A/cm\(^2\), equal to \( f_{0, \text{pH7}}^{\text{max}} \) (equation 5.15) by application of equation 5.9b. The value thus obtained for \( D_{\text{H, out}} \), \( 8.5 \times 10^{-5} \) cm\(^2\)/s, is in excellent agreement with literature values (38, 9.3 \( \times \) \( 10^{-5} \) cm\(^2\)/s), showing

**Figure 5.10.** Tafel plots of 200 nm Co–P films operated in 0.1 M NaClO\(_4\) with no buffer present, pH: 6.0 (blue), 6.2 (green), 6.4 (red), 6.6 (yellow), 6.8 (magenta), 7.2 (orange), at two rotation rates. (a) 2500 rpm and (b) 625 rpm. The slopes of the straight lines are F/2RT\(\ln 10\) (1/120 mV).
the excellent consistency of the data obtained with high buffer concentrations on the one hand and those obtained with no buffer at all on the other.

The effect of varying the pH is shown in Figure 5.10. As shown in Section 5.2.2 (equation 5.11), the variation of the Tafel data with pH is predicted to follow the variation of the formal $O_2/H_2O$ potential with pH (equation 5.13), which served as reference for the definition of the overpotential. The results are therefore best represented by plotting $\log j$ as a function of the electrode potential, $E$, rather than vs. $\eta$ leading as expected to a pH-independent plot as indeed seen in Figure 5.10.

5.3.3. Weakly buffered electrolytes (0.3 – 10 mM $Pi$).

The mechanism thus established is further confirmed by the results obtained in weakly buffered solutions, which are displayed in Figure 5.11. The Tafel plots under these conditions are strikingly similar to the predictions displayed in Figure 5.6. Whereas a slope equaling $F/R T \ln 10 (1/60 \text{ mV})$ is observed at low overpotential, a slope of $F/2RT \ln 10$ is observed at high overpotential with a transition that depends both on buffer concentration and rotation rate. From the intercepts of the straight lines possessing slopes of $F/RT \ln 10$.

![Figure 5.11](image-url)

**Figure 5.11.** Tafel plots of a 200 nm Co–Pi films operated in 0 (blue •), 0.3 (green ▲), 0.55 (red □), 1 (yellow ◆), 3 (magenta □), 5.5 (orange ○), 10 (turquoise ▼) mM NaPi pH 6 electrolyte with 0.1 M NaClO₄ as supporting electrolyte at various rotation rate. (a) 2500 rpm. b: 625 rpm data at other rotation rates are given in the SI.3). The slopes of the straight lines are $F/RT \ln 10$ (dashed black) and $F/2RT \ln 10$ and (solid blue).
we obtain $j_0 = 2.7 \times 10^{-11}$ A/cm² in agreement with the data shown in Figure 5.7b and from the intercepts of the lines with a slope of $F/2RT\ln 10$, we obtain $j_{H,\text{out}} \times j_0$ as function of $1/\delta$, thus leading to $D_{H,\text{out}} = 8 \times 10^{-5}$ cm²/s in full agreement with the buffer-free experiments described in the preceding section. Knowing $j_0$ as well as $j_{H,\text{out}}$ at each rotation rate, the whole set of data can be fit at any buffer concentration with a single parameter, $D_{Z,\text{out}}$, through $j_{Z,\text{out}} = FD_{Z,\text{out}}C_2^0/\delta$ according to equation 5.12. This is in line with the fact that the transition between both limiting behaviors is controlled by buffer diffusion in solution.$^{40}$ Fitting, as shown in Figure 5.10 leads to $D_{Z,\text{out}} = 6 \times 10^{-6}$ cm²/s in agreement with literature values of the diffusion coefficient of $\text{HPO}_4^{2-}$ ($7.6 \times 10^{-6}$ cm²/s$^38$). The effect of film thickness was systematically investigated at a low Pᵢ concentration (3 mM) at pH 6 at various rotation rates (Figure 5.12). The data are satisfactorily fit with equation 5.12 using the same diffusion parameters as above, i.e. $D_{H,\text{out}} = 8 \times 10^{-5}$ cm²/s and $D_{Z,\text{out}} = 6 \times 10^{-6}$ cm²/s, as well as the same intrinsic parameter $j_{0,\text{pH}6}^{\text{max}} = 1.75 \times 10^{-10}$ A/cm². This confirms the full consistency of our mechanism.

![Figure 5.12](image-url) **Figure 5.12.** Tafel plots of Co–Pᵢ films operated in 3 mM NaPᵢ pH 6 electrolyte with 0.1 M NaClO₄ as supporting electrolyte with increasing film thicknesses 48 nm (red ■), 200 nm (green ▲), 575 nm (blue ●) at various rotation rates: (a) 2500 rpm. (b) 625 rpm. The solid colored lines correspond to fitting of data.
5.4. Kinetic and thermodynamic parameters of Co–OEC.

One remarkable aspect of our mechanistic analysis is that the data obtained at high buffer concentrations, with no buffer at all and in weakly buffered solutions, are perfectly consistent and in agreement with the same set of kinetic and thermodynamic characteristics. It is worth having a closer look into what can be precisely derived from the experimental data in terms of kinetic and thermodynamic characteristics. The rate constant of the catalytic reaction, $k_{\text{cat}}$, the equivalent diffusion coefficient of proton-electron hopping, $D_{H,e}$ and the standard potential of the catalyst, $E^0_{Q+ZH/PH+Z}$ (or $E^0_{Q+H^+/PH}$) are three unknowns related by two equations deriving from the experimental determination of $D_{H,e}/k_{\text{cat}}$ from $d_f^{\text{opt}}$ (eq. 5.8) and $k_{\text{cat}}C_{\text{cat}} \exp\left[-(F/RT)(E^0_{Q+ZH/PH+Z})\right]$ or $k_{\text{cat}}C_{\text{cat}} \exp\left[-(F/RT)(E^0_{Q+H^+/PH})\right]$ from $j_0^{\text{max}}$ (eq. 5.9). At the present stage, we do not know these three parameters independently from one another. Progress in this direction might require resorting to faster electrochemical techniques in order to detect the proton–electron hopping rate in conditions where catalysis is made negligible. For the time being, knowing the combined parameter $k_{\text{cat}}C_{\text{cat}} \exp\left[-(F/RT)(E^0_{Q+ZH/PH+Z})\right]$ will nevertheless allow benchmarking catalysts of a given reaction similarly to the recently advocated comparison between turnover frequencies at zero overpotential.\textsuperscript{\text{41,42}}

In the present case of a catalytic film whose thickness may be varied, the proton–electron conduction is an additional benchmarking factor, the larger $D_{H,e}/k_{\text{cat}}$, the more globally efficient the catalysis. The optimal thickness, $d_f^{\text{opt}} = \sqrt{D_{H,e}/k_{\text{cat}}}$ can be determined experimentally and preparing a film at this thickness will allow the global benchmarking factor may then be derived from $j_0^{\text{max}}$ as: $F\sqrt{D_{H,e}/k_{\text{cat}}}C_{\text{cat}} \exp\left[-(F/RT)(E^0_{Q+ZH/PH+Z})\right].$

5.5. Conclusions

A methodology has been established to predict the current responses expected in rotating-disk electrode voltammetry for the semi-general catalytic reaction scheme depicted in Figure 5.1. The predictions concern the Tafel plots and their dependence on
buffer concentration (including absence of buffer), film thickness and rotation rate, which are the main operational parameters that can be experimentally varied to uncover the reaction mechanism and determine its kinetic characteristics. To avoid unmanageable complexity, the scheme investigated is not completely general but it can be easily implemented for other reactions and controlling factors along the same principles, thanks particularly to the use of characteristic current densities that stand for each particular rate-governing factor involved. One important outcome of this theoretical analysis, whose pertinence is confirmed experimentally, is that the Tafel plots may have a variety of slopes—\( F/R T \ln 10, F/2R T \ln 10, \text{zero} \)—that not only may be observed along the whole plot but may also coexist within the overpotential range of a single plot. It is also remarkable that Koutecky–Levich plots, relating the inverse of the current density to the inverse of the square root of the rotation rate, are not always linear, making somewhat more cumbersome, albeit still reachable, the separation of the events inside the film from reactant transport in the solution.

Application to water oxidation by films of a cobalt-based oxidic catalyst had a dual purpose. One was to provide an experimental example of the viability of the proposed methodology and of its ability to uncover the reaction mechanism and determine its kinetic characteristics. The second was to actually establish kinetic characteristics of this particular catalyst in action, with a new focus on elucidating the reasons for the previously observed behavior in buffer-free electrolytes and the effect of film thickness on OER activity\(^{22}\) (as also observed in Ni–B\(_i\) catalyst films, Chapter 3). These catalysts are highly promising materials for the oxidation of water in solar–fuels devices such as those required for the resolution of modern energy challenges. Thus understanding the factors that control and limit their activity is important and may serve as a methodological model for future studies.

Some of the features of the oxidic cobalt-based catalyst are remarkable and are worth emphasizing since they may be relevant to other OECs or in other catalytic reactions. One of these is that the current response is controlled jointly by the catalytic reaction and
proton–electron hopping. This mixed control results in an optimal thickness beyond which any increase is at best useless or may even afford rapidly diminishing returns in net catalytic activity.

Intuitively one might expect that the best catalysts would possess a high catalytic rate constant, a high catalyst concentration in the film, a low catalyst standard potential and also a fast proton–electron hopping conduction in the film. However what counts eventually is the value of the combination of all these parameters into a global benchmarking index. The exact expression of the benchmarking index depends on the catalytic electron and proton stoichiometries in the electrochemical rate law. These are reflected in the Tafel slopes and \( \text{H}^+ \) reaction order, respectively. When the stoichiometries are the same a single index can be used. In the opposite case, the comparison should involve the entire Tafel plots with the possibility that the first catalyst is better than the second in a certain range of overpotentials or \( \text{pH} \) and \textit{vice versa} (as shown in Chapter 3). Furthermore, if the catalyst is to be employed in a photoelectrochemical cell, the matching requirements of the targeted semiconductor substrates/assemblies will define the appropriate catalyst to be used (Chapter 4).\(^{43}\)

Deconvolution of the kinetics of the catalytic reaction and of proton–electron hopping conduction is a necessary requirement for a future assessment of the catalytic and conduction mechanisms that may \textit{a priori} involve stepwise or concerted pathways. Examination of kinetic H/D isotope effects should also be useful in this endeavor.

### 5.6. Experimental Section

**Materials.** Co(NO\(_3\))\(_2\).6H\(_2\)O 99.999% (Strem) and NaClO\(_4\) 99.99% metals basis (Aldrich) were used as received. NaH\(_2\)PO\(_4\) 99%, KH\(_2\)PO\(_4\) 99%, NaOH 99%, KOH 88% and KNO\(_3\) 99.0–100.5% were reagent grade and used as received from Macron. All H\(_2\)O electrolyte solutions were prepared with type I water (EMD Millipore, 18.2 MΩ cm resistivity).
**Electrochemical Methods.** All electrochemical experiments were conducted using a CH Instruments 760C or 760D bipotentiostat, a BASi Ag/AgCl reference electrode (soaked in saturated NaCl), and a Pt-mesh counter electrode. Measurements were conducted using a Pine Instruments MSR rotator and a 5 mm diameter Pt-disk rotating electrode (RDE). Electrochemical experiments were performed using a three-electrode electrochemical cell with a porous glass frit separating the working and auxiliary compartments. Experiments were performed at room temperature (24 ± 1 °C) and electrode potentials were converted to the NHE scale using $E_{\text{NHE}} = E_{\text{Ag/AgCl}} + 0.197$ V.

**Film Preparation.** Catalyst films were prepared via controlled-potential electrolysis of 0.1 M potassium phosphate (KP$_i$), pH 7.0 electrolyte solutions containing 0.5 mM Co$^{2+}$. To minimize precipitation of cobalt(II) phosphate, 25 mL of 0.2 M KP$_i$ was added to 25 mL of 1.0 mM Co$^{2+}$ solution. The solutions thus prepared remained clear over the course of all depositions. Depositions were carried out using a 5 mm diameter Pt disk as the working electrode. Deposition by controlled potential electrolysis was carried out on quiescent solutions at 1.047 V without $iR$ compensation. A typical deposition lasted 40 minutes for a 24 mC/cm$^2$ film (~48 nm thick). Following deposition, films were rinsed thoroughly in type I water to remove any adventitious Co$^{2+}$ and P$_i$. Thinner films were deposited under identical conditions but with passage of the desired amount of charge. Evaluation of film thickness was performed from an estimation of the volume occupied by each Co atom as previously described. The amount of mol Co/cm$^2$ was determined from ICP analysis of films digested in 2% nitric acid (Fluka TraceSelect). Film thicknesses of 10, 30, 100, 262 and 637 nm (as shown in Figure 5.7) correspond respectively to 5, 15, 30, 150 and 400 mC/cm$^2$ deposition.

**Potentiostatic Tafel Data Collection in well-buffered P$_i$ electrolyte.** Current–potential data were obtained by controlled potential electrolysis of 0.1 M KP$_i$ electrolyte pH 7.0 at a variety of applied potentials. Prior to film deposition, the solution resistance of
the electrolyte to be used for Tafel data collection was measured using the iR test function. The electrolysis solution was exchanged for Co\textsuperscript{2+}-containing KP\textsubscript{i} electrolyte, without modifying the relative positions of the working and reference electrodes. The film was prepared by controlled-potential electrolysis as described above. Following film preparation, the working electrode was rinsed in water and transferred, without drying, to the same electrolysis bath in which the solution resistance was measured. The electrode was allowed to equilibrate with the electrolysis solution for 5 min while being held at the open circuit potential. The rotation rate was set to 1000 rpm, and steady-state currents were then measured at applied potentials that descended from 1.267 V to 1.097 V in 10 mV steps. For current densities greater than 10 \( \mu \text{A cm}^{-2} \), a steady state was reached at a particular potential in less than 400 sec. For current densities lower than 10 \( \mu \text{A cm}^{-2} \), longer electrolysis times (15–20 minutes) were utilized to ensure that a steady state had been achieved. The solution resistance measured prior to the data collection was used to correct the Tafel plot for ohmic potential losses.

**Tafel data in low \([\text{P}_i]\) electrolyte, pH 6.** A 24 mC/cm\textsuperscript{2} catalyst film was prepared onto a Pt RDE as described above. Following Tafel data acquisition in 0.1 M KP\textsubscript{i} electrolyte, the electrode was rinsed thoroughly with type I water, and steady state current densities were acquired in weakly buffered electrolytes (1.0 M NaClO\textsubscript{4}, pH 6 electrolyte containing \([\text{NaP}_i]\) between 30 mM and 0.1 \( \mu \text{M} \)) with iR compensation (measured prior to film deposition) at rotation rates of 2500, 1600, 1225, 900 and 625 rpm at 20 mV intervals over the desired potential range. When necessary 0.5–5 \( \mu \text{L} \) aliquots of 1 M aqueous NaOH were added periodically to ensure minimal drift in bulk pH (± 0.01) over the course of the experiment. The experiment was repeated twice more using the same catalyst film. Consecutive runs displayed excellent reproducibility. Following operation in P\textsubscript{i}-free electrolyte the electrode was rinsed and data acquisition was repeated in 0.1 M KP\textsubscript{i} electrolyte, as described above.
Background Pt RDE Tafel data. Tafel data were acquired using a Pt RDE in the absence of a catalyst film. The electrode surface was polished to a mirror finish with 0.05 µm alumina, sonicated for 2 minutes, rinsed in 1 M H₂SO₄, and rinsed thoroughly in type I water. Those data were compared to data acquired with a 24 mC/cm² catalyst film (d_f = 48 nm) deposited onto a Pt RDE and operated in 1 M NaClO₄ pH 7.0 electrolyte. Between 1.39 V and 1.2 V the current measured with the catalyst film is one order of magnitude higher than the current measured on Pt in the absence of a catalyst film.

Tafel data in P_i-free electrolyte, pH 6. A 24 mC/cm² catalyst film was prepared onto a Pt RDE as described above. Following Tafel data acquisition in 0.1 M KP_i electrolyte, the electrode was rinsed thoroughly with type I water, and steady state current densities were acquired in P_i-free 1 M NaClO₄ pH 6.0 electrolyte in a manner identical to that described above. Experiments were repeated for films operated in 0.5 M NaClO₄ and 1.0 M KNO₃. Within experimental uncertainty (less than the size of data points), data acquired are identical irrespective of electrolyte concentration or composition. To compare data in an electrolyte, completely lacking dissolved CO₂ and carbonate, O₂ was bubbled through a 1.0 M NaClO₄ solution overnight (>12 hrs) and data were acquired as described previously. Data arising from this measurement were identical to that acquired in 1 M NaClO₄ without bubbling O₂, indicating that dissolved carbonate species do not play a role in proton transfers during O₂ evolution in P_i-free media.

5.7. Appendix: Analysis of the kinetic responses

5.7.1. Proton–electron hopping: equivalent Fick’s law and expressions of the “diffusion coefficient”

The formation of the catalytic species (noted Q) throughout the film can occur through various PCET processes between adjacent sites. Although one might expect that a buffer couple (ZH⁺/Z) present can be part of the process, thus making the transport an electron hopping process with proton release to the buffer, we will not consider this
possibility because transport occurs at very low buffer concentration and even in the absence of buffer. Hence, we only consider proton–electron hopping processes between adjacent sites across the film.

The purpose of this section is to show that proton–electron hopping through the film may be phenomenologically likened to a linear diffusion process obeying Fick’s laws of diffusion and hence, in presence of a catalytic reaction, leads to the following expressions of reaction–diffusion equations:

\[
D_{H,e} \frac{d^2C_{PH}}{dx^2} + k_{cat}C_Q = 0 \quad (A5.1)
\]

\[
D_{H,e} \frac{d^2C_Q}{dx^2} - k_{cat}C_Q = 0 \quad (A5.2)
\]

As shown below, insofar as proton transfer steps are at equilibrium, those reaction-diffusion equations apply whatever the mechanism of proton–electron hopping albeit \(D_{H,e}\) may have different expressions in each case.

The film is divided in successive monolayers (j) and three different cases for proton-electron self-exchange between PH and Q species have to be considered: a concerted proton–electron transfer (CPET) transport (involving the equivalent transfer of a H atom) or a stepwise proton transfer, followed by electron transfer (PTET) or electron transfer, followed by proton transfer (ETPT) transport involving both electron transfer and proton transfer between P, PH, Q, QH species. In all cases, we consider that there is no electric field effect in the film.

5.7.1.1. CPET transport

In the monolayer #j the two members of the PCET redox couple undergo the electron transfer reactions depicted in Scheme A1 with the sites located in # j+1 and # j–1 layers while the catalytic reaction (A → B) transforms Q back into PH. The concentration

![Scheme A5.1](image)
of the substrate A is included in the pseudo-first order catalytic rate constant, $k$, and hence A does not appear explicitly in the reaction schemes above and below. Thus:

$$-\frac{dC_{Q_j}}{dt} = -k_{(j-1)C_{PH}}C_{Q_{j-1}} + k_{(j-1)C_{PH}}C_{Q_{j+1}} + k_{(j+1)C_{PH}}C_{Q_j} - k_{(j+1)C_{PH}}C_{Q_{j+1}} + k_{cat}C_{Q_j}$$

after introduction of the self-exchange rate constant:

$$k_0 = k_{(j-1)} = k_{(j+1)} = k_{-(j+1)}$$

Substitution in the above equations and replacement of the finite difference expression by the corresponding differential expression finally leads to:

$$\frac{\partial C_Q}{\partial t} = D_{c pet} \frac{\partial^2 C_Q}{\partial x^2} - k_{cat}C_Q$$

with $D_{c pet} = k_0C_{cat}(d_r)^2$, $C_{cat}$ being the total concentration of redox sites and $d_r$, the center-to-center distance between the sites.

Similarly:

$$\frac{\partial C_{PH}}{\partial t} = D_{c pet} \frac{\partial^2 C_{PH}}{\partial x^2} + k_{cat}C_Q$$

In the case of the RDEV stationary method, equations A5.1 and A5.2 ensue with:

$$D_{H,e} = D_{c pet} = k_0C_{cat}d_r^2$$

5.7.1.2. PTET transport

In the monolayer # j the four members of the (P/Q) and (PH/QH) couples undergo the PCET reactions depicted below (Scheme A5.2) with the molecules located in # j+1 and # j–1 layers while the catalytic reaction transforms Q back into PH.

Thus:

$$-\frac{dC_{Q_j}}{dt} = -k_{c,(j-1)C_{P}}C_{Q_{j-1}} + k_{c,(j-1)C_{PH}}C_{Q_{j+1}} + k_{H,(j+1)C_{PH}}C_{Q_j} - k_{H,(j-1)C_{QH}}C_{P_{j+1}} + k_{cat}C_{Q_j}$$

The electron transfer and proton transfer reactions in Scheme A5.2 have the same driving force. Hence:

$$k_{c,(j-1)} = k_c, k_{c,(j-1)} = k_c K_{a,QH} K_{a,PH} \text{ and } k_{H,(j+1)} = k_p, k_{H,(j-1)} = k_p K_{a,QH} K_{a,PH} (K_{a,PH}, K_{a,QH} \text{ are the acidity constants of PH and QH respectively})$$

leading to:

$$-\frac{dC_{Q_j}}{dt} = \left[ -k_c K_{a,QH} K_{a,PH} C_{QH_{j-1}} + k_c C_{PH_{j-1}} C_{Q_{j+1}} + k_p C_{PH_{j+1}} C_{Q_j} - k_p K_{a,QH} K_{a,PH} C_{QH_{j+1}} C_{P_{j+1}} \right] + k_{cat}C_{Q_j}$$

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Steady-state approximation on P and QH gives:

\[
\frac{dC_P}{dt} = -k_e \cdot j_{(j-1)} C_P C_{QH_{j-1}} + k_e \cdot j_{(j-1)} C_{PH_{j-1}} C_{Qj} + k_H \cdot j_{(j-1)} C_{PH} C_{Qj_{j-1}} - k_{H, (j-1)} C_{QH_{j-1}} C_P = 0
\]

\[
k_e C_{PH_{j-1}} C_{Qj} + k_p C_{PH} C_{Qj_{j-1}} = k_e \frac{K_{a, PH}}{K_{a, QH}} C_P C_{QH_{j-1}} + k_p \frac{K_{a, PH}}{K_{a, QH}} C_{QH_{j-1}} C_P
\]

leading to

\[
C_P C_{QH_{j-1}} = \frac{K_{a, PH}}{K_{a, QH}} \left( \frac{k_e}{k_e + k_p} C_{Qj} + \frac{k_p}{k_e + k_p} C_{Qj_{j-1}} \right)
\]

\[
\frac{dC_{QH_{j}}}{dt} = -k_e \cdot j_{(j+1)} C_{P_{j+1}} C_{QH_{j+1}} + k_e \cdot j_{(j+1)} C_{PH_{j+1}} C_{Qj_{j+1}} + k_H \cdot j_{(j+1)} C_{PH_{j+1}} C_{Qj} - k_{H, (j+1)} C_{QH_{j+1}} C_{P_{j+1}} = 0
\]

\[
(k_e + k_p) C_{QH_{j}} C_{P_{j+1}} = K_{a, PH} \frac{K_{a, QH}}{k_e C_{PH_{j+1}} C_{Qj_{j+1}} + k_p C_{PH_{j+1}} C_{Qj}}
\]

leading to

\[
C_{QH_{j}} C_{P_{j+1}} = \frac{K_{a, PH}}{K_{a, QH}} \left( \frac{k_e}{k_e + k_p} C_{Qj_{j+1}} + \frac{k_p}{k_e + k_p} C_{Qj} \right)
\]

Thus:

\[
\frac{dC_{Qj}}{dt} = C_{cat} \left[ -k_e \left( \frac{k_e}{k_e + k_p} C_{Qj} + \frac{k_p}{k_e + k_p} C_{Qj_{j-1}} \right) + k_e C_{Qj} + k_p C_{Qj} - k_p \left( \frac{k_e}{k_e + k_p} C_{Qj_{j-1}} + \frac{k_p}{k_e + k_p} C_{Qj} \right) \right] + k_{cat} C_{Qj}
\]

\[
\frac{dC_{Qj_{j+1}}}{dt} = C_{cat} \left[ -k_e \left( \frac{k_e}{k_e + k_p} C_{Qj_{j+1}} - \frac{2k_e k_p}{k_e + k_p} C_{Qj} - \frac{k_e k_p}{k_e + k_p} C_{Qj_{j-1}} \right) + k_e C_{Qj} - k_{cat} \left( \frac{-C_{Qj_{j+1}} - 2C_{Qj} - C_{Qj_{j-1}}}{C_{Qj}^2} \right) \right] + k_{cat} C_{Qj_{j+1}}
\]

Replacement of the finite difference expression by the corresponding differential expression finally leads to:

\[
\frac{\partial C_{Qj}}{\partial t} = D_{pet} \frac{\partial^2 C_{Qj}}{\partial x^2} - k_{cat} C_{Qj}
\]
with $D_{\text{pet}} = \frac{k_p k_r}{(k_c + k_p)} C_{\text{cat}} d_t^2$ and $C_{\text{cat}}$ the total concentration of redox sites and $d_t$, the center-to-center distance between the sites.

Similarly:

$$\frac{\partial C_{\text{PH}}}{\partial t} = D_{\text{pet}} \frac{\partial^2 C_{\text{PH}}}{\partial x^2} + k_{\text{cat}} C_{\text{Q}}$$

In the case of the RDEV stationary method, equations A5.1 and A5.2 ensue with:

$$D_{H,e} = D_{\text{pet}} = \frac{k_p k_r}{(k_c + k_p)} C_{\text{cat}} d_t^2$$

5.7.1.3. ETPT transport

In the monolayer # j the four members of the (P/Q) and (PH/QH) couples undergo the PCET reactions depicted below (scheme A5.3) with the molecules located in # j+1 and # j−1 layers while the catalytic reaction transforms Q back into PH. The situation is symmetrical to the PTET transport, hence we end up with the same relationships and $D_{\text{pet}} = D_{\text{opt}}$

\[\text{Scheme A5.3}\]

5.7.1.4 Comparison between $D_{\text{cpet}}$ and $D_{\text{pet}} = D_{\text{etpt}}$:

$$D_{\text{pet}} = D_{\text{opt}} = \frac{k_p k_r}{(k_c + k_p)} C_{\text{cat}} d_t^2 \text{ and } D_{\text{cpet}} = k_0 C_{\text{cat}} d_t^2$$
Assuming a linear activation–driving force relationship for both electron transfer (linearized Marcus theory) and proton transfer (Bronstêd) with a symmetry factor equal to 0.5 in both cases:

\[ k_e = k_{0e} \exp \left( -\frac{\Delta G^0}{2RT} \right), \quad k_p = k_{0p} \exp \left( -\frac{\Delta G^0}{2RT} \right) \quad \text{with} \quad \exp \left( -\frac{\Delta G^0}{RT} \right) = \frac{K_{a,PH}}{K_{a,QH}} \]

Hence,

\[ D_{pet} = D_{ept} = \frac{k_{0e}k_{0p}}{(k_{0e} + k_{0p})} \left( \frac{K_{a,PH}}{K_{a,QH}} \right) C_{cat} q^2 \]

leading to a comparison between:

\[ k_0 \quad \text{and} \quad \frac{k_{0e}k_{0p}}{(k_{0e} + k_{0p})} \left( \frac{K_{a,PH}}{K_{a,QH}} \right) \]

5.7.2. Derivation of the current density–potential relationships (Here \( I = \) current density)*

As shown in the preceding section, proton–electron hopping through the film (thickness: \( d_f \)) may be likened to a linear diffusional transport obeying Fick’s laws of diffusion. The buffer components, if present and the solvated protons diffuse freely in the pores of the film and in solution. The system can then be expressed by means of the following set of derivative equations and boundary conditions.

**In the film, \( 0 < x < d_f \):**

\[ D_{H,e} \frac{d^2C_{PH}}{dx^2} + k_{cat} C_Q = 0 \]

\[ D_{H,e} \frac{d^2C_Q}{dx^2} - k_{cat} C_Q = 0 \]

with \( k_{cat} = k_{2nd} C_{substr} \), where the concentration of the substrate A, is assumed to be constant as it is the case when the solvent, e.g., water, is the substrate.

* To avoid confusion with the layer number “j”, the current density is denoted as “I” in this appendix.
We assume that diffusion coefficients for \(Z\) and \(ZH^+\) are identical.

\[
D_{Z,\text{in}} \frac{d^2C_Z}{dx^2} - k_{\text{in}}^{\text{in}} C_Z \times C_{H^+} + k_{\text{in}}^{\text{in}} C_{ZH} = 0
\]

\[
D_{Z,\text{in}} \frac{d^2C_{ZH}}{dx^2} + k_{\text{in}}^{\text{in}} C_Z \times C_{H^+} - k_{\text{in}}^{\text{in}} C_{ZH} = 0
\]

\[
D_{H,\text{in}} \frac{d^2C_{H^+}}{dx^2} - k_{\text{in}}^{\text{in}} C_Z \times C_{H^+} + k_{\text{in}}^{\text{in}} C_{ZH} = 0
\]

\(k_{\text{in}}^{\text{in}}\) and \(k_{\text{in}}^{\text{in}}\) are the proton transfer rate constants inside the film.

Thus:

\[
\frac{d^2 (C_Z + C_{ZH})}{dx^2} = 0 \quad \text{throughout the film and:}
\]

\[
D_{H,\text{in}} \frac{d^2C_{H^+}}{dx^2} + D_{Z,\text{in}} \frac{d^2C_{ZH}}{dx^2} = 0
\]

**In the solution, \(d_f < x < \delta\):**

\(c_{\text{pH}} = 0, \quad c_Q = 0\) \hspace{1cm} (A5.3)

\[
D_{Z,\text{out}} \frac{d^2C_Z}{dx^2} - k_{\text{out}}^{\text{out}} C_Z \times C_{H^+} + k_{\text{out}}^{\text{out}} C_{ZH} = 0
\]

\[
D_{Z,\text{out}} \frac{d^2C_{ZH}}{dx^2} + k_{\text{out}}^{\text{out}} C_Z \times C_{H^+} - k_{\text{out}}^{\text{out}} C_{ZH} = 0
\]

\[
D_{H,\text{out}} \frac{d^2C_{H^+}}{dx^2} - k_{\text{out}}^{\text{out}} C_Z \times C_{H^+} + k_{\text{out}}^{\text{out}} C_{ZH} = 0
\]

\(k_{\text{in}}^{\text{out}}\) and \(k_{\text{in}}^{\text{out}}\) are the proton transfer rate constants in the solution.

Thus:

\[
\frac{d^2 (C_Z + C_{ZH})}{dx^2} = 0 \quad \text{and:}
\]

\[
D_{H,\text{out}} \frac{d^2C_{H^+}}{dx^2} + D_{Z,\text{out}} \frac{d^2C_{ZH}}{dx^2} = 0
\]

**At the diffusion layer–solution interface, \(x = \delta\):**

\[
(C_{H^+})_{x=\delta} = C_{H^+}^0, \quad (C_Z)_{x=\delta} = C_Z^0, \quad (C_{ZH})_{x=\delta} = C_{ZH}^0
\]

**At the film–diffusion layer interface, \(x = d_f\):**
\[
\frac{dC_Q}{dx}_{x=d_f} = \frac{dC_{PH}}{dx}_{x=d_f} = 0 \quad (4S)
\]

Conservation of fluxes across the interface for the buffer components, if present, and for the solvated proton in any case:

\[
D_{H, in} \left( \frac{dC_{H^+}}{dx} \right)_{x=d_{f-}} = D_{H, out} \left( \frac{dC_{H^+}}{dx} \right)_{x=d_{f+}} , \quad D_{Z, in} \left( \frac{dC_Z}{dx} \right)_{x=d_{f-}} = D_{Z, out} \left( \frac{dC_Z}{dx} \right)_{x=d_{f+}} ,
\]

\[
D_{Z, in} \left( \frac{dC_{ZH}}{dx} \right)_{x=d_{f-}} = D_{Z, out} \left( \frac{dC_{ZH}}{dx} \right)_{x=d_{f+}}
\]

Note that we do not consider penetration of the buffer components and solvated proton as a possible rate-determining step. It can be done when necessary by adaptation of the present model with the help of previous analyses.[31]

We further assume that the partition coefficients of \(H^+, ZH^+\) and \(Z\) between the solution in the pores and the solution outside the film are approximately equal to unity. Thus:

\[
(C_Z)_{x=d_{f-}} = (C_Z)_{x=d_{f+}} , \quad (C_{ZH})_{x=d_{f-}} = (C_{ZH})_{x=d_{f+}} , \quad (C_{H^+})_{x=d_{f-}} = (C_{H^+})_{x=d_{f+}}
\]

**At the electrode surface, \(x = 0\):**

One may consider several ways to oxidize the catalyst \(PH\).

**CPET with water and/or buffer base as proton acceptor**

\[
\left( \frac{C_Q}{C_{PH}} \right)_{x=0} \times \left( \frac{C_{ZH}}{C_Z} \right)_{x=0} = \exp \left[ \frac{F}{RT} \left( E - E_0^{Q+ZH/PH+Z} \right) \right] \quad (A5.5a)
\]

and

\[
\left( \frac{C_Q}{C_{PH}} \right)_{x=0} \times \left( \frac{C_{H^+}}{C^0} \right)_{x=0} = \exp \left[ \frac{F}{RT} \left( E - E_0^{Q+H^+/PH} \right) \right] \quad (A5.5b)
\]

\((E\) is the electrode potential\)

Since the electrode reactions and proton transfer reactions are at equilibrium, the two Nernst equations are equivalent:

\[
E_{Q+ZH/PH+Z}^0 = E_{Q+H^+/PH}^0 + \frac{RT}{F} \ln \left( \frac{K_a}{C^0} \right);
\]

with:

\[
\left( \frac{C_{H^+}}{C_{ZH}} \right)_{x=0} \left( \frac{C_Z}{C^0} \right)_{x=0} = K_a \quad (A5.6)
\]

The Nernst equations may also be expressed as a function of the overpotential, \(\eta\), with:

\[
= E - E_A^{eq} \quad \text{where} \quad E_A^{eq} \quad \text{is the equilibrium potential of the reaction to be catalyzed}
\]
The buffer, when present, serves to neutralize the protons generated by the CPET electrode reaction and to convert, at least partially, its diffusion toward the solution into a \(\text{ZH}^+\) diffusion toward the solution and a diffusion of \(Z\) toward the electrode and, additionally, to participate as reactants to the CPET electrode reaction. Hence,

\[
\frac{(C_Q)_{x=0} \times (C_{ZH})_{x=0}}{(C_{PH})_{x=0} \times (C_Z)_{x=0}} = \exp\left(\frac{F \eta}{RT}\right) \exp\left[\frac{F}{RT} \left(\frac{E_{eq}^0}{E_{A} - E_{Q+ZH/PH+Z}}\right)\right]
\]  

(A5.7a)

\[
\frac{(C_Q)_{x=0} \times (C_{H^+})_{x=0}}{(C_{PH})_{x=0} \times C^0} = \exp\left(\frac{F \eta}{RT}\right) \exp\left[\frac{F}{RT} \left(\frac{E_{eq}^0}{E_{A} - E_{Q+H^+/PH}}\right)\right]
\]  

(A5.7b)

If both reactions take place at the electrode, the current density, \(I\), is:

\[
I = D_{H,e} \left(\frac{dC_{PH}}{dx}\right)_{x=0} = -D_{H,e} \left(\frac{dC_Q}{dx}\right)_{x=0} = -D_{H,in} \left(\frac{dC_{H^+}}{dx}\right)_{x=0} - D_{Z,in} \left(\frac{dC_{ZH}}{dx}\right)_{x=0}
\]  

(A5.8)

**PTET (deprotonation of PH followed by oxidation of P):**

Fast electron transfer leads to

\[
\frac{(C_Q)_{x=0}}{(C_P)_{x=0}} = \exp\left[\frac{F}{RT} \left(E - E_{Q/P}^0\right)\right]
\]

where \(E_{Q/P}^0\) is the standard potential of the \(Q/P\) redox couple.

The buffer, if present, serves to neutralize the protons generated by the electrode reaction and to convert, at least partially, its diffusion toward the solution into a diffusion of \(\text{ZH}^+\) toward the solution and a diffusion of \(Z\) toward the electrode. In these conditions,

\[
D_{Z,in} \left(\frac{dC_Z}{dx}\right)_{x=0} = -D_{Z,in} \left(\frac{dC_{ZH}}{dx}\right)_{x=0}
\]

Since proton transfer is assumed to be at equilibrium:

\[
K = \frac{(C_P)_{x=0} \times (C_{ZH})_{x=0}}{(C_{PH})_{x=0} \times (C_Z)_{x=0}} \quad \text{and} \quad K' = \frac{(C_P)_{x=0} \times (C_{H^+})_{x=0}}{(C_{PH})_{x=0} \times C^0}
\]

leading to the same expressions for the Nernst equations as in the CPET case, i.e., equations (A5.5a), (A5.5b), (A5.7a), (A5.7b).

The current density, \(I = j\) is given by:

\[
\frac{I}{F} = -D_{H,e} \left(\frac{dC_Q}{dx}\right)_{x=0}
\]
We can consider that P only exists in a very thin layer close to the electrode; within this thin layer, we can write at steady state:

\[
\frac{dC_P}{dt} = \frac{1}{F} \left( k_+ (C_Z)_{x=0} + k'_+ (C_{PH})_{x=0} - \left( k_- (C_{ZH})_{x=0} + k'_- (C_{H^+})_{x=0} \right) \right) (C_P)_{x=0} = 0
\]

\[
\frac{dC_{ZH}}{dt} = D_{Z, in} \left( \frac{dC_{ZH}}{dx} \right)_{x=0} + k_+ (C_{PH})_{x=0} (C_Z)_{x=0} - k_- (C_P)_{x=0} (C_{ZH})_{x=0} = 0
\]

\[
\frac{dC_{H^+}}{dt} = D_{H, in} \left( \frac{dC_{H^+}}{dx} \right)_{x=0} + k'_+ (C_{PH})_{x=0} - k'_- (C_P)_{x=0} (C_{H^+})_{x=0} = 0
\]

leading to:

\[
\frac{I}{F} = -D_{H, in} \left( \frac{dC_{H^+}}{dx} \right)_{x=0} - D_{Z, in} \left( \frac{dC_{ZH}}{dx} \right)_{x=0}
\]

We thus obtain the same set of equations as in the CPET case.

**ETPT (oxidation of PH followed by deprotonation of QH):**

Fast electron transfer leads to:

\[
\frac{(C_{QH})_{x=0}}{(C_{PH})_{x=0}} = \exp \left[ \frac{F}{RT} \left( E - E_{QH/PH}^0 \right) \right]
\]

where \( E_{QH/PH}^0 \) is the standard potential of the QH/PH redox couple.

The buffer, if present, serves to neutralize the protons generated by the electrode reaction and to convert, at least partially, its diffusion toward the solution into a diffusion of \( ZH^+ \) toward the solution and a diffusion of \( Z \) toward the electrode. Under these conditions,

\[
D_{Z, in} \left( \frac{dC_Z}{dx} \right)_{x=0} = -D_{Z, in} \left( \frac{dC_{ZH}}{dx} \right)_{x=0}
\]

Since proton transfer is assumed to be at equilibrium:

\[
K = \frac{(C_Q)_{x=0} \times (C_{ZH})_{x=0}}{(C_{QH})_{x=0} \times (C_Z)_{x=0}} \text{ and } K' = \frac{(C_Q)_{x=0} \times (C_{H^+})_{x=0}}{(C_{QH})_{x=0} \times C^0}
\]

leading to the same expressions for the Nernst equations as in the CPET case, i.e., equations (A5.5a), (A5.5b), (A5.7a), (A5.7b).

The current density, \( I \) is given by:

\[
\frac{I}{F} = D_{H, e} \left( \frac{dC_{PH}}{dx} \right)_{x=0}
\]

We can consider that QH only exists in a very thin layer close to the electrode; within this thin layer, we can write at steady state:

\[
\frac{dC_{QH}}{dt} = \frac{1}{F} \left[ k_+ (C_Z)_{x=0} + k'_+ \right] (C_{QH})_{x=0} + \left[ k_- (C_{ZH})_{x=0} + k'_- (C_{H^+})_{x=0} \right] (C_Q)_{x=0} = 0
\]
$$\frac{dC_{ZH}}{dt} = D_{Z,\text{in}} \left( \frac{dC_{ZH}}{dx} \right)_{x=0} + k_+ (C_{QH})_{x=0} (C_Z)_{x=0} - k_- (C_Q)_{x=0} (C_{ZH})_{x=0} = 0$$

$$\frac{dC^+}{dt} = D_{H,\text{in}} \left( \frac{dC^+}{dx} \right)_{x=0} + k'_+ (C_{QH})_{x=0} - k'_- (C_Q)_{x=0} (C^+_{H})_{x=0} = 0$$

leading to:

$$\frac{I}{F} = -D_{H,\text{in}} \left( \frac{dC^+}{dx} \right)_{x=0} - D_{Z,\text{in}} \left( \frac{dC_{ZH}}{dx} \right)_{x=0}$$

Moreover, the net flux of Q from the electrode surface is:

$$-D_{H,e} \left( \frac{dC_Q}{dx} \right)_{x=0} = \left[ k_+ (C_Z)_{x=0} + k'_+ (C_{QH})_{x=0} \right] (C_Q)_{x=0} - \left[ k_- (C_{ZH})_{x=0} + k'_- (C^+_{H})_{x=0} \right] (C_Q)_{x=0}$$

Hence: $$\frac{I}{F} = -D_{H,e} \left( \frac{dC_Q}{dx} \right)_{x=0}$$

We thus obtain the same set of equations as in the CPET case.

**Resolution**

From what precedes, the resolution of the above set of derivatives equations and boundary conditions is the same for all three pathways of the PCET reaction, CPET, PTET and ETPT.

In the film and in the solution:

$$\frac{d^2 (C_Z + C_{ZH})}{dx^2} = 0$$

It follows, taking into account the boundary conditions, that:

$$(C_Z)_{x=0} + (C_{ZH})_{x=0} = (C_Z)_{x=d_{f,\text{in}}} + (C_{ZH})_{x=d_{f,\text{in}}} = (C_Z)_{x=d_{f,\text{in}}} + (C_{ZH})_{x=d_{f,\text{in}}} = C_{Z}^0 + C_{ZH} \quad (A5.9)$$

In addition:

$$D_{H,\text{in}} \left( \frac{dC^+}{dx} \right)_{x=0} + D_{Z,\text{in}} \left( \frac{dC_{ZH}}{dx} \right)_{x=0} = -\frac{I}{F}$$

Hence:

$$\frac{I}{F} = \left( \frac{D_{H,\text{in}} C^+ + D_{Z,\text{in}} C_{ZH}}{d_f} \right)_{x=d_{f,\text{in}}} - \left( \frac{D_{H,\text{in}} C^+ + D_{Z,\text{in}} C_{ZH}}{d_f} \right)_{x=0}$$

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Leading to:
\[
\left( C_{H^+} + \frac{D_{Z,\text{out}}}{D_{H,\text{out}}} C_{ZH} \right)_{x=\delta} - \left( C_{H^+} + \frac{D_{Z,\text{in}}}{D_{H,\text{in}}} C_{ZH} \right)_{x=0} = \frac{I_f}{D_{H,\text{in}}} \left( C_{H^+} + \frac{D_{Z,\text{in}}}{D_{H,\text{in}}} C_{ZH} \right)_{x=0} + \frac{I_H}{D_{H,\text{in}}} \left( C_{H^+} + \frac{D_{Z,\text{in}}}{D_{H,\text{in}}} C_{ZH} \right)_{x=0}
\]

It may be assumed that: \( \frac{D_{Z,\text{in}}}{D_{H,\text{in}}} \approx \frac{D_{Z,\text{out}}}{D_{H,\text{out}}} \). Thus:
\[
\left( C_{H^+} \right)_{x=0} + \frac{D_{Z,\text{in}}}{D_{H,\text{in}}} (C_{ZH})_{x=0} = \frac{I_f}{D_{H,\text{out}}} \left( D_{H,\text{out}} \left( \frac{d_f}{D_{H,\text{in}}} + \delta \right) \right) - \left( C_{H^+} \right)_{x=0} + \frac{D_{Z,\text{out}}}{D_{H,\text{out}}} C_{ZH}
\]

Since \( \frac{D_{H,\text{out}}}{D_{H,\text{in}}} d_f \ll \delta \):
\[
\left( C_{H^+} \right)_{x=0} + \frac{D_{Z,\text{in}}}{D_{H,\text{in}}} (C_{ZH})_{x=0} = \frac{I_f}{D_{H,\text{out}}} \left( \frac{d_f}{D_{H,\text{in}}} + \delta \right) - \left( C_{H^+} \right)_{x=0} + \frac{D_{Z,\text{out}}}{D_{H,\text{out}}} C_{ZH}
\]

It follows that:
\[
(C_{ZH})_{x=0} = C_{ZH}^0 + \frac{D_{H,\text{out}}}{D_{Z,\text{out}}} \left( \frac{I_f}{D_{H,\text{out}}} \right) \left( -\left( C_{H^+} \right)_{x=0} \right)
\]

Application of equation (A5.6) thus leads to the following second order equation for \( (C_{H^+})_{x=0} \):
\[
\left( (C_{H^+})_{x=0} \right)^2 + \left( (C_{H^+})_{x=0} \right) \frac{D_{Z,\text{out}}}{D_{H,\text{out}}} C_{ZH}^0 - \frac{I_f}{D_{H,\text{out}}} C_{H^+}^0 - \frac{K_a}{1 - \frac{I_f}{I_{Z,\text{out}}} \frac{C_{ZH}^0}{C_{Z}^0}} \left( C_{H^+}^0 \right) \left( \frac{1}{I_{Z,\text{out}}} \frac{C_{ZH}^0}{C_{Z}^0} \right) = 0
\]

In most practical cases, \( K_a \) is small and the pH is close to the pK\(_a\) of ZH\(^+\), leading to:
\[
\left( (C_{H^+})_{x=0} \right)^2 + \left( (C_{H^+})_{x=0} \right) C_{H^+}^0 \left( \frac{I_{Z,\text{out}}}{I_{H,\text{out}}} \left( 1 - \frac{I_{Z,\text{out}}}{I_{H,\text{out}}} \right) \right) \left( C_{H^+}^0 \right) \left( \frac{1}{I_{Z,\text{out}}} \frac{C_{ZH}^0}{C_{Z}^0} \right) = 0
\]

Thus:
\[
\left( \frac{C_{H^+}}{C_{H^+}^0} \right)_{x=0} = \frac{1}{1 - \frac{I_{Z,\text{out}}}{I_{H,\text{out}}} \left( 1 - \frac{I_{Z,\text{out}}}{I_{H,\text{out}}} \right)} \left( \frac{1}{I_{Z,\text{out}}} \frac{C_{ZH}^0}{C_{Z}^0} \right) = 0
\]

Moreover, integration of (A5.2) taking into account (A5.4) and (A5.8) and the fact taking into account that \( (C_{PH})_{x=0} = C_{cat} \)  at the foot of the current-potential response leads to:
\[
\left(\frac{C_Q}{k}\right)_{k=0} = \frac{1}{\sqrt{k_{\text{cat}}}} \frac{1}{\tanh \left( \frac{k_{\text{cat}}}{I_{H,e}} \right)}
\]

(A5.11)

with \( I_k = F_k \text{cat} d_f \), \( I_{H,e} = \frac{FC_{\text{cat}}D_{H,e}}{d_f} \)

Combination of equations (A5.10) and (A5.11) with the Nernst law expressed by equation (A5.7a) leads to an implicit expression of the Tafel plot that is valid for any buffer concentration.

\[
\frac{F}{RT \ln 10} \eta = \log \left( \frac{1}{I_0} \right) + \log \left[ \frac{1 - \frac{1}{I_{Z,\text{out}}}}{I_{H,\text{out}}} \right] + \frac{1}{2} \left( 1 - \frac{I_{Z,\text{out}}}{I_{H,\text{out}}} \right) + 4 \left( \frac{1}{I_{Z,\text{out}}} \right) \left( \frac{C_{ZH}^0}{C_Z^0} \right) \left( \frac{C_{ZH}^0}{I_{H,\text{out}}} \right)
\]

(A5.13)

after introduction of the exchange current density, \( I_0 \):

\[
I_0 = \left( \frac{C_{H^+}^0}{C_{H^+}} \right) \sqrt{k_{\text{cat}}} \frac{1}{I_{H,e}} \tanh \left( \frac{k_{\text{cat}}}{I_{H,e}} \right) \exp \left( \frac{F \left( E_{A^\text{eq}} - E_{Q+H^+/PH} \right)}{RT} \right)
\]

(A5.14)

(equations 5.7a and 5.7b in Section 5.2.1, where \( I = j \) and \( I_0 = j_0 \)).

As shown below, the two limiting cases that we have treated in the previous sections corresponding to perfect buffering throughout the film and the solution on the one hand (Sections 5.2.1 and 5.3.1) and to the total absence of buffer on the other (5.2.2 and 5.3.2) can be derived from equations (A5.13) and (A5.14), as follows.

**High buffer concentration:**

Then \( I_{Z,\text{out}} \) is large and \( \frac{1}{I_{Z,\text{out}}} \ll 1 \) and therefore the Tafel plot is simply expressed by:

\[
\log I = \log I_0 + \frac{F}{RT \ln 10} \eta
\]

(equation 5.6)

with the same expression of the exchange current (equation A5.14), corresponding to equations 5.7a and 5.7b.
It should be noted that this limiting Tafel plot behavior is reached for high buffer concentrations but also, at a given buffer concentration (and therefore a given value of $I_{Z,\text{out}}$), upon decreasing the overpotential, which entails a decrease of the current density and consequently of $1/I_{Z,\text{out}}$.

**Buffer-free solution:**

The expression of the proton concentration at the electrode is:

$$
\left( C_{H^+} \right)_{x=0} = \frac{1}{FD_{H,\text{out}}} \left( \frac{D_{H,\text{out}}}{D_{H,\text{in}}} d_f + \delta \right) + C_{H^+}^0
$$

i.e. $\frac{\left( C_{H^+} \right)_{x=0}}{C_{H^+}^0} = 1 + \frac{1}{I_{H,\text{in}}} \left( \frac{1}{I_{H,\text{out}}} + \frac{1}{I_{H,\text{out}}} \right)$ with $I_{H,\text{out}} = \frac{FD_{H,\text{out}} C_{H^+}^0}{\delta}$ and $I_{H,\text{in}} = \frac{FD_{H,\text{in}} C_{H^+}^0}{d_f}$.

We have $\frac{1}{I_{Z,\text{out}}} \gg 1$, and from equation (A5.13):

$$
\frac{F}{RT \ln 10} \eta \rightarrow \log \frac{I}{I_0} + \log \left[ \frac{I_{Z,\text{out}}}{I_{H,\text{out}}} \frac{I}{I_{Z,\text{out}}} \right], \text{i.e.}
$$

$$
\log I = \frac{1}{2} \left( \log I_0 + \log I_{H,\text{out}} \right) + \frac{F}{2RT \ln 10} \eta \text{ (equation 5.11)}
$$

### 5.8 References


(32) It may alternatively be expressed in terms of $E_{Q+ZH/PH+Z}^0$ by application of equation (5.4):

$$
\log j_0 = \log \left[ \frac{C_Z^0}{C_{ZH}^0} \sqrt{j_k j_{H,e}} \tanh \left( \frac{j_k}{j_{H,e}} \right) \right] + \frac{F(E_A^{eq} - E_{Q+ZH/PH+Z}^0)}{RT \ln 10}
$$

$$
= \log \left[ F \frac{C_Z^0}{C_{ZH}^0} C_{cat} k_{cat} d_{f}^{opt} \tanh \left( \frac{d_f}{d_{f}^{opt}} \right) \right] + \frac{F(E_A^{eq} - E_{Q+ZH/PH+Z}^0)}{RT \ln 10} \quad (5.7b)
$$
or, alternatively by:

\[ j_0^{\text{max}} = F \frac{c_0}{c_{ZH}} C_{cat} k_{cat} \sqrt{k_{cat} D_{H,e}} \exp \left( \frac{F(E_A^{eq} - E_0^{eq} + z + z)}{RT} \right) \]

\[ = F \frac{c_0}{c_{ZH}^{eq}} C_{cat} k_{cat} a_f^{eq} \exp \left( \frac{F(E_A^{eq} - E_0^{eq} + z + z)}{RT} \right) \] \hspace{1cm} (5.9b)

For details on the notion of “pure kinetic conditions” see reference 13, p. 82.


Above pH = 7, OH\(^{-}\) ions appear to start to interfere as an additional CPET proton acceptors. The reactions that have OH\(^{-}\) and other species as proton acceptor require further investigation.

A similar behavior is observed with Ni–B, films in unbuffered pH 8.5 electrolyte as described in Chapter 3 (see Bediako, D. K.; Surendranath, Y.; Nocera, D. G. *J. Am. Chem. Soc.* 2013, *135*, 3662) where the slopes of the Koutecký-Levich plots change suggesting that in the latter case the limiting factor is diffusion of OH\(^{-}\), which is the acting base in the PCET processes. This ultimately leads to current density plateaus (Chapter 3, Figure 3.10).


Chapter 6 — Intermediate-Range Structure and Redox Conductivity of Co–P\textsubscript{i} and Co–B\textsubscript{i} Oxygen Evolution Catalysts

Portions of this chapter have been published:

6.1 Introduction

In the preceding chapter we discussed how charge transport through these films occurs by proton–electron hopping down a gradient in electrochemical potential. Conceivably, the rate of this “diffusive” hopping process may be influenced by the nanoscale structure of the material. In this chapter we highlight studies to interrogate the structure of two cobalt-based catalyst films that are prepared by electrodeposition from aqueous phosphate- or borate-buffered Co(II) solutions (Co–P_i and Co–B_i, respectively). Extended X-ray absorption fine structure (EXAFS) investigations\(^1\)\(^-\)\(^3\) of these cobalt oxygen evolution catalyst (Co–OEC) films establish that they are composed of edge-sharing CoO\(_6\) clusters of molecular dimensions.

Recently an X-ray scattering and PDF analysis study\(^4\) confirmed the previous EXAFS results for Co–P_i films. Whereas EXAFS provides key insight into the local order in these films, atomic pair distribution function (PDF) has the added benefit that it affords a direct probe that is also sensitive to intermediate-range structure on the nanoscale.\(^5\)\(^,\)\(^6\) Nanoscale structure is a crucial determinant of the electronic structure of a variety of functional materials. In the case of the self-assembled OER catalysts, intermediate-range order in these porous thin films is also anticipated to be critical to charge/mass transport between active sites and hence overall catalytic activity. Indeed, changes in microstructure of thin films and electronic structure would be expected to impact the activity and performance of any OER anode. The kinetics of Co–P_i nucleation and film deposition indicates that the electrolyte plays a pivotal role in modulating catalyst self-assembly.\(^7\) We surmised that the identity of the electrolyte could impact the structure of Co–OEC, and in the future permit the tuning of catalytic activity. To this end, the self-assembled Co–P/B_i films offer a unique platform to explore nanoscale structure–activity relationships of OER catalysts at length scales beyond the molecular dimension.
We couple these structural studies to electrochemical results that show a divergence in activity of Co–P_i and Co–B_i as the film thickness is increased. Using the concepts developed in Chapter 5, we resolve this disparity in activity in terms of the rates of proton-electron hopping diffusion. We also use redox trans-conductance measurements to directly probe the bulk conductivity of these materials.

6.2 Results

6.2.1 Catalyst Preparation, X-ray total scattering and PDF analysis

Catalyst films were electrodeposited onto FTO plates (Hartford Glass) by controlled-potential electrolysis of Co^{2+}_{(aq)} solutions containing P_i or B_i at pH 7.0, and 9.2, respectively. Following electrodeposition, films were rinsed, dried in air, and catalyst material was removed from the substrate surface. Nanoparticulate (50 nm) Co_3O_4 was used as received (Sigma-Aldrich) and CoO(OH) was prepared according to an established procedure.\(^8\) Samples were packed into polyimide capillary tubes for x-ray analysis. X-ray analysis was performed at the X7B beamline at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. Diffraction data were collected using the rapid acquisition pair distribution function (RaPDF) technique,\(^9\) utilizing a 2D X-ray detector.

All raw 2D data images were azimuthally integrated and converted to intensity versus 2\(\theta\) using the software Fit2D,\(^{10}\) where the 2\(\theta\) is the angle between the incident and scattered X-rays. The data were corrected using PDFget\(\chi\)3,\(^{11}\) a home-written data analysis program, to obtain the total scattering structure function, \(S(Q)\), where Q is the magnitude of the scattering vector (as defined in Section 6.5) and the PDF, \(G(r)\). Plots of Q(S(Q)–1) for all samples are shown in Figure 6.1a and \(G(r)\) plots for Co–P_i and Co–B_i are shown in Figure 6.1b. PDFs of all samples are presented in Figure 6.1c.
Unlike the crystalline analogs, which exhibit sharp Bragg peaks in the diffraction pattern (Figure 6.1a) and possess PDFs that extend to high-r (Figure 6.1c), the catalyst samples exhibit only diffuse scattering due to finite size effects (Figure 6.1a). However, PDFs of Co–P₁ and Co–B₁ display sharp peaks in real-space (Figure 6.1b) indicating a well-defined local order (i.e., they are not glassy). The peaks diminish with increasing r signifying that the samples are nanocrystalline with domain sizes between 15 and 30 Å. It is also evident from Figure 6.1b that Co–B₁ possesses more structural coherence than Co–P₁, since there is a wider range of r for the former over which structural correlations persist. In addition, the peaks in Co–P₁ at higher r appear slightly broader than those in Co–B₁.

**Figure 6.1.** (a) Structure functions and PDFs (b, c) for Co₃O₄ (green), CoOOH (gray), Co–B₁ (blue) and Co–P₁ (red). In (b) PDFs of Co–B₁ and Co–P₁ are compared and the difference curve is shown by the lower purple trace (offset for clarity). PDFs have been truncated around r = 20 Å to highlight the differences.
suggesting that there is greater disorder in Co–P₁. Whereas Du and co-workers have observed extra features in their PDF data that was attributed to CoO cube defects and distortions to the terminal Co–O positions⁴ we do not observe any evidence for such features. The fact that our samples are catalytically active without the presence of the defect features suggests that they are not essential for the activity, though additional studies are required to resolve this issue.

Two crystalline structural analogs, Co₃O₄ and CoOOH, were also measured for structural comparison to the Co–P₁/B₁ samples. Their PDFs were truncated to simulate

![Figure 6.2](image)

**Figure 6.2.** Comparison between Co–OECs—blue: Co–B₁ (a and c), red: Co–P₁ (b and d)—and truncated PDFs of Co oxide model compounds—green: Co₃O₄ (a and b), grey: CoOOH (c and d). The model compound signals were scaled and truncated with a spherical characteristic function to simulate nanoparticle effects. The purple lines (—) represent the difference curves (offset for clarity) between the PDF of each model compound and that of the specified Co–OEC.
nanoparticle effects and compared to the PDFs of Co–P₁ and Co–B₁ (Figure 6.2). In general, there is poorer agreement of Co–Pᵢ/Bᵢ to Co₃O₄ (Figures 6.1a and 6.1b) as compared to CoOOH (Figures 6.1c and 6.1d), indicating that the Co–Pᵢ/Bᵢ samples are of the cobaltate structure, in agreement with previous EXAFS and PDF structural studies. However, there is significantly poorer agreement between CoOOH and the Co–Pᵢ/Bᵢ at high r compared to low r, representing some difference in intermediate range structure. For example, a significant discrepancy in peak position between CoOOH and either Co–P₁ and Co–B₁ is found in the doublet between 4 and 5 Å.

The CoOOH structure consists of aligned layers of edge-shared CoO₆ octahedra with hydrogen atoms in the interlayer region. The first peak in the doublet arises from the nearest-neighbor interlayer Co–Co distance in the CoOOH structure, and the second peak is from the nearest-neighbor intralayer Co–Co distance. Since the largest discrepancy is in the position of first peak of the doublet, this indicates that Co–P₁ and Co–B₁ have the CoOOH structure, but with diminished coherence in the stacking direction due to turbostratic disorder between stacked layers, or because the clusters are not coherently stacked at all.

Preliminary modeling was performed using the PDFGUI software, with the model PDFs attenuated by the characteristic function for a sphere. Modeling was performed according to standard procedures using the maximum number of parameters allowed by the space groups of the model structures. In agreement with our initial observations, the CoOOH model performed better by a considerable margin than Co₃O₄ (Figures 6.3a and 6.3b) as evidenced by the greatly improved goodness-of-fit parameter, Rw. Both models refined with large cobalt atomic displacement parameters (ADPs) along the c-axis of the cell, providing evidence for turbostratic disorder among the stacked layers.
More advanced modeling was performed using atomistic nanoparticle models created from the CoOOH structure. These models were fit using the recently developed SRREAL and SRFIT programs. Models were created for refinement using a nanoparticle template approach; a geometric shape is used to excise a nanoparticulate model from a crystal structure. This allows us to vary not only the crystal structure, but also the dimensions of the nanoparticle by varying the template. It also allows us to decorate the model with additional scatterers and to distort the model. This was not done here, but will

Figure 6.3. Preliminary model fits to (a) Co–B (blue) and (b) Co–P (red) data using the (top) CoOOH (gray) model and (bottom) Co₃O₄ (green) model. The difference is the purple line offset below. Goodness-of-fit, R_w, parameters equal (a) top: 0.307; bottom: 0.515 and (b) top: 0.336; bottom: 0.403.
be explored in future modeling efforts. The nanoparticle models for Co–Bi and Co–Pi were created using a cylindrical template. The template was allowed variable dimensions and location, with the axis of the cylinder aligned with the c-axis of the CoOOH structure. For simplicity, hydrogen atoms were excluded from the models. Since circular cuts were made in the hexagonal layers, the resulting structures that were used for modeling did not necessarily have fully coordinated Co ions at the perimeter.

The refined PDF fits and models for Co–Bi and Co–Pi catalysts are shown in Figures 6.4 and 6.5, and some structural parameters are tabulated in Table 6.1. The Co–Bi model has three layers on average, and the diameter of the layers is approximately 35 Å. We attempted to constrain the model to a single layer, but this results in a poorer fit (Figure 6.6) suggesting that the coherent domains of Co–Bi do indeed consist of multiple layers of clusters with weak, but significant interlayer correlations. Compared to the crystalline CoOOH compound, the c–axis is significantly larger (Table 6.1), which indicates an expansion of the layers, perhaps to accommodate something larger than protons in the

**Figure 6.4.** (a) Cylindrical atomistic model fit (black lines) to the Co–Bi catalyst PDF data (blue circles). The difference curve is shown in purple, and is offset for clarity. (b) View of the refined model for the average coherent domain in Co–Bi films.
interlayer region such as weakly scattering or disordered electrolyte ions, though these were not identified. The refined Co–P\textsubscript{i} model and fit (Figure 6.5) indicate that the diameter of the clusters is approximately 14 Å, considerably smaller than those of Co–B\textsubscript{i}. This model was given the flexibility to form layers, but did not. This suggests that unlike Co–B\textsubscript{i}, the coherent domains of the catalyst consist of single-layer clusters like those shown in Figure 6.5b whose arrangements are significantly disordered in the film.

The dependence of structure on deposition potential was evaluated for fixed electrolyte conditions. Co–P\textsubscript{i} films were deposited at 1.0–1.1 V vs. NHE and CoB\textsubscript{i} films were deposited at 0.9–1.0 V vs. NHE. No significant differences were observed for films grown in P\textsubscript{i} or B\textsubscript{i} at varying potentials, indicating that it is the electrolyte, and not the potential, that directs the nanoscale structure of catalyst films.

Figure 6.5. (a) Cylindrical atomistic model fit (black lines) to the Co–P\textsubscript{i} catalyst PDF data (red circles). The difference curve is shown in purple, and is offset for clarity. (b) Two views of the refined model for the average coherent domain in Co–P\textsubscript{i} films.
6.2.2 Steady-state electrocatalytic studies.

Catalyst films of Co–B\textsubscript{i} and Co–P\textsubscript{i} were electrodeposited onto FTO-coated glass slides by controlled potential electrolysis with limits set on the amount of charge passed. Films were prepared by passage of 5, 15, 50, 150, 400, and (only in the case of Co–B\textsubscript{i})...
films) 1000 mC/cm². Full details on deposition conditions are provided in Section 6.5.

Following deposition, films were transferred without drying to solutions of 1 M KB₃ pH 9.2 (for Co–B₃) or 0.1 M KP₃ pH 7.0 (for Co–P₃) electrolytes and Tafel data was acquired by application of potential steps from overpotential values of ~0.45 V to ~0.25 V with stirring. Voltages were post hoc corrected for ohmic losses due to solution resistance (measured prior to film deposition). Films were subsequently digested in ultrapure nitric acid and analyzed for Co content.

**Figure 6.7.** Tafel plots ($\eta = E - E^\circ - iR$) of (a) Co–B₃ and (b) Co–P₃ in 1 M KB₃ pH 9.2 and 1 M KP₃ pH 7.0, respectively. Films were prepared by passage of 5 (■), 15 (□), 50 (■), 150 (△), 400 (▲), and 1000 mC/cm² (♦). (c) Exchange current density, $j_0$, vs. catalyst loading plots of Co–B₃ (■) and Co–P₃ (●) obtained by fitting the linear regions of the Tafel plots in a and b to a straight line with a slope of $2.3 \times RT/F$ (59 mV). Lines are fits to $j_0 = j_0^{max} \tanh(d_f/d_f^{opt})$ (eq. 5.10). (d) Activity vs. catalyst loading (film thickness) plots of Co–B₃ (■) and Co–P₃ (●) at $\eta = 0.4$ V obtained by direct interpolation of Tafel plots in Figure 6.7a and 6.7b. Lines are drawn as guides to the eye.
The resultant Tafel plots are shown in Figure 6.7a and 6.7b. It is evident that while films prepared by passage of <50 mC/cm² (0.5 µmol/cm² Co) display similar activity over the overpotential range 0.25–0.45 V, for thicker films Co–Bi and Co–Pi display very disparate activities. Fitting the linear regions of the Tafel plots to slopes of \(2.3 \times \frac{RT}{F}\) (59 mV) and extrapolating to zero overpotential enables the construction of the plots of exchange current density against catalyst loading (Co ions per unit area) shown in Figure 6.7c. Here we observe a plateau in Co–Pi activity that occurs prior to the plateau in Co–Bi activity. Fitting the data in Figure 6.7c according to equation 5.10 (Chapter 5) leads to values of \(d_f^{opt}\) of 4.3 µmol Co/cm² (Co–Bi) and 1.8 µmol Co/cm² (Co–Pi). Interpolation of the data in Figures 6.7a and 6.7b at an overpotential of 0.4 V also affords plots of current density against catalyst loading as shown in Figure 6.7d. From Figure 6.7d we observe that Co–Pi films exhibit a severe attenuation in activity at elevated overpotentials (\(\eta > 0.35\) V) for catalyst loadings in excess of 1 µmol/cm², giving rise to a sharp plateau. Contrarily, Co–Bi films display continued increases in anode performance with film thicknesses in excess of 1 µmol/cm².

6.2.3. Redox conductivity measurements

Co catalyst films were electrodeposited onto platinum interdigitated microsensor electrodes (ABTECH Scientific) for conductivity measurements. These microelectrode devices were comprised of 25 platinum electrode pairs (50 total), 5 µm wide and 5 mm long, separated by a 5-µm gap. Each of the two sets of 25 microelectrodes could be addressable independently. Films were deposited such that a connection was formed between the microelectrodes through the overlaid catalyst film. For both types of catalyst material, the same amount of charge was passed, ensuring that the catalyst loading was identical. Following deposition, film conductivity was measured in a 0.1 M solution of the appropriate buffer by varying the voltage, \(E\), at one set of microelectrodes within the 0.7 – 1.3 V range, while adjusting the potential at the other set of microelectrodes such that a
voltage difference, $\Delta E$, of 5 mV would be sustained. A schematic of the setup is shown in Figure 6.8a. Here, there are two separate currents that may be measured ($i_1$ and $i_2$) associated with each set of microelectrodes. Each current also has contributions from two processes. One is the current associated with any steady-state redox reactions within the film (such as catalysis) ($i_{cat1}$ and $i_{cat2}$) and the other has to do with current flowing between the two sets of electrodes ($i_\sigma$) due to the 5 mV offset and the gradient in electrochemical potential (redox speciation) thereby engendered.\textsuperscript{17,18}

![Diagram of the setup](image)

**Figure 6.8.** (a) Schematic diagram showing the cross-sectional configuration of the interdigitated microsensor electrodes used in redox conductivity measurements (showing only one of 25 electrode pairs on the glass substrate). (b, c) Redox conductivity, $\sigma$, of Co–Bi (■) and Co–P (●) deposited by passage of 5.96 mC operated in 0.1 M KB$_i$ pH 9.2 and 0.1 M KP$_i$ pH 7, respectively, using a voltage offset of 5 mV. Each data point was the result of a 300 s step.
Thus
\[ i_1 = i_{\text{cat}1} + i_\sigma \] (6.1)
\[ i_2 = i_{\text{cat}2} + i_\sigma \] (6.2)

If the voltage offset \( \Delta E \) is sufficiently small that \( i_{\text{cat}1} - i_{\text{cat}2} \to 0 \), then\(^{19}\)
\[ i_\sigma = \frac{(i_1 - i_2)}{2} \] (6.3)

The redox conductivity, \( \sigma \), is then given by\(^{19}\)
\[ \sigma = \frac{i_\sigma}{\left( \frac{\Delta E}{d} \cdot A \right)} \] (6.4)

where \( A \) is the total effective area of the two arrays of electrodes and \( d \) is the distance between electrode pairs.

The resultant bulk redox conductivity data for Co–P\(_i\) and Co–B\(_i\) are shown in Figures 6.8b and 6.8c. In both cases, the conductivity of the films increases with potential (i.e. average Co oxidation state of the film) and then approaches a plateau within the region of oxygen evolution. The conductivity curve of Co–B\(_i\) (acquired at pH 9.2) is shifted to more negative potentials than that of Co–P\(_i\) (acquired at pH 7). This observation is what is expected for a hopping process that is driven by a proton-coupled redox reaction that possesses a pH-dependent equilibrium potential. However, it is particularly interesting that Co–B\(_i\) displays higher plateau conductivity than Co–P\(_i\), implying that the charge hopping process is intrinsically faster in the borate-deposited films.

### 6.3. Discussion

X-ray total scattering and PDF analysis reveals distinct cobalt-catalyst structural archetypes that are dependent on the buffering electrolyte that is present during oxidative self-assembly of the film. Co–P\(_i\) films are comprised of domains of edge-sharing CoO\(_6\) octahedra organized into nanoscale clusters as shown in in Figure 6.5b. This result confirms our previous interpretation of EXAFS data and shows that the corner-sharing model is not the structural motif present in these films. PDF results also give information into the
intermediate-range structure in these materials, and reveal that unlike Co–P$_i$ (Figure 6.5b), whose individual cobaltate layers are highly disordered, Co–B$_i$ films consist of more ordered domains of larger clusters that are more coherently stacked into slabs of about three layers (Figure 6.4b).

Electrochemical data indicate that the intrinsic activity of Co–B$_i$ films is considerably better than that of Co–P$_i$ films as film thickness is increased. This is evident in Figure 6.7c where the linear regions of the Tafel plots are extrapolated to zero overpotential and the resultant $j_0$ values are plotted as a function of the catalyst loading. In both cases, the performance of the anode can be improved by depositing thicker films. However, the behavior for Co–B$_i$ and Co–P$_i$ differs. In general we might expect that for porous catalyst films of this type, as discussed in Chapter 5, the exchange current density ($j_0$) should eventually plateau as the thickness is increased, and this is certainly what is observed in Figure 6.7c. However, we also expect the Tafel slope to remain constant. From the Tafel data in Figure 6.7a and 6.7b, it is clear that particularly in the case of Co–P$_i$ films, higher Tafel slopes are reached at overpotentials in excess of 350 mV. This leads to an additional attenuation in activity and a more severe plateau in Figure 6.7d ($j$ at $\eta = 400$ mV) compared to that observed in Figure 6.7c ($j$ at $\eta = 0$ mV).

The PDF results now offer a concrete difference in Co–P$_i$ and Co–B$_i$, thus allowing the first insight into a tangible structure–function correlation. Electrochemical and stopped-flow spectroscopic studies using molecular model compounds establish that the mechanism for charge transport in these films is best thought of as involving a series of PCET self-exchange reactions between Co$^{III}$ and Co$^{IV}$ centers of different cluster subunits. The behavior observed in Figure 6.7c is precisely what is expected for a catalytic film whose steady-state current is jointly controlled by proton–electron hopping and a catalytic reaction as discussed in detail in Chapter 5. Since the behavior of these two catalyst variants is similar for thin films, we surmise that the catalytic rate constant is unchanged over this
range in domain size. The disparity between Co–Bi and Co–Pi for thick films is associated with a faster rate of the effective proton–electron hopping diffusion rate ($D_{H,e}$), and consequently the optimal catalyst loading is larger for Co–Bi (4.3 µmol Co/cm$^2$) than for Co–Pi (1.8 µmol Co/cm$^2$).

Along these lines, the larger domain size of Co–Bi relative to Co–Pi provides a mechanism to delocalize the mobile holes over a larger region, which can be manifest in more efficient charge transport owing to: (1) fewer discrete hole hops needed in a given distance for charge transport among clusters and (2) a reduced reorganizational energy for electron transfer since charge is delocalized over a larger cluster area. Indeed, charge delocalization has been observed to enhance apparent self-exchange rates and attendant hole mobility on polymer$^{21,22}$ and nanoparticulate$^{23}$ films. In addition, interlayer hopping of holes may be facilitated by less disorder in a film comprising a multi-layer Co–Bi structure as compared to more disorder in the single layer structure of Co–Pi films. Together, these factors will contribute to an enhanced proton–electron/hole hopping rate, and hence a greater charge transport mobility in Co–Bi films, accounting for the ability of these films to sustain higher net activity than Co–Pi. In addition, we hypothesize that such nanoscale differences may impact a long-range morphology of these materials, such as their porosity, and by extension, their capacity for mass transport. Some of these other phenomena may explain the change in Tafel slope at overpotentials greater than 400 mV in Co–Pi and the resulting more severe plateau in Figure 6.7d.

The redox conductivity data presented in Figure 6.8 validates these conclusions. The bulk conductivity for both film types is dependent on the potential, since the potential defines the average concentration of oxidized Co centers (Figure 5.3d in Chapter 5). The voltage offset engenders a gradient in electrochemical potential along which protons and electrons hop. Co–Bi shows a lower voltage onset of conductance owing to the higher pH of the solution, which shifts the formal potential of the bulk proton-coupled redox (e.g.
Co^{IV/III}) waves of the material to lower potentials. Thus, this observation is expected. It is noteworthy, however, that Co–B\textsubscript{i} has a maximal conductance value that is three times greater than that of Co–P\textsubscript{i}, in line with the fits to data in Figure 6.7c which reveal a ~2.4-fold greater rate of proton-coupled electron hopping diffusion in Co–B\textsubscript{i} than Co–P\textsubscript{i}. We note that since the conductivity onset occurs at lower potentials than the catalytic wave, it must be concluded that the conductance values measured here relate to the bulk conductance, and not to the catalytic-hole hopping process. Nevertheless, the correspondence between Figure 6.7c and Figure 6.8b,c indicates that these measurements may serve as a proxy for the relative rates of catalytic-hole hopping as well.

6.4 Conclusion

The electrolyte in the OER and self-assembly reactions of Co and Ni/P\textsubscript{i} and B\textsubscript{i} films has several important roles. First, the electrolyte is a structural element of the molecular cluster subunit, terminating the growth of the oxidic clusters. Second, the anionic electrolyte is a mechanistic element of film nucleation and film growth. Third, the electrolyte is a proton acceptor in the PCET reaction of OER. Fourth, the electrolyte is the critical determinant of the self-healing nature of these films. The structural insights uncovered here by PDF analysis now indicate yet another important role of the electrolyte as a templating element that directs the intermediate-range structural order of the oxidic cobalt clusters within the films. Previous kinetic studies have provided a mechanistic framework for understanding the conflicting interactions between the buffering electrolyte as both proton acceptor and coordinating anion\textsuperscript{7} Whereas the latter role inhibits catalyst assembly, the former serves to assist formation and growth of clusters by facilitating the PCET oxidation of Co\textsuperscript{2+} precursors\textsuperscript{7} Thus, it is reasonable to expect that the size of the domains formed would depend critically on the balance between these factors; a high binding constant or irreversible binding between buffering anion and cobalt centers—most likely at the edges of nascent clusters—would favor the formation of new domains versus the growth of
existing ones, whereas a weaker adsorption isotherm and/or rapid binding–dissociation kinetics could promote larger domain sizes. The fundamental thermodynamic and kinetic parameters that directly regulate catalyst size warrant further investigation, since electrochemical studies show that these nanoscale morphological changes have a marked impact on the activity with film thickness (Figure 6.7), which are attributed to changes in the rate of proton–electron hopping through the film.

The Co–P/Bi clusters are dimensionally reduced analogs of extended cobalt oxides. These PDF studies now show that this dimensional reduction extends beyond molecular subunits and in Co–Bi, a mesostructure is realized that captures the nascent layered structure of cobaltates such as LiCoO₂. Hence, the results described herein suggest that when traditional metal oxides restructure to give metallate cluster active sites of the type observed in this study, the morphology of the domains might be regulated by the electrolyte composition. Insights such as these, which provide a bridge between molecular and extended solids, should be useful to accelerating the discovery of both homogeneous and heterogeneous catalysts systems.

6.5. Experimental Methods

Materials. Co(NO₃)₂•6H₂O 99.999% was used as received from Strem. KOH 88%, KH₂PO₄, and H₃BO₃ 99.9% were reagent grade and used as received from Macron. All electrolyte solutions were prepared with type I water (EMD Millipore, 18.2 MΩ cm resistivity). Fluorine-tin-oxide coated glass (FTO; TEC-7) was purchased as pre-cut 9” × 11” and 1 cm × 2.5 cm glass pieces from Hartford Glass. Unless stated otherwise, all experiments used FTO with 7 Ω/sq surface resistivity.

General Electrochemical Methods. All electrochemical experiments were conducted using a CH Instruments 760C or 760D bipotentiotstat, a BASi Ag/AgCl reference electrode, a Ni-foam counter electrode for the synthesis of catalyst powders for
X-ray PDF, and a Pt-mesh counter electrode for steady state electrochemical measurements. Catalyst synthesis for X-ray PDF was performed using a 27 cm × 7.5 cm × 26 cm thin-layer chromatography (TLC) developing chamber (VWR). Steady-state electrochemical experiments were performed using a three-electrode electrochemical cell with a porous glass frit separating the working and auxiliary compartments. All experiments were performed at room temperature (23 ± 1 °C) and electrode potentials were converted to the NHE scale using $E_{\text{NHE}} = E_{\text{Ag/AgCl}} + 0.197$ V. Oxygen evolution overpotentials, $\eta$, were calculated as $\eta = E_{\text{NHE}} - (1.23 - 0.059 \times \text{pH})$. Unless stated otherwise, the electrolyte comprised 0.1 M potassium borate (KBo$_3$), or 0.1 M potassium phosphate (KP$_3$) electrolytes.

**Co–B$_3$ Film Preparation for X-ray PDF Analysis.** Co–B$_3$ catalyst films for X-ray PDF analysis were prepared via controlled-potential electrolysis of 0.1 M KB$_i$, pH 9.2 electrolyte solutions containing 0.5 mM Co$^{2+}$. To minimize precipitation of Co(OH)$_2$ from these solutions, 2.0 L of 0.2 M KB$_i$ was added to 2.0 L of 1.0 mM Co$^{2+}$ solution. Depositions were carried out using an FTO-coated glass piece (9” × 11”) as the working electrode. These FTO-coated glass electrodes were rinsed with acetone and water prior to use in all experiments. Unless stated otherwise, deposition by controlled potential electrolysis was carried out on quiescent solutions at 0.9 V vs. NHE (accounting for ohmic potential losses due to solution resistances). Typical depositions lasted 14–16 h. Following deposition, films were rinsed in type I water (18.2 MΩ cm), and dried in a flow of air. Catalyst material was isolated from the FTO plate using a razor blade, and packed into polyimide capillary tubes: 0.0360” ID × 0.0400” OD (Cole Parmer). The ends of these tubes were sealed with epoxy.

**Co–P$_3$ Film Preparation for X-ray PDF Analysis.** Co–P$_3$ catalyst films for X-ray PDF analysis were prepared via controlled-potential electrolysis of 0.1 M KP$_3$, pH 7.0 electrolyte solutions containing 0.5 mM Co$^{2+}$. To minimize precipitation of Co$_3$(PO$_4$)$_2$ from
these solutions, 2.0 L of 0.2 M KP$_i$ was added to 2.0 L of 1.0 mM Co$^{2+}$ solution. Depositions were carried out using an FTO-coated glass piece (9” × 11”) as the working electrode. These FTO-coated glass electrodes were rinsed with acetone and water prior to use in all experiments. Unless stated otherwise, deposition by controlled potential electrolysis was carried out on quiescent solutions at 1.04 V vs. NHE (accounting for ohmic potential losses due to solution resistances). Typical depositions lasted 14–16 h. Following deposition, films were rinsed in type I water (18.2 MΩ cm), and dried in a flow of air. Catalyst material was isolated from the FTO plate using a razor blade, and packed into polyimide capillary tubes: 0.0360” ID × 0.0400” OD (Cole Parmer). The ends of these tubes were sealed with epoxy.

**X-ray Analysis.** The diffraction experiment was performed at the X7B beamline at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. Diffraction data were collected using the rapid acquisition pair distribution function (RaPDF) technique. Data were collected at a temperature of 100 K with an X-ray energy of 38.94 keV ($\lambda = 0.3184$ Å). A large area 2-D Perkin Elmer detector (2084 × 2084 pixels, 200 × 200 micron pixel size) was mounted orthogonal to the beam path with a sample to detector distance of 135 mm. The samples were rocked during the measurement to increase powder averaging. For each sample, the image plate was exposed for ca. 2 h. The catalyst samples gave unusable data past Q ≈ 17 Å$^{-1}$ due to the poor signal-to-noise. The CoOOH data were usable up to Q ≈ 19 Å$^{-1}$ and the Co$_3$O$_4$ data were usable up to Q ≈ 21 Å$^{-1}$. All raw 2D data were integrated and converted to intensity versus 2$\theta$ using the software Fit2D, where the 2$\theta$ is the angle between the incident and scattered x-rays. The data were corrected using PDFgetX3 to obtain the total scattering structure function, S(Q) and the PDF, G(r).

**Potentiostatic Steady-State Electrochemical Measurements.** FTO-coated glass plates (1 cm × 2.5 cm) were used as the substrates for deposition of Co–P$_i$ and Co–B$_i$ films for steady-state electrochemical measurements. Deposition was carried out in KP$_i$ pH 7 or
KB\textsubscript{i} pH 9.2 electrolytes containing 0.5 mM Co\textsuperscript{2+}. Co–P\textsubscript{i} films were deposited at 1.05 V vs. NHE and Co–B\textsubscript{i} films were deposited at 0.92 V vs. NHE. The deposition time was regulated by modulating the amount of charge passed. Cobalt content was verified by ICP-OES (using a Horiba ACTIVA-S inductively coupled plasma optical emission spectrometer, MIT Center for Materials Science and Engineering). The instrument was calibrated using commercial Co ICP standards (Fluka). For depositions at 1.05 V in KP\textsubscript{i}, we find there is a 1:1 correlation between the number of electrons discharged and the number of Co ions deposited to form the Co–P\textsubscript{i} film. However, at 0.92 V in KB\textsubscript{i} electrolyte, as the film loading is increased, a decreasing fraction of the charge passed correlates with Co deposition in the Co–B\textsubscript{i} film. This is due to a non-trivial amount of water oxidation occurring at this potential, with the associated current increasing in proportion to the number of active sites as the thickness increases. Thus, in this particular case elemental analysis was vital for determining the actual catalyst loading.

Steady-state current densities were measured as a function of the applied potential (with correction for ohmic potential losses due to the solution resistance) for Co–P\textsubscript{i} and Co–B\textsubscript{i} catalyst films in 1.0 M KP\textsubscript{i} pH 7 and 1.0 M KB\textsubscript{i} pH 9.2 electrolytes, respectively. Films were operated for at least 5 min at each applied potential to ensure that catalysis had achieved steady state conditions. Oxygen evolution overpotential (\(\bar{\eta}\)) ranges between 0.25 and 0.45 V were sampled. These Tafel plots were fit to slopes of \(2.3 \times RT/F\) and extrapolated to \(\eta = 0\) to obtain the plots in Figure 6.7c. Interpolation at \(\eta = 0.4\) V afforded the plots shown in Figure 6.7d.

**Redox conductivity Measurements.** Co catalyst films were electrodeposited onto platinum interdigitated microsensor electrodes (ABTECH Scientific, Part#: IME.0525.5-FD-Pt-U). Film deposition was accomplished initially by short-circuiting the two sets of electrodes and electrolyzing a 0.5 mM Co\textsuperscript{2+ (aq)} solution containing 0.1 M KB\textsubscript{i} pH 9.2 or 0.1 M KP\textsubscript{i} pH 7.0 at a potential of 0.92 V or 1.05 V (vs. NHE), respectively. After three hours
(passage of 3.15 mC), a voltage offset was applied to the two sets of microelectrodes in order to detect whether a catalyst “bridge” had been formed between source and drain (Figure 6.8). Since no cross-current was observed, the deposition was carried out for another 3 h, passing 2.81 mC (for a total of 5.96 mC). Upon subsequently applying a voltage offset to the microelectrodes a cross-current was observed. As such it was identified that 5.96 mC was sufficient to coat the electrodes and in subsequent measurements electrolysis was terminated once 5.96 mC of charge was passed. Following deposition, the electrode assembly was transferred into Co-free electrolyte (P_i or B_i) and the average voltage of the two sets of electrodes was varied from 1.16 V – 0.72 V (Co–B_i) and 1.3 V – 0.86 V (Co–P_i) in 30 mV increments while an voltage offset of 5 mV was maintained. The current through each microelectrode set was recorded and the conductance calculated as described by equations 6.1 – 6.4.

6.6 References


Chapter 7 — Facile, Rapid, and Large-Area Periodic Patterning of Conducting and Semiconducting Substrates with Sub-Micron Inorganic Structures

Portions of this chapter have been published:


7.1 Introduction

Having established in the previous chapter that the buffering electrolyte can be used to modulate the nanoscale morphology and activity of catalyst films, we now turn our attention to the discussion of a method that allows the morphology of a metal/semimetal/oxide film to be patterned at the sub-micron scale over macroscopic areas. The ability to effect a regular distribution of such materials is crucially important since the direct integration of oxidic catalysts for water splitting with semiconductor surfaces forms the basis of promising solar-to-fuel conversion devices such as the artificial leaf. Moreover, semiconductors patterned periodically with metallic and dielectric materials are desirable for enhancing light absorption in solar cells and present opportunities in the context of electrocatalyst-semiconductor devices. Although a repertoire of patterning methods exists, development of techniques that are high throughput, scalable and simple to implement is useful for the facile fabrication of optimized performance of energy conversion devices, such as the artificial leaf and more generally buried junction devices. Here we demonstrate a facile and rapid electrochemical method termed RIPPLE (reactive interface patterning promoted by lithographic electrochemistry) for patterning periodic metallic, non-metallic, and catalytic sub-micron structures over large areas of silicon.

7.2 Results

7.2.1. Electrochemical patterning of Ge and Cu films

Substrates were prepared by chemical vapor deposition of Ge (see Section 7.5) onto a silicon substrate. Following Ge deposition, a polymer electron (e)-beam resist layer was spin-coated onto the film, and periodic apertures (lines or dots) were defined in this polymer by e-beam lithography, to expose the Ge layer beneath. Cyclic voltammetry of this electrode in 0.1 M H$_2$SO$_4$ between 0.3 and 1.4 V (vs. NHE) promotes film etching
Figure 7.1. Top and Bottom: Schematics of the RIPPLE method showing a 2-compartment electrochemical cell with a Pt mesh electrode submerged in the left chamber and the working electrode, which undergoes patterning, submerged in the right chamber (together with a reference electrode, which is not shown). The working electrode, whose axial cross-section is shown at right, consists, for example, of a Ge thin film (green) that is exposed at defined sites (e.g. dots) through a resist layer (beige). Top: Both electrodes are immersed in acidic solution (blue) and a linearly ramped potential sweep (thick red line) is applied (e.g. between 0.3 and 1.4 V vs. NHE). Lateral etching of Ge proceeds underneath the resist layer. Bottom: A return potential sweep is applied leading to continued etching of Ge and site-selective formation of patterned features.

(Figure 7.1). The etching originates at the site of the lines/dots, which were defined through the resist, and then propagates underneath the resist.

Figure 7.2 shows various patterns derived from performing RIPPLE on a Ge film. After applying several cyclic voltammogram (CV) scans to the Ge-coated electrode and removing the resist, the substrate was examined by scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDS), and atomic force microscopy (AFM). Periodically spaced lines and rings patterned onto planar (Figures 7.2a,b) or microstructured (Figure 7.2c) Si substrates are observed in SEM images. The parallel lines or concentric rings emanate from the initially defined line or dot, respectively. The scan rate influences the pattern spacing (Figure 7.2b). An SEM survey of several patterns in an
array shows that they are composed of well-defined uniform circles (Figure 7.2d). The number of lines or rings formed is given by the empirical expression $N_F = N_{CV} - 1$, where $N_F$ is the number of patterned features and $N_{CV}$ is the number of CVs. Elemental mapping of the pattern shows that these features give rise to Ge signal (Figure 7.2e).

The RIPPLE technique is capable of patterning over three-dimensional (3D) surfaces. A Si substrate containing an array of square platforms of 7 µm height was
prepared and overlaid with Ge (Figure 7.2c). Nine lines patterned at a voltage scan rate of 230 mV/s, originating from the 2 µm wide line positioned atop one of these raised platforms, seamlessly propagate from the top of the platform and then over the edge of the platform (3 lines are positioned on the surface of the vertical edge) and onto the substrate below (Figure 7.2c).

An AFM map and line section analysis of the topography of the Ge ring structures show that the periodic, concentric rings are 20(±1) nm high and 360(±15) nm wide and that these dimensions are conserved across the structure (Figure 7.2f, left). More complicated 2D to 3D features can be patterned by modifying the electrolyte conditions. An experiment conducted over the same voltage range (0.3 – 1.4 V) and with a Ge substrate, but at pH 5.9 in the presence of Na₂SO₄, reveals a complex 3D pattern consisting of concentric terraces (R<sub>rms</sub> = 3.9 nm) which step down in ~20 nm increments from the center region (Figure 7.2f, right).

A detailed analysis of the structure and composition of the patterned features was afforded by high-resolution transmission electron microscopy (TEM) and EDS. For imaging purposes, a ~15 nm metal layer was deposited prior to RIPPLE to assist in differentiation of patterned features. Several important features are established by TEM images and EDS maps of an axial cross-section taken at the periphery of a feature containing patterned concentric rings. First, as established by Figure 7.3a, besides the patterned ring (bright contrast between substrate and metal layer), there is no material positioned elsewhere on the flat Si substrate. Second, from the high-resolution TEM of Figure 7.3b, it appears that the ring has a morphology distinct from that of the underlying <111> Si substrate whose lattice-fringes are visible. EDS elemental Ge and O maps of an area encompassing the ring cross-section (Figure 7.3c) show significant overlap only in the region of the ring.
The production of an oxidic Ge material is consistent with the CV conditions employed for ring formation. The evolution of a single pattern was correlated to SEM images (Figure 7.3e) taken after each forward, 0.3 to 1.4 V, (solid lines, Figure 7.3e) and reverse, 1.4 to 0.3 V, (dashed lines, Figure 7.3e) sweep. At 100 mV s$^{-1}$, the first forward sweep (solid red line) is characterized by rapid onset of anodic current at ~0.5 V, a broad irreversible peak at 1.01 V, and a linear regime for potentials greater than 1.1 V. These features are preserved in subsequent forward sweeps and the current associated with the peak at 1.01 V increases monotonically as the pattern increases in size. Reverse sweeps show nearly identical profiles and are absent of any distinguishing features. EDS data reveals that the rings comprise Ge and O (Figure 7.3c). Furthermore, rings appear during

Figure 7.3. (a) Bright-field TEM images of the axial cross-section of a substrate patterned with concentric rings. (b) High-resolution bright-field TEM image of the interface between the patterned ring and underlying Si substrate marked by the pink box in (a). (c) From top to bottom, EDS elemental maps of Ge, O, and Si for the cross-section of a patterned ring. (e) Left: Cyclic voltammograms at 100 mV s$^{-1}$ performed in 0.1 M H$_2$SO$_4$; Right: Accompanying SEM images of patterned structures. Three CVs, each composed of a forward (solid lines) and reverse (dashed lines) sweep, were performed between 0.3 and 1.4 V.
reverse sweeps (Figure 7.3e, images 4 and 6) at a location coincident with the periphery of the etched region formed after the previous forward sweep (Figure 7.3e, images 3 and 5). Finally, when the voltage scan rate was altered in the middle of a patterning process, the period for the first set of rings is consistent with that expected from patterning solely at the first scan rate.

The periodicity of patterned structures produced by the RIPPLE method may be tuned reliably. CVs acquired using voltage scan rates from 30 to 500 mV s$^{-1}$ result in patterned concentric rings with period tunable from 6.9 µm to 537 nm, respectively (Figure 7.4a). The period for the last ring pair shows a power law dependence on scan rate (Figure 7.4 inset) and exhibits <3.0% deviation from the mean among 10 out of 81 patterns randomly sampled over a 0.25 mm$^2$ area, for each scan rate. For a scan rate of 100 mV s$^{-1}$ there is a 13.3% difference in period between the first and last pair of concentric rings within a pattern (Figure 7.4b). Notably, for scan rates >300 mV s$^{-1}$, which yield sub-micron periods, the deviation in period among all rings within a pattern is <3.1%.

Figure 7.4 (a) Average period for the last ring pair within randomly sampled patterns as a function of voltage scan rate. Error bars denote % deviation from the mean and the dashed line is a power law fit to the data. Inset: Data presented on a logarithmic plot with linear fit to data. (b) Average period for the 1$^{st}$ through 4$^{th}$ ring pairs within randomly sampled patterns at 3 different voltage scan rates: 65 mV s$^{-1}$ (green circle), 100 mV s$^{-1}$ (red square), and 300 mV s$^{-1}$ (blue triangle).
The RIPPLE technique may be used to furnish more complex patterns. Hollow Ge squares with micrometer-scale features are formed at the interstices of a square array of closely-spaced Ge concentric ring patterns (Figure 7.5a), which were patterned by performing a 5-cycle CV at 30 mV s\(^{-1}\). The combination of rings and squares after one round of patterning demonstrates the potential of the RIPPLE technique with regard to creating variegated patterns over large areas of a Si substrate.

This methodology may also be extended to patterning metallic materials and over large substrate areas. A thin Cu film subjected to 5 CVs between 0.6 and 1.5 V in 0.1 M sulfuric acid leads to formation of concentric rings of Cu over Si (Figure 7.5b). Copper and oxygen EDS maps of the axial cross-section of a single ring do not overlap suggesting that the patterned structures are composed of metallic Cu as opposed to an oxide of Cu (Figure 7.5c). Furthermore, a large shape was patterned from a Cu film on transparent substrate where each "pixel" consisted of a single pattern of concentric Cu rings arranged in a square array (Figure 7.5d). Together, these data verify that the method may be used to pattern sub-micron non-metallic and metallic structures over large areas with control over their shape.

**Figure 7.5** (a) (top) Schematic of a square array of periodic ring patterns. (bottom) SEM image of the region where rings from adjacent patterns overlap with each other. Inset: EDS Ge map of the square. (b) (left) SEM image of an array of rings patterned from a Cu film on Si. (right) Composite Cu (orange) and Si (blue) EDS map of one pattern. (c) (left) High-resolution STEM image of a 60 nm thick axial cross-section of a patterned Cu ring. (middle and right) Cu (orange) and O (red) EDS maps of the same cross-section. (d) (left) Photograph of a Cu-structure patterned over a transparent substrate. (right) SEM image of periodic rings that serve as the “pixels” in design of the patterns.
7.2.2. Electrochemical patterning of Co and Co OER catalyst films

The ability to pattern large substrate areas with metal and oxidic materials suggests the potential for integrating inorganic catalysts with semiconductors for energy conversion applications. We turned our attention to patterning Si with the cobalt-based water splitting catalyst discussed in chapters 5 and 6, Co–P. Using similar electrochemical conditions as for Cu patterning, a Co film was patterned into concentric ring structures (Figure 7.6a). Anodization of this patterned Co substrate was performed (see Section 7.5) in accordance with methods that have previously been shown to yield Co–P. SEM and Co and O EDS maps of the patterned and anodized Co sample reveal well-defined concentric rings composed of the anticipated Co–P catalyst (Figure 7.6b). CVs of the Co–P film exhibit a catalytic wave at 1.0 V (Figure 7.6c) indicative of the water splitting reaction.

Figure 7.6 (a) Top: SEM of patterned metallic Co (left), Co EDS map (middle), and O EDS map (right); scale bar, 10 µm. Bottom: Cyclic voltammogram in 0.1 M H$_2$SO$_4$ of a 250 nm metallic Co film (see Section 7.5) on a platinum/silicon substrate. The gray arrow indicates the direction of progression in the voltammograms. (b) RIPPLE-patterned cobalt phosphate (Co–P) water splitting catalyst. Top: SEM image of Co–P catalyst patterned into concentric rings; Co (yellow) and O (red) EDS maps of a single Co–P catalyst pattern are shown in the middle and bottom, respectively. (c) Cyclic voltammogram of a substrate bearing arrays of patterned Co–P in 0.1 M KP$_4$ pH 7 electrolyte at a scan rate of 100 mV/s. (d) O$_2$ evolved by patterned Co–P catalyst as measured by a fluorescent probe (red) and O$_2$ calculated from charge passed assuming a Faradaic efficiency of 100% (black).
Furthermore, the significant steady-state catalytic current for potentials $\geq 1.1$ V is consistent with that reported for electrodeposited Co–P$_i$ films.\textsuperscript{22} We conclude from these data that the performance of these patterned systems is comparable to that of bulk films. An oxygen probe experiment carried out over 10 h using this patterned substrate verified the competence of this catalyst towards O$_2$ generation from water with a Faradaic efficiency of $>99\%$ (Figure 7.6d). Electrolysis performed for over 20 h also verified the well-established stability of the catalyst.

7.3. Discussion

Reactive interface patterning promoted by lithographic electrochemistry (RIPPLE) entails a simple experimental setup (Figure 7.1) and leads to the formation and propagation of periodically spaced sub-micron structures over large areas (Figure 7.2a,b). This new method performs concerted redox etching and patterning of an inorganic material when it is subjected to applied cyclic potentials in the presence of appropriate electrolyte. The use of cyclic potentials and a 3-electrode configuration affords a high degree of control over the redox processes leading to patterning that is uncommon to electrochemically-based patterning methods.\textsuperscript{16,17} In addition, a unique feature of RIPPLE is the ability to pattern over 3D surfaces and position patterns onto the vertical sidewalls of a raised feature (Figure 7.2c). Thus, unlike most lithographic techniques,\textsuperscript{6} the RIPPLE technique is not limited to “line-of-sight” patterning.

When patterning germanium, the resultant CVs are consistent with oxidation of Ge, which is thermodynamically favored to form GeO$_2$ and soluble H$_2$GeO$_3$ (solubility of 43 mM) at pH 1 and at potentials greater than 0.2 V.\textsuperscript{25} Indeed, the presence of rings comprising Ge and O concurs with EDS data of Figure 7.3c. These results suggest a relation between Ge redox chemistry and germanium oxide solubility, at a given potential and pH, which could be used to tune the profile and composition of the patterns. The formation of an oxide suggests that pH might be important in the morphology of patterned features. Indeed, an
identical patterning experiment conducted at pH 5.9 in the presence of Na$_2$SO$_4$ revealed a CV with quasi-reversible waves between 0.4 and 0.8 V and a pattern consisting of concentric terraces (Figure 7.2f, right). Pattern periodicity is clearly dependent on the scan rate with feature spacings between ~500 nm and 7 µm accessible by utilization of scan rates between 30 and 500 mV/s.

Patterning is not restricted to germanium and has been straightforwardly extended to metallic films of Cu and Co (Figures 7.5 and 7.6). In both cases, the electrochemical data obtained during etching is similar to that obtained in the case of Ge, inasmuch as oxidative currents are observed throughout the patterning process with a steady progression in the average current. However, there are key differences as well; a more pronounced peak is observed in CVs of Ge (Figure 7.3) compared to Co (Figure 7.6), and it would also appear as though the Cu patterns are more metallic than Ge or Co analogs.

In spite of these differences, which will require additional studies to explain, these data generally suggest that pattern evolution occurs through oxidation and dissolution of the metal/semi-metal film in concert with localization of a residual oxide/metallic feature, which is stable during subsequent electrochemical cycles. Through an apparent interplay of electrochemical and hydrodynamic effects the RIPPLE method allows us to control: (a) the lateral extent of Ge etching via CV and electrolyte conditions, and (b) the formation of features mediated by specific solution conditions such as pH. The patterns we obtain are akin to those obtained from moving boundary simulations of etching processes. Where our results emphasize that pattern formation is electrochemically mediated, capillary flows may lead to contact line pinning and de-pinning at the periphery of the un-etched parent material, mediating the formation of periodic features. Work currently underway will allow the proposed mechanism to be more fully defined.
7.4. Conclusion

The RIPPLE technique directly patterns arrays of periodically spaced sub-micron scale structures of inorganic materials onto planar and 3D semiconducting substrates. The process is reliable, applicable to wafer-scale and even larger substrates, and fast with the CV cycling directly associated with patterning. Considering all steps intrinsic to preparation and patterning, the process takes less than 30 min and can yield multiple substrates patterned in parallel. The ability to perform non-line-of-site patterning may allow for positioning of catalyst layers over textured substrates, such as those with high aspect ratio features. Optimized integration of catalysts with semiconductors may enable improved solar-to-fuel conversion devices, which benefit from photon management and reduced optical losses owing to absorption by the catalyst material. Given the fidelity of and in situ control over RIPPLE patterned structures and their period, future work will also investigate their role in photonic and plasmonic applications.\textsuperscript{28–31} Capitalizing on such applications requires fabricating high quality optical elements characterized by low surface roughness, sharp pattern profiles, and a small dispersion in sub-micron periods. It may be beneficial from the standpoint of materials efficiency to modify RIPPLE so that it functions in a strictly additive sense with periodic deposition occurring from solution-phase precursors supplied via microfluidic arrays. These and other imperatives will motivate future efforts, including exploration of the fundamental resolution, material limits, and mechanism of this patterning. The high-throughput, facile, and large area patterning of sub-micron inorganic structures by RIPPLE could enable new and emerging opportunities in energy conversion and storage.

7.5. Experimental Methods

Substrate Preparation. Si $<111>$ p-type doped substrates (Prime Grade 3-5 $\Omega$ cm, Nova Electronic Materials) were cleaned using a UV/ozone system at 300 $^\circ$C for 5 min.
The substrates were etched for 10 s in buffered hydrogen fluoride and then inserted into a home-built chemical vapor deposition (CVD) reactor, which was evacuated to a base pressure of 5.4 mTorr. A poly-crystalline p-type Ge film was grown initially at 360 °C for 3 min and then at 330 °C for another 30 min. The growth pressure was 28 Torr with flow rates of 10, 14 and 100 standard cubic centimeters per minute (sccm) for germane (GeH₄), diborane (B₂H₆, 100 ppm in He) and hydrogen (H₂, Semiconductor Grade), respectively. The film growth rate under these conditions was ~7.5 nm min⁻¹ for a total film thickness of ~250 nm. For n-type Ge film growth a 2.8 sccm PH₃ flow rate was used instead of B₂H₆. For Cu patterning experiments, a 250 nm thick Cu film was deposited on p-type Si substrate by DC sputtering (Orion 3, AJA International, Inc.) at a pressure of 4 mTorr with 12 sccm of Ar and a gun process current and voltage of 1 A and 455 V, respectively. For Co patterning and catalyst studies, electron-beam evaporation was used to deposit a 300 nm thick Pt film on p-type Si substrate followed by a 250 nm film of Co.

For the 3D surface patterning in Fig. 1d, a Si <111> p-type substrate was patterned with 45 µm × 45 µm regions using electron beam lithography through PMMA (400 µC cm⁻², 1.4 nA beam current). A 150 nm Cr film was deposited by thermal evaporation followed by acetone lift-off. A Si deep reactive ion etch (SF₆) was performed for 10 min in an inductively coupled plasma reactor (Surface Technology Systems ICP RIE, SPTS). A room temperature Cr etch was performed for 2 min in ceric ammonium nitrate (Cr etchant, Sigma Aldrich) to remove the Cr RIE mask. Thereafter, Ge CVD deposition was performed as described above.

After material (Ge or Cu) deposition, the substrate was coated with a 500 nm thick layer of S1805 photo-resist (S1805, MicroChem Corp.) or PMMA e-beam resist (PMMA C5, MicroChem Corp.). Using photolithography (5 s exposure) or electron beam lithography (400 µC cm⁻², 1.4 nA beam current), 80 µm × 2 µm (length × width) lines or 2 µm × 2 µm dots were defined through the aforementioned resists to the underlying Ge
film. A small region at the top of the substrate was left uncovered by resist in order to facilitate electrical contact via a Cu alligator clip to the potentiostat. The back and sides of the substrate were covered with a lacquer (Microshield, Tolber Chemical) to electrically passivate the substrate. For the cross-sectional sample characterized in Fig. 2a-d, a ~15 nm thick Au/Pd film was deposited to assist in clear differentiation of the patterned feature from the carbon film intentionally deposited to protect the sample during FIB milling.

**Cyclic Voltammetry.** A two-compartment (50 mL compartments separated by a glass frit of medium porosity) electrochemical cell was filled with 0.1 M sulfuric acid and the substrate (see Substrate Preparation) was submerged into one compartment. iR compensation was performed prior to every patterning experiment and yielded typical resistance values in the range of 500 – 1500 Ω. Standard three-electrode cyclic voltammetry experiments were conducted using a Ag/AgCl reference electrode (BAS Inc.), a Pt mesh counter electrode, and potentiostat (760D series, CH Instruments Inc.). Potentials versus the normal hydrogen electrode (NHE) were determined by: E (NHE) = E (Ag/AgCl) + 0.197 V. After concluding the cyclic voltammetry, the resists and lacquer were removed by soaking in acetone for ~1 min followed by a 10 s rinse in isopropanol. For Ge patterning, scans were initiated at the open circuit potential, which was 0.3 V (vs. NHE). For the data shown in Figure 7.2f, a 0.1 M sodium sulfate solution was used. All electrolytes were prepared from reagent grade chemicals and type I water (18 MΩ resistivity).

**Catalyst Preparation and Characterization.** The patterned cobalt was oxidized to the CoP₁ catalyst at 1.15 V (vs. NHE) for 30 min in 0.1 M KPO₄ (pH 7.0), at which point steady-state was observed. Faradaic efficiency was calculated using a fluorescent oxygen sensor (Ocean Optics) in a gas-tight electrochemical cell. The solution and headspace were purged with N₂ for an hour and the sensor was placed in the headspace. Electrolysis was performed at 1.2 V (vs. NHE) in 0.1 M KPO₄ (pH 7.0) for 10 h.
**SEM.** SEMs were acquired using the SE2 detector on a Zeiss Supra55VP (Carl Zeiss AG) operating at 7 kV. The SEM images in Figure 7.3e were false colored using the Copper Color Table in Igor Pro (WaveMetrics, Inc.) in order to aid in clear visualization of the rings.

**EDS.** Low-resolution EDS maps (Figs. 7.2e and 7.6a,b) were acquired on an SEM operating at 7 kV with 60 µm aperture size and WD = 8.5 mm. EDS parameters included a dwell time of 200 ms and a frame resolution of 1024 × 800. High-resolution EDS maps (Fig. 7.3d) were acquired on an aberration corrected STEM (Libra 200 MC, Carl Zeiss AG) operating at 200 kV with twin EDS detectors and drift correction. EDS parameters included a dwell time of 500 ms and a frame resolution of 1024 × 800.

**AFM.** Topographic maps were acquired using an MFP-3D AFM (Asylum Research) with an Al coated Si AFM tip (f ~ 300 kHz, AC160TS). Data were acquired in AC mode at a 0.6 kHz scan rate. Using the Asylum software package, a 1st order Flatten procedure was applied to the raw data to correct for a mild distortion of the substrate plane. For the AFM maps in Fig. 1e, a N×N median filter (size = 1) was applied as was the "Mocha" color table for the z-axis data (Asylum software).

**TEM of cross-sections.** The axial cross-section of a substrate patterned with rings was prepared by Ga⁺ focused ion-beam milling (Zeiss NVision 40, Carl Zeiss AG). To protect against subsequent FIB damage, the sample was first coated with a ~50 nm thick carbon film inside the FIB under SEM mode followed by ~550 nm of carbon under FIB mode. FIB milling was used to excise a wedge from the substrate and was followed by FIB welding of the wedge to a nano-manipulator needle with tungsten. The wedge was subsequently transferred and welded to a specialty Cu TEM grid. The section was reduced to a thickness of ~60 nm using FIB milling. Bright-field TEM images were acquired on a TEM operating at 200 kV (JEOL 2100, JEOL Ltd.).
7.6 References


(18) James, B. D.; Baum, G. N.; Perez, J.; Baum, K. N. Technoeconomic Analysis of Photoelectrochemical (PEC) Hydrogen Production; U.S. DOE, 2009.


Chapter 8 — PCET kinetics of homogeneous H₂ evolution by cobalt and nickel hangman porphyrins

Portions of this chapter have been published:


8.1 Introduction

As highlighted in Chapter 1, the efficient catalysis of transformations of energy consequence\textsuperscript{1–7} mandates the coupling of electron transfer (ET) to proton transfer (PT) in proton-coupled electron transfer (PCET) reactions. \textsuperscript{8–14} In the absence of PCET, intermediates possessing equilibrium potentials that are prohibitively large depreciate the storage capacity offered by the solar-to-fuels conversion process. The coupling of protons to changes in electron equivalency offers the possibility of restricting the equilibrium potentials of the redox steps to a more narrow potential range, thereby minimizing the overpotential required to sustain catalysis at a desired turnover rate. Thus, the exploitation of PCET pathways to permit potential-leveling effects is a crucial prerequisite for the efficient catalytic conversion reactions of energy relevant molecules.

PCET reactions may be classified into stepwise and concerted pathways. \textsuperscript{8,10,14,15} Stepwise PCET may involve ET first followed by PT (ETPT), or PT followed by ET (PTET). In concerted proton-electron transfers (CPET), the proton and electron traverse a common transition state. While concerted pathways avoid the formation of thermodynamically costly intermediates, CPET reactions may incur kinetic penalties associated with the requirements for proton tunneling. \textsuperscript{13,14,16} The competition between these dynamics during catalysis determines the most efficient route of reaction. Studies that explore the interplay between these factors are crucial to designing catalytic reactions of high efficiency. Along these lines, the incorporation of proton relays in the second coordination sphere of molecular catalysts has emerged as a useful tool in optimizing PCET transformations.\textsuperscript{17–23} We have focused on the synthesis and mechanistic investigation of a class of metalloporphyrin molecules attached to a xanthene backbone bearing a carboxylic acid functional group —“hangman” porphyrins (such as 1-M in Figure 8.1).\textsuperscript{17,24,25} Hangman porphyrins of this type (substituents appended to the meso-positions of the
In this chapter, we examine the role of proton relays in influencing PCET in the context of the homogeneous electrocatalytic production of H₂ from non-aqueous solutions containing weak acids. We discuss the quantitative value of the hangman group by comparing the PCET kinetics of 1-Co with 2-Co and 3-Co. In previous studies, it has been shown that 1-Co serves as a catalyst for H₂ production, as evidenced by cyclic voltammetry and bulk (preparative-scale)-electrolysis.²⁹ It was also demonstrated that 1-Co displayed a shift in the catalytic wave to more positive potentials, relative to 2-Co, and a Co(II)H species appeared to be a key intermediate in the electrocatalytic reaction. We therefore set out to investigate the details of the PCET pathway involved in the formation of this Co(II)H intermediate. Our studies reveal that the hangman effect gives rise to a rate enhancement that is equivalent to effective acid concentrations in excess of what is physically possible. We then turned our attention to exploring the influence of the metal center, and by extension the pKₐ difference between proton donor and acceptor, on PCET kinetics by studying the electrokinetics of Ni porphyrins 1-Ni and 2-Ni. These nickel catalysts are shown to offer improved activity over their cobalt analogs, and the improvement in activity is rationalized in terms of a change in mechanism upon alteration of the metal center.

**Figure 8.1.** Metalloporphyrin catalysts used in this study, including hangman complexes (1-M) and non-hangman analogs (2-M and 3-M).
8.2 Cobalt hangman porphyrin H₂ electrocatalysis

8.2.1. Results

8.2.1.1. Electrochemical interrogation of reversible waves and trumpet plots

Porphyrins 1–3-CoII were synthesized in short synthesis times and in good yields according to previously published procedures. Figure 8.2a shows the voltammetric waves of the formal Co²⁺/⁺ couple of 3-Co acquired from cyclic voltammetry (CV) over a range of scan rates. For simplicity, the formal metal oxidation state will be used herein though we note that the metal orbitals are likely mixed with the porphyrin ring and hence the formal reduction of the metal invariably involves delocalization of the reducing equivalent onto the porphyrin ring. The “trumpet plot” for the Co²⁺/⁺ couple (Figure 8.2b) of 3-Co shows the difference between the anodic or cathodic peak potential and midpoint potential (Eₚ – E⁰) as a function of the logarithm of scan rate (log v). Simulation of CVs

Figure 8.2. (a) Overlay of representative normalized (iₚ = i/v¹/₂) CVs taken of a 0.3 mM solution of Co(C₆F₅)₄ porphyrin in acetonitrile with 0.03 ( ), 0.3 ( ), and 3 ( ) V/s scan rates, using a glassy carbon electrode. (b) Difference between anodic or cathodic peak potential and midpoint potential (Eₚ – E⁰) vs. log of scan rate (E⁰ = –1.00 V for the CoIII/II couple ( ), and –1.98 V for the CoI/0 couple ( ))). Simulated curves are plotted for kₛ = 0.011 cm/s ( ) and kₛ = 0.2 cm/s ( ). The diffusion coefficient (D) for the Co(C₆F₅)₄ porphyrin was determined to be 8 × 10⁻⁶ cm² s⁻¹ from the peak current, i, in the reversible limit: i = 0.446FAC⁰D¹/₂(Fv/RT)¹/₂ (where F is the faraday constant, A is the area of the electrode and C⁰ is the bulk porphyrin concentration).
(see Section 8.5.1) to replicate the shape of the trumpet plot furnishes a value of 0.011 cm/s for the standard heterogeneous electron transfer rate constant, \( k_s \), of the Co\(^{2+/+} \) couple. The trumpet plot for the Co\(^{+/0} \) couple of 3-Co is also shown in Figure 8.2b. The \( k_s \) value extracted from the trumpet plot for the Co\(^{+/0} \) couple of 3-Co is at least an order of magnitude higher than that of the Co\(^{2+/+} \), on the order of 0.2 cm/s. The \( k_s \) of 0.012 cm/s for the Co\(^{2+/+} \) couple of 1-Co is the same as that of 3-Co.

### 8.2.1.2. PCET electrokinetics of cobalt hangman porphyrin

As previously reported,\(^{29} \) the presence of the carboxylic acid hanging group in 1-Co results in irreversibility of the Co\(^{+/0} \) wave owing to an irreversible reaction between the reduced metal center and the internal acid group. However, the similarity in Co\(^{2+/+} \) midpoint potential between 1-Co and 2-Co suggests that the position of the irreversible Co\(^{+/0} \) wave of 2-Co (\( E^0 \) at \(-2.14 \) V vs. Fc\(^+/0 \)) is a good estimate of the Co\(^{+/0} \) midpoint potential of 1-Co as well. The \~200 mV positive shift in the peak position of the irreversible “Co\(^{+/0} \)” peak can be indicative of what is classically considered an “EC” mechanism, where a heterogeneous electron transfer reaction is followed by a homogeneous chemical reaction.\(^{32} \) In the context of this hangman-promoted reaction, the “C” step logically involves an intramolecular proton transfer from the hanging group to the metal center to furnish a Co\(^{II} \) hydride:

\[
\begin{align*}
H \cdots Co^I + e^- & \rightleftharpoons H \cdots Co^0 & E^0, k_s & \quad (8.1) \\
H \cdots Co^0 & \rightarrow H \cdots Co^{II}H & k_{PT} & \quad (8.2)
\end{align*}
\]

Where \( H \cdots Co^I \) designates the presence of a proton in the secondary coordination sphere of the cobalt center (by virtue of the pendant carboxylic acid group). Such an EC mechanism within a PCET framework is the stepwise ETPT pathway. In this case, the peak potential of a CV (\( E_p \)) should be independent of the bulk concentration of the complex.\(^{32,33} \) In addition, when electron transfer is reversible and fast enough so as not to interfere kinetically in the electrochemical response, \( E_p \) can be expressed as a function of the
The reversible potential of the ET step $E^\circ$, the proton transfer rate constant $k_{PT}$, and the scan rate ($v$) as follows:

$$E_p = E^\circ - 0.78 \frac{RT}{F} + \frac{RT}{2F} \ln \left( \frac{RT k_{PT}}{F} \right)$$  \hspace{1cm} (8.3)$$

As shown in Figure 8.3a, the peak potential of the irreversible wave of 1-Co is indeed independent of concentration over a range of scan rates. To extract information on the kinetics of the proton transfer reaction, CVs were acquired by varying the scan rate between 30 mV/s and 30 V/s (Figure 8.3b) at a fixed metalloporphyrin concentration of 0.2 mM. Equation 8.3 predicts a linear correlation between the dimensionless parameter $(E_p - E^\circ)F/RT$ and $\ln(v)$ with a slope of $-0.5$. The experimental data, however, display a distinct curvature that becomes more pronounced at higher scan rates (Figure 8.3c).

8.2.1.3. PCET electrokinetics of non-hangman Co porphyrins

In order to compare the kinetics of the intramolecular PT for 1-Co, to an intermolecular PT from an external acid source, CVs of 3-Co were recorded in the presence of varying amounts of benzoic acid (Fig. 8.4a). The Co$^{+0}$ redox wave becomes completely
irreversible in the presence of excess benzoic acid and a catalytic wave is observed in the CV. In this case, catalytic \( \text{H}_2 \) production is observed upon reduction to Co(0), and thus, a second protonation step must be taken into consideration.

Kinetic resolution of the system requires knowledge of which of the two following protonation steps is rate limiting in the overall catalytic reaction:

\[
\text{Co}^0 + \text{H}^+ \xrightleftharpoons{ k_{PT1} } \text{Co}^{\text{II}}\text{H} \\
\text{Co}^{\text{II}}\text{H} + \text{H}^+ \xrightarrow{k_{PT2}} \text{Co}^{\text{II}} + \text{H}_2
\]

There are three parameters that govern the rate of \( \text{H}_2 \) evolution catalysis, and therefore the magnitude of the peak catalytic current \( i_{\text{cat}} \):

(i) The ratio of substrate (acid) to catalyst (porphyrin) concentration, i.e. the excess factor \( \gamma \):

\[
\gamma = \frac{[\text{PhCOOH}]_{\text{bulk}}}{[3-\text{Co}]_{\text{bulk}}} \tag{8.6}
\]

(ii) The dimensionless parameter \( \lambda_{\text{PT1}} \) which defines the kinetics of equation 8.4:

\[
\lambda_{\text{PT1}}
\]

Figure 8.4. (a) CVs of a 0.1 mM solution of 3-Co in the absence of benzoic acid (---) and in the presence of 0.05 (••••), 0.3 (---), and 0.6 (---) mM benzoic acid. Scan rate, 30 mV/s; 0.2 M TBAPF\(_6\) in acetonitrile. (b) CVs of 0.1 (---), 0.3 (---), and 1 mM (---) solutions of 3 in the absence of benzoic acid and in the presence of 0.05 (••••), 0.15 (---), and 0.5 (••••) mM benzoic acid, respectively. Scan rate, 30 mV/s; 0.2 M TBAPF\(_6\) in acetonitrile. Glassy carbon working electrode, Ag/AgNO\(_3\) reference electrode, and Pt wire counter electrode.
\[ \lambda_{PT1} = \frac{RT [3-Co]_{bulk} k_{PT1}}{v} \]  

(8.7)

(iii) The competition between equations 8.4 and 8.5, given by \( \rho \) where:

\[ \rho = \frac{\lambda_{PT1}}{\lambda_{PT2}} = \frac{k_{PT1}}{k_{PT2}} \]  

(8.8)

In general, equation 8.4 will be rate limiting for \( \rho > 10 \) and equation 8.5 is rate limiting for \( \rho < 0.1 \). Because the waves for catalysis and for the catalyst in the absence of acid occur at similar potentials, the peak in the CV is due to both substrate and catalyst consumption. The confluence of these two processes precludes an analytical solution to the problem at hand, and mandates the use of CV simulation to generate working curves that relate peak current values to kinetic parameters (Section 8.2.2).

To assist in the determination of which value of \( \rho \) is operative during \( H_2 \) production mediated by 3-Co, and therefore the identity of the rate-limiting step, CVs of solutions containing 0.1, 0.3, and 1 mM 3-Co were recorded (Figure 8.4b), and the Co\(^{+0}\) peak currents \( (i_0) \) were determined in each case. CVs were also acquired for solutions with identical concentrations of 3-Co, but containing 0.5 equivalents of benzoic acid (i.e. \( \gamma = 0.5 \)) (Figure 8.4b), permitting measurement of the corresponding catalytic peak currents \( (i_{cat}) \).

8.2.2. Discussion

Cobalt porphyrins have been shown to mediate the production of \( H_2 \) from non-aqueous solutions containing a weak acid.\(^{29}\) Here we analyze the electrochemical responses of these molecules with an emphasis on elucidating the effect of a pendant proton relay in the second coordination sphere of the cobalt center. To this end, comparing the behavior of catalysts bearing a proton relay with those for which a proton relay is absent, is a useful strategy. The non-hangman complexes (2-Co and 3-Co) also permit access to ET rate constants in the absence of any proton transfer. Varying the scan rate while monitoring the peak potentials of a reversible feature allows the extraction of the standard heterogeneous
electrochemical rate constant, \( k_s \). As the scan rate is increased, the anodic and cathodic peaks begin to separate. This increasing separation between cathodic and anodic peak potentials as the scan rate is increased is indicative of deviation away from strict Nernstian behavior towards electrochemical irreversibility. Accordingly, the degree of separation for a given scan rate relies on \( k_s \). CV simulation software\textsuperscript{34} provides a reliable means of determining \( k_s \) from the trumpet plot generated by simulating CVs over a range of scan rates. As shown in Figure 8.2, the \( k_s \) values for the formal Co\textsuperscript{2+/+} redox couples of 2-Co and 3-Co are at least an order of magnitude lower (ca. 0.01 cm/s) than those of the subsequent Co\textsuperscript{+0} couples (~0.2 cm/s). This greater kinetic sluggishness of the Co\textsuperscript{2+/+} process may be a result of the requisite dissociation of an axially coordinated solvent ligand (observed in the crystal structure of a Co porphyrin).\textsuperscript{26}

The presence of a hangman group engenders irreversibility in the Co\textsuperscript{+0} couple (Figure 8.3b). The peak potentials become severely dependent on \( \ln v \) as shown in Figure 8.3c, but do not comply with the simple linear dependence predicted by equation 8.3 (Figure 8.3c, dashed line). These observations are consistent with kinetic competition between the heterogeneous ET step (equation 8.1) and the irreversible homogeneous PT (equation 8.2).\textsuperscript{32} As the scan rate is increased, we observe effects attendant to passage into a regime where the ET (along with diffusion) limits the electrochemical response. Although this complication precludes the straightforward determination of \( k_{PT} \) from equation 8.3, the presence of this mixed control permits determination of the kinetic parameters governing both ET and PT steps from a simulation of the dependence of peak potential on scan rate. The peak potential of the slow scan (30 mV/s) voltammogram was substituted into equation 8.3 to obtain an initial estimate of the intramolecular PT rate constant of \( 3 \times 10^6 \) s\textsuperscript{-1}. In addition, the \( k_s \) value of 0.2 cm/s associated with the Co\textsuperscript{+0} couple of 3-Co (Figure 8.2b) was used as an initial approximation for that of the hangman system. These parameters were optimized by CV simulation iteratively until the simulated peak potential over the
range of scan rates agreed with the experimental data, resulting in the fit displayed in Figure 8.5. The results of this fit yielded a heterogeneous ET rate constant of 0.24 cm/s for the reaction represented by equation 8.1 and \( k_{PT} = 8.5 \times 10^6 \text{s}^{-1} \) for the formation of the Co(II)H species via equation 8.2. As expected, deviation away from \( k_s = 0.24 \text{ cm s}^{-1} \) influences the peak potential more at higher scan rates (Figure 8.5, left) whereas deviation away from the optimized \( k_{PT} = 8.5 \times 10^6 \text{s}^{-1} \) influences peak potentials at low scan rates to a greater extent.

In order to shed light on the kinetics that govern H\(_2\) catalysis in the case of the non-hangman complexes, working curves that relate the parameters \( \gamma, \lambda_{PT1} \), and \( \rho \) were generated as follows. A CV was simulated for the case of a catalyst at a specified concentration in the absence of substrate (PhCOOH). The peak current associated with the Co\(^{+}/0\) couple was recorded as \( i_0 \). Next, a CV was simulated for the same catalyst concentration, but with substrate added at an excess factor, \( \gamma \), of 0.5 for a reaction scheme in which \( k_{PT2} \) is 100 times a specified value of \( k_{PT1} (\rho = 100) \). The peak current associated with this voltammogram was recorded as \( i_{cat} \). The normalized current value \( i_{cat}/(i_0 \cdot \gamma) \) was calculated. Varying \( k_{PT1} \) — and thus \( \log(\lambda_{PT1}) \) — while maintaining \( \gamma = 0.5 \) and \( \rho = 100 \), and determining the corresponding \( i_{cat} \) (and therefore \( i_{cat}/(i_0 \cdot \gamma) \) values), furnished the black
This was repeated for $\gamma = 10, 1, 0.1, 0.01, \text{ and } 0.001$ to generate the remaining plots in Figure 8.6a. The maxima in these working curves define the maximum normalized current values attainable, for a specific $\gamma$. The resultant normalized current ratios ($i_{\text{cat}}/i_0 \cdot \gamma$), obtained from the experimental data in Figure 8.4b (designated by horizontal lines in the working curves of Figure 8.6a) are only consistent with equation 8.4 as the rate-limiting step ($\rho \geq 10$), since in the case of 1 mM catalyst concentration, $i_{\text{cat}}/i_0 \cdot \gamma = 2.9$ (Figure 8.6a). In contrast, the maximum value for the cases where $\rho \leq 1$ is 2.7. Notably, since equation 8.4 is rate limiting, the precise value of $\rho$ cannot be determined; the working curves associated with $\rho = 100$ and $\rho = 10$ are almost identical, and the discrepancy between $\rho = 1000$ and $\rho = 100$ can be shown to be even less. For that matter, whereas $k_{\text{PT1}}$ may be determined, $k_{\text{PT2}}$ cannot.

To estimate the value of $k_{\text{PT1}}$, we again generated working curves of $i_{\text{cat}}/i_0 \cdot \gamma$ vs. $\log \lambda_{\text{PT1}}$ based on the $i_{\text{cat}}$ and $i_0$ values extracted from simulated CVs. In this case, we fixed $\rho = 10$ for all simulations (since this furnishes the upper limit for $k_{\text{PT1}}$ compared to all other
\( \rho > 10 \) and varied \( \lambda_{PT1} \) for different values of the excess factor, \( \gamma \) (Figure 8.6b). Therefore, one value of \( \gamma \) is associated with each curve in Figure 8.6b. Experimental \( i_{cat} \) and \( i_0 \) values were then extracted from CVs of a 1.0 mM solution of 3-Co with increasing concentrations of benzoic acid between 0 (affording \( i_0 \)) and 20 mM. Normalized current ratios (\( i_{cat}/i_0\gamma \)) from these CVs give five distinct points on the vertical axis of the \( i_{cat}/i_0\gamma \) vs. \( \log \lambda_{PT1} \) plots in Figure 8.6b (□). Each one of these values corresponds to a point on the specific working curve associated with the benzoic acid concentration (\( \gamma \) value) of that CV. For each point on the working curves, a \( \log \lambda \) value may be determined (grey arrows, Figure 8.6b). Each dimensionless parameter, \( \lambda_{PT1} \), thus obtained permitted the calculation of a discrete value of \( k_{PT1} \) (equation 8.7). The calculated rate constants ranged between \( \sim 400 \) to 1600 M\(^{-1}\) s\(^{-1}\). We thus determined that the intermolecular (2nd order) PT rate constant between benzoic acid and 3-Co in its reduced Co(0) state is on the order of 1000 M\(^{-1}\) s\(^{-1}\). Previous experimental CV data (\( i_0 \) and \( i_{cat} \) values) from the titration of 2-Co with benzoic acid were evaluated in an identical manner to yield a similar intermolecular PT rate constant of \( \sim 2500 \) M\(^{-1}\) s\(^{-1}\) for the reaction between the Co(0) centre in 2-Co and benzoic acid.

### 8.3. Nickel hangman porphyrin H\(_2\) generation electrocatalysis

#### 8.3.1. Results

8.3.1.1. Synthesis and structure of nickel hangman porphyrins

Insertion of nickel into the free-base porphyrin (1) to generate 1-Ni was performed by an 8 – 10 h microwave irradiation of 1 and excess NiBr\(_2\) in a chloroform:methanol solvent mixture (4:1) at 65 °C. Purification was accomplished by column chromatography. Full synthetic procedures are provided in Section 8.5.2, and complete characterization data is published elsewhere.
1-Ni was crystallized by slow evaporation of a dichloromethane-hexane solution of the compound; the crystal structure is shown in Figure 8.7. The distance between the oxygen center of the hangman group and the metal center is 4.510 Å in the solid state. Other structural metrics are similar to those of a similar Co(II) hangman porphyrin possessing mesityl meso-substituents. The distances of the proton of the hanging group to the metal centers are 4.46 Å (Co) and 4.25 Å (Ni), a 0.21 Å difference.

8.3.1.2. Cyclic voltammetry of Ni metalloporphyrins

Cyclic voltammograms (CVs) of 1-Ni and 2-Ni in acetonitrile are shown in Figure 8.8a. The CV of 2-Ni (Figure 8.8d, − black) simply displays two reversible waves centered at −1.39 and −1.96 V, which we ascribe to the formal Ni$^{2+/+}$ (2-Ni/[2-Ni]$^-$) and
Ni\textsuperscript{+/0} (\(\mathrm{[2-Ni]}^+/\mathrm{[2-Ni]}^2\)) redox couples. Electrochemical reversible behavior is also observed for the \(A_4\) porphyrin \(3\)-\(Ni\); the reduction potentials are shifted to more positive potentials as a result of the additional electron-withdrawing \(\text{C}_6\text{F}_5\) substituent. The CV of \(1\)-\(Ni\) (Figure 8.8a, \(\textcolor{red}{\text{red}}\)) displays two reversible waves possessing midpoint potentials of \(-1.37\) V and
–2.01 V that flank an irreversible wave with a peak potential of –1.76 V. By analogy to 2-Ni, we assign the first reversible wave observed in the case of 1-Ni to the formal Ni\(^{2+/+}\) redox couple (i.e., 1-Ni/[1-Ni]\(^-\)) and the second reversible wave to the formal Ni\(^{+0}\) couple.

As described in section 8.2.1.1, variable scan rate voltammetry permits isolation of the standard heterogeneous ET rate constants (k\(_s\)) associated with the electrochemically reversible processes of all complexes. Trumpet plots of the 1-Ni/[1-Ni]\(^-\) peak potentials (blue circles) as a function of the logarithm of the scan rate, shown in Figure 8.8b, furnish a k\(_s\) value of 0.025 cm/s. Owing to the influence of the irreversible wave on the peak potential of the second reversible wave, the k\(_s\) value for the [1-Ni]\(^+\)/[1-Ni]\(^2-\) couple was determined at a later stage from fits to the entire CV (vide infra). Similarly k\(_s\) values were obtained for the 2-Ni/[2-Ni]\(^-\) and [2-Ni]\(^+\)/[2-Ni]\(^2-\) reversible redox couples (both found to be about 0.06 cm/s) and the 3-Ni/[3-Ni]\(^-\) and [3-Ni]\(^+\)/[3-Ni]\(^2-\) couples (0.05 and 0.03 cm/s, respectively).

Titration of 1-Ni with benzoic acid results in the growth of the irreversible wave centered at –1.76 V, which is indicative of an electrocatalytic reaction. Treatment of 1-Ni with solid potassium carbonate in order to deprotonate the pendant acid group results in the elimination of the central irreversible feature (Figure 8.8c, ) as well as a ~70 mV negative shift in the midpoint potential of the first reversible wave to –1.43 V. The midpoint potential of the second reversible wave shifts in the positive direction to approximately –1.88 V following treatment with K\(_2\)CO\(_3\). These data confirm that the middle, irreversible peak is associated with an electrocatalytic reaction involving an acid species along with proton transfer from the hangman group. Titration of the deprotonated 1-Ni with increasing amounts of benzoic acid leads to the return of the irreversible wave (Figure 8.8c, green – dot –) and subsequent growth with increasing benzoic acid concentration (blue and purple traces) is also in agreement with the occurrence of an electrocatalytic reaction involving an acid source. Indeed, chronocoulometry of a 0.4 mM solution of 1-Ni in the presence of 15
mM benzoic acid at –1.77 V leads to the generation of H₂ with a faradaic efficiency of 92% over the course of an electrolysis that passed a total of 20.0 C.

Following treatment of 1-Ni with K₂CO₃ to deprotonate the pendant acid as described above, a batch of this deprotonated hangman porphyrin was titrated with C₆H₅COOH and an identical batch was titrated with C₆H₅COOD. The difference in catalytic peak potential in the case of the two isotopes is plotted as a function of the number of equivalents of acid titrated in Figure 8.9. No isotope effect is observed here, ruling out the possibility of a rate-limiting reaction involving proton transfer.

![Figure 8.9. Plot of difference in catalytic peak potential between C₆H₅COOH- and C₆H₅COOD-titrated 1-Ni (following treatment with K₂CO₃) as a function of the number of acid equivalents introduced.](image)

Titration of 2-Ni with benzoic acid also results in the emergence and growth of an irreversible catalytic wave as shown in Figure 8.8d. However this catalytic feature is offset toward more negative potentials relative to what is observed in 1-Ni. The presence of the pendant proton relay is therefore integral to the observance of a catalytic wave that is markedly shifted toward more positive potentials (i.e., the hangman effect).

8.3.1.3. Spectroelectrochemical analysis of Ni metalloporphyrins

Thin-layer spectroelectrochemical analysis of 3-Ni was undertaken to provide insight into the electronic structure of the Ni(II), Ni(I) and formally Ni(0) states of the...
controlled-potential electrolysis of $[\text{3-Ni}]$– in acetonitrile at $–1.3\ \text{V}$ cleanly generates the spectrum of $[\text{3-Ni}]$– with good isosbestic points (Figure 8.10a). Electrolysis at $–1.9\ \text{V}$ generates the spectrum of the two-electron reduced species, $[\text{3-Ni}]^{2–}$ (Figure 8.10b). The absorption spectrum of $\text{3-Ni}$ is quantitatively recovered upon electrolysis at $0\ \text{V}$ following the generation of $[\text{3-Ni}]^{2–}$, supporting the CV data that indicates that the reduction processes are reversible. The UV-vis absorption spectra of the three species are shown in Figure 8.10c.

**8.3.1.4. Density functional theory (DFT) computational studies**

Density functional theory (DFT) calculations (see Section 8.5.2 on the computational method) were used to probe the electronic structure of the compounds in the different oxidation states. For computational tractability, the tert-butyl groups on the xanthene backbone and pentafluorophenyl meso-substituents of the porphyrin ring were truncated to methyl groups and chlorine atoms, respectively. These truncations were chosen based on Hammett constants$^{36}$ of similar values (see Section 8.5.2), and we have

---

*Figure 8.10.* Thin layer spectroelectrochemistry of 0.3 mM NiTFPP in 0.1 M TBAPF$_6$ in MeCN during electrolysis at (a) $–1.3\ \text{V}$ and (b) $–1.9\ \text{V}$ vs. Fc$^+/\text{Fc}$. Spectra were acquired every 8 seconds during electrolysis. Initial spectra are represented by black traces, and final spectra are in (a) red, and (b) green. (c) UV-vis absorption spectra of $\text{3-Ni}$ (dark gray), $[\text{3-Ni}]^–$ (red), and $[\text{3-Ni}]^{2–}$ (blue) in 0.1 M TBAPF$_6$ in acetonitrile obtained using thin layer spectroelectrochemistry.
exploited this protocol successfully in recent studies to compute the equilibrium potentials of intermediates involved in homogeneous hydrogen evolution.\textsuperscript{37}

From our calculations, we find that the Ni(II) closed shell singlet of the 3-Ni resting state is 8.5 kcal/mol lower in energy than the triplet. In addition, upon reduction to [3-Ni]\textsuperscript{−} the results of calculations using five different functionals (Table 8.1) all agree that the spin density on Ni is near unity, suggesting that the unpaired electron is localized on the nickel

**Table 8.1. Calculated spin density on Ni of [3-Ni]\textsuperscript{−}**

<table>
<thead>
<tr>
<th>Functional</th>
<th>Spins</th>
<th>Gas-Phase Geometries</th>
<th>Solvated Geometries</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3P86</td>
<td>0.00</td>
<td>1.010179</td>
<td>0.936177</td>
</tr>
<tr>
<td>B3LYP</td>
<td>0.00</td>
<td>1.017783</td>
<td>0.948812</td>
</tr>
<tr>
<td>TPSSh</td>
<td>0.00</td>
<td>1.060435</td>
<td>0.988065</td>
</tr>
<tr>
<td>ωB97xD</td>
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<td>0.984440</td>
<td>0.924697</td>
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<tr>
<td>M06L</td>
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<td>1.070799</td>
<td>1.017061</td>
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**Table 8.2. Calculated relative Free Energies and spin density (SD) on Ni of [3-Ni]\textsuperscript{2−}**

<table>
<thead>
<tr>
<th>Functional</th>
<th>S</th>
<th>Relative Energy (kcal/mol)</th>
<th>SD on Ni</th>
<th>Relative Energy (kcal/mol)</th>
<th>SD on Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3P86</td>
<td>0</td>
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<td>0.000000</td>
<td>0.00</td>
<td>0.000000</td>
</tr>
<tr>
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<tr>
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<td>1.098609</td>
<td>−10.27</td>
<td>1.036479</td>
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</table>
center. DFT calculations on the doubly reduced molecule \([3\text{-Ni}]^{2-}\) with 7 different functionals (Table 8.2) all show that only one electron is localized on Ni, and the triplet state is lower in energy than the closed shell singlet.

Figure 8.11 displays the singly occupied molecular orbitals (SOMOs) calculated for \([3\text{-Ni}]^-\) (Figure 8.11a) and \([3\text{-Ni}]^{2-}\) (Figures 8.11b and 8.11c), showing that in the case of the monoanion \((S = \frac{1}{2})\), the electron is localized primarily on the \(\sigma^*(d_{x^2-y^2})\) orbital of the Ni center, whereas subsequent reduction to the dianion \((S = 1)\) leads to the highest energy SOMO possessing electron density primarily localized on the porphyrin ligand while the other SOMO resembles the SOMO for \([3\text{-Ni}]^{2-}\).

**Figure 8.11.** Calculated (B3P86 solvated phase; IsoValue: 0.05): (a) singly occupied molecular orbital (SOMO) of \([3\text{-Ni}]^-\) showing electron density localized on the nickel center. (b) SOMO and (c) SOMO–1 of \([3\text{-Ni}]^{2-}\) showing that the second electron is localized primarily on the ligands.

8.3.2. Discussion

Nickel porphyrins display higher catalytic activity for H\(_2\) evolution than Co porphyrins; catalytic waves are shifted towards more positive potentials in 1–3 Ni relative to those observed with 1–3 Co. We therefore set out to identify the mechanistic basis for these disparities in intrinsic activity. While the solid-state structures for cobalt and nickel hangman porphyrins (Figure 8.7) are very similar, one minor difference in the crystallographic structures of these two molecules is the presence of an apical (acetone) ligand bound to cobalt. The absence of an apical ligand in the Ni complex is a result of the \(d^8\) electron count of the nickel; consequently the \(d_{z^2}\) orbital is fully populated and thus
unavailable for interaction with an apical ligand. The 0.21 Å difference in M–H distance is a result of a larger tilt angle of the xanthene relative to the porphyrin ring for the cobalt porphyrin (13.9° for Co, 7.1° for Ni), which positions the hanging group farther from the Co center. We believe this difference is likely due to packing effects in the solid state and thus of little consequence of the molecule’s behavior in solution. Thus differences in subsequent HER chemistry between the Co and Ni complexes is attributed to electronic effects and not to an inherent structural difference between the two complexes.

The greater kinetic facility of the Ni^{2+/+} reduction (Figure 8.8b; \( k_s = 0.025 \text{ cm/s} \)) relative to the Co^{2+/+} reduction (Figure 8.2b; 0.01 cm/s) may be attributed to the requisite dissociation of a solvent (acetonitrile) ligand that is axially coordinated to the low-spin \( d^7 \) Co^{2+} molecule as observed in the solid-state. No axial ligand is expected from our theoretical computations nor observed in the solid-state structure (Figure 8.7) of the low-spin \( d^8 \) Ni^{II} species.

The CV characteristics displayed in Figures 8.8a and 8.8c—specifically the two reversible waves, one irreversible wave, following 1-Ni reduction—are reminiscent of what Savéant classifies as “total catalysis.” This term denotes a mechanistic regime wherein owing to a high catalytic rate and/or a dearth of reactant, the rate of reactant consumption is very rapid, leading to control of the electrocatalytic response by diffusion of the reactant from the bulk electrolyte. This behavior results in the presence of two waves: (1) an irreversible wave involving the reactant-diffusion-controlled catalytic process, followed by (2) a reversible wave associated with the molecular catalyst, centered at the potential where it appears in the absence of reactant. The catalytic rate constant influences the peak potential of the irreversible wave, but not the peak current. In the case of 1-Ni, notwithstanding the absence of exogenous benzoic acid, one equivalent of acid from each hangman porphyrin is available. These acid functional groups should permit \( \text{H}_2 \) production, and catalytic turnover would regenerate the [1-Ni]^{-} state. Hence, we infer that
the second reversible wave involves the formal Ni$^{+0}$ reduction of the molecule in its deprotonated (i.e. hanging carboxylate group) state. We ascribe the positive shift in the second reduction potential upon addition of potassium carbonate (Figure 8.8c) to the greater stabilizing effect of the smaller and likely ion-paired K$^+$ counter cations present in this case, compared to tetrabutylammonium cations that serve to provide charge balance upon electrochemical reduction. The effect of the more charge dense potassium ions would be pronounced particularly in the reduction to the highly charged deprotonated and doubly reduced state.

Spectroelectrochemical interrogation (Figure 8.10) of the reversible electrochemistry of 3-Ni provides insight into the electronic structure of the complex upon reduction to [3-Ni]$^-$ and [3-Ni]$^{2-}$. Upon electrolysis of a solution of 3-Ni at $-1.3$ V vs. Fc$^+$/Fc, the spectrum of [3-Ni]$^-$ is obtained (Figure 8.10a). The bathochromic shift and concomitant loss of intensity of the Soret band along with the growth of new bands at 358 nm and 608 nm are consistent with spectra obtained by Savéant and coworkers for the one-electron reduction products of similar Ni porphyrins that were assigned as formal Ni(I) species based on UV-vis absorption and ESR data. These data therefore support the contention that the first reduction of 3-Ni to [3-Ni]$^-$ is metal-centered. Upon electrolysis at $-1.9$ V, in order to doubly reduce 3-Ni, we observe the growth of a broad absorption band at 615 nm that extends into the near-infrared region (Figure 8.10b), which is consistent with a ligand-centered second reduction to form [3-Ni]$^{2-}$. These spectroscopic data are validated by DFT computational results (Figure 8.11) which show that the Ni$^{2+/+}$ reduction reaction involves ET to a Ni-based orbital, and subsequent reduction to the formally Ni$^0$ complex entails the reduction of the ligand. The fact that these results are reached irrespective of the type of functional used (Tables 8.1 and 8.2), gives us confidence in our computations.
The electrocatalytic generation of hydrogen from the \([\text{1-Ni}]^-\) resting state must proceed through an initial step consisting of either one of two stepwise PCET pathways or a concerted one (Figure 8.12). Insight into the operative PCET pathway comes from modeling the CV responses in concert with using the insights garnered from DFT computations as a guide. We computed the equilibrium potentials, \(E_{\text{eq}}\), of plausible intermediates using the experimentally determined Ni\(^{2+/+}\) reduction potential of \(\text{1-Ni}\) (\(i.e. -1.37\) V) as a reference value (Table 8.3). The correspondence between experimental and computed equilibrium potentials of non-hangman porphyrins \(\text{2-Ni}\) and \(\text{3-Ni}\) is very satisfying, and gives us confidence in the relevance of the computational results. Moreover, the computed reduction potential for a putative Ni\(^{II}\)H intermediate (calculated as \(-1.84\) V) is found to lie between the reduction potentials of \(\text{1-Ni}\) and \([\text{1-Ni}]^-\), within our voltage sweep window. As such, a subsequent reduction of this Ni\(^{II}\)H to Ni\(^{I}\)H could be favored. Theoretical studies on the mechanism of hydrogen production by cobaloximes have revealed that the equilibrium potential of the Co\(^{II}\)/Co\(^{I}\) couple in those systems also lies between that of Co\(^{2+/+}\) and Co\(^{+/0}\).

**Figure 8.12.** Stepwise (ETPT and PTET) and concerted (CPET) proton-coupled electron transfer pathways from \([\text{1-Ni}]^-\) leading to the generation of a formally Ni(II) hydride, \([\text{1-NiH}]^2-\). HOOC--NiP is synonymous with \(\text{1-Ni}\), indicating the presence of a proton on the carboxylate group in the second coordination sphere of the Ni\(^{2+}\) metal center.
We first set out to determine whether the ETPT framework that is operative in the case of 1-Co (Section 8.2) could account for the electrocatalytic behavior manifest in Figures 8.8a and 8.8c. In the context of such an ETPT mechanism (top route of Figure 8.12), three critical parameters that control the electrochemical response are: (1) the reduction potential of [1-Ni]−, (2) the associated standard heterogeneous ET rate constant, and (3) the rate of the subsequent intramolecular PT. The experimentally measured equilibrium potential and standard heterogeneous ET rate constant of the non-hangman analog (i.e., the [2-Ni]−/[2-Ni]2− couple, which possesses $E^0 = -1.96$ V and $k_s = 0.06$ cm/s) provide an estimate for (1) and (2). However, this still leaves the intramolecular PT rate constant (3) as well any equilibrium/rate constant and reduction potential values associated with follow up reactions (such as the protonation of a hydride to evolve H2) as unknowns. If these are fast and post-rate-limiting they will not influence the electrokinetic response.

### Table 8.3. Computed reduction potentials of nickel hangman porphyrins

<table>
<thead>
<tr>
<th>Oxidized Species</th>
<th>$S_{ox}$</th>
<th>Reduced Species</th>
<th>$S_{red}$</th>
<th>$E^0 / V$ (vs. Fc+/Fc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOOC--NiP</td>
<td>0</td>
<td>[HOOC--NiP]−</td>
<td>1/2</td>
<td>−1.37 (−1.37)</td>
</tr>
<tr>
<td>[HOOC--NiP]−</td>
<td>1/2</td>
<td>[HOOC--NiP]2−</td>
<td>1</td>
<td>−1.85</td>
</tr>
<tr>
<td>[OOC--NiP]−</td>
<td>0</td>
<td>[OOC--NiP]2−</td>
<td>1/2</td>
<td>−1.40 (−1.43)</td>
</tr>
<tr>
<td>[OOC--NiP]2−</td>
<td>1/2</td>
<td>[OOC--NiP]3−</td>
<td>1</td>
<td>−2.01 (−1.99)</td>
</tr>
<tr>
<td>[OOC--Ni(H)P]−</td>
<td>1/2</td>
<td>[OOC--Ni(H)P]2−</td>
<td>1</td>
<td>−0.81</td>
</tr>
<tr>
<td>[OOC--Ni(H)P]2−</td>
<td>1</td>
<td>[OOC--Ni(H)P]3−</td>
<td>3/2</td>
<td>−1.84</td>
</tr>
</tbody>
</table>

Calculation were performed with DFT using the B3P86 functional, 6-31+G(d), and 6-31+G(d,p) basis sets, and C-PCM solvation. Geometries were optimized in solution. Experimental midpoint potential ($E_{1/2}$) values are given in parentheses. These experimental and computational values are the same by construction since this is the reference reaction used in computation. This reduced species refers to the formally Ni(I) hydride; the spin density on nickel remains ~2, indicating that the reduction is ligand-based.
As in the case for the one-electron ET reactions, CV simulation is a powerful tool for gaining mechanistic insight in homogeneous electrocatalytic reactions, especially in cases where substrate limitation cannot be avoided. In the case of 1-Co, we used CV simulation to construct working curves (Section 8.2.2) from which we extracted kinetic information. Here, we use CV simulation more directly, since we have catalytic waves are well-separated from the redox waves that are obtained in the absence of substrate (Figures 8.8a,c). CV simulations of an ETPT pathway using the aforementioned parameters are shown in Figure 8.13a and 8.13b. In these simulations, we also assumed that all bimolecular reactions proceed at the diffusion limit with a rate constant on the order of $10^{10}$ M$^{-1}$ s$^{-1}$. Moreover, the intramolecular rate constant, $k_{PT}^{intra}$ is set to $10^{13}$ s$^{-1}$, such that it is many orders of magnitude faster than the bimolecular reactions (i.e., we ensure that the product of the diffusion-limited rate constant, $10^{10}$ M$^{-1}$ s$^{-1}$, and the concentration of the catalyst/substrate (<1 mM) will be much less than $k_{PT}^{intra}$). We also set the reduction potential of the Ni$^{II}$H that is formed by protonation of the formally Ni$^{0}$ species to be equal

![Figure 8.13](image.png)

**Figure 8.13.** Experimental (thick yellow-green curves) and simulated (thin red curves) cyclic voltammograms of a 0.4 mM solution of 1-Ni at a scan rate of (a, c) 30 mV/s. and (b) 3 V/s. Voltammograms were simulated according to a mechanistic framework consisting of an ETPT pathway (Figure 8.12) from 1-Ni$^+$ to [1-NiH]$^{2-}$, followed by reduction to the formally Ni(I) hydride, [1-NiH]$^{3-}$, which is subsequently protonated by the pendant acid group of another porphyrin molecule to liberate H$_2$. Parameters used in simulation of (a) and (b) are tabulated in Table 8.4. Parameters pertinent to simulation (c) are tabulated in Table 8.5.
to \(-1.4\) V, close to that of the Ni\(^{2+/+}\) reduction potential. This value is considerably more positive than the potential at which catalysis is observed (\(ca.\ -1.76\) V) and also more positive than that computed by DFT (\(-1.84\) V).

These parameters (Tabulated in Table 8.4) were specifically chosen in order to be representative of a best-case scenario for the ETPT mechanism. These governing factors will lead to the most positive peak potentials possible for an ETPT process, which proceeds through the \([1-Ni]^{2-}\) intermediate: in a reaction scheme governed by these parameters the most negative reduction potential is that of \([1-Ni]^{+}/[1-Ni]^{2-}\) and all bimolecular reactions proceed at the diffusion limit. Even though the resulting simulation reveals a

<table>
<thead>
<tr>
<th>Oxidized Species</th>
<th>Reduced Species</th>
<th>(E_{\text{sim}}^0)</th>
<th>(k_s / \text{cm s}^{-1})</th>
</tr>
</thead>
<tbody>
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<td>[HOOC--NiP](^+)</td>
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</tr>
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<td>0.05(^d)</td>
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<table>
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<th>(k_{\text{forward}})</th>
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<td>[OOC--NiP(H)](^3-) + [OOC--NiP](^2-)</td>
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<td>(k_{\text{diff}}^f)</td>
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<td>[OOC--NiP(H)](^3-) + acid(^g)</td>
<td>H(_2) + [OOC--NiP](^2-) + conjugate base</td>
<td>(&gt;10^6)</td>
<td>(k_{\text{diff}}^f)</td>
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\(^a\) Reduction potentials are relative to the reduction potential of Fc\(^+\). Values in italics are obtained by from simulating experimental CV data. \(^b\)Values estimated from that of non-hangman compound 2-Ni. \(^c\) Value determined from treatment of 1-Ni with potassium carbonate, and further refined by simulating shoulder near anodic return peak of 1-Ni/[1-Ni]\(^+\) wave. \(^d\) Value set equal to that obtained from trumpet plots of the corresponding protonated species. \(^e\) These equilibrium constants are governed by the difference in reduction potentials of the two sets of species. \(^f\) The forward rate constants of these downhill reactions are assumed to be the diffusion limited rate constant: \(10^{10}\) M\(^{-1}\) s\(^{-1}\). \(^g\) All nickel porphyrins with protonated hanging groups are permitted as acid sources in the model.
voltammogram that displays the general “total catalysis” behavior, the ETPT model leads
to voltammetric features that are not fully coincident with the experimental results (Figure
8.13a); anticipated peak potentials are too negative and peak current values remain too low
to account for the experimental result. These observations are conserved over a scan rate
range of two orders of magnitude (Figure 8.13b).

To explore the possibility of this ETPT mechanism further, we also simulated CVs
using the computed \([1-\text{Ni}]^-/1-\text{Ni}^2-\) and \([1-\text{Ni}]^2-/1-\text{Ni}^3-\) \(E^\circ\) values (−1.85 and −1.84 V, respectively Table 8.3) as opposed to using that of the non-hangman analog. The resulting
simulated voltammogram is shown in Figure 8.13c. Using these computed parameters a

Table 8.5. CV Simulation Parameters for ETPT mechanisms using DFT-computed
\([1-\text{Ni}]^-/1-\text{Ni}^2-\) reduction potential.

<table>
<thead>
<tr>
<th>Oxidized Species</th>
<th>Reduced Species</th>
<th>(E^\circ_{\text{sim}})</th>
<th>(k_s / \text{cm s}^{-1})</th>
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<tr>
<th>Reactants</th>
<th>Products</th>
<th>(K_q)</th>
<th>(k_{\text{forward}})</th>
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<td>([\text{OOC--NiP(H)}^2^-]^-)</td>
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<td>([\text{OOC--NiP(H)}^3^-]^-) + ([\text{OOC--NiP}^2^-]^-)</td>
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<td>([\text{OOC--NiP(H)}^3^-]^-) + acid(^h)</td>
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<td>(&gt;10^6)</td>
<td>(k_{\text{diff}})</td>
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</table>

\(a\) Reduction potentials are relative to the reduction potential of \(\text{Fe}^{2+}\). Values in italics are obtained by from
simulating experimental CV data. \(^b\) Value computed using DFT (Table 8.3). \(^c\) Value estimated from that
of non-hangman compound \(2-\text{Ni}\). \(^d\) Value determined from treatment of \(1-\text{Ni}\) with potassium carbonate,
and further refined by simulating shoulder near anodic return peak of \(1-\text{Ni}^[1-\text{Ni}]^\circ\) wave. \(^e\) Value set equal
to that obtained from trumpet plots of the corresponding protonated species. \(^f\) These equilibrium constants
are governed by the difference in reduction potentials of the two sets of species. \(^g\) The forward rate
constants of these downhill reactions are assumed to be the diffusion limited rate constant: \(10^{10}\) \text{M}^{-1} \text{s}^{-1}. \(^h\)
All nickel porphyrins with protonated hanging groups are permitted as acid sources in the model.
much slower intramolecular PT rate constant of 2000 s⁻¹ is needed to replicate the peak potential of the irreversible catalytic wave (Table 8.5). However, the simulations show that additional peaks expected at 30 mV in the return sweep are inconsistent with experimental data (Figure 8.13c). Thus, simulations of the ETPT pathway under any reasonable fitting condition do not match the experimental CVs of 1-Ni. We therefore turned our attention to the interrogation of the PTET and CPET mechanisms displayed in Figure 8.12.

To assist in differentiating between the PTET and CPET mechanisms, we set out to measure the H/D isotope effect. In the case of the PTET mechanism, no significant isotope is expected since the proton transfer exists in a rapid pre-equilibrium, and any equilibrium isotope effect is expected to be too small to lead to a detectable change in peak position. In contrast, any change in the standard CPET rate constant, \( k_{\text{CPET}} \), associated with H–D isotopic substitution would lead to a shift in peak position if that reaction were to be the rate-determining step. Indeed, as shown by CV simulations (Figure 8.14, Table 8.6) a
CPET-based framework accommodates the voltammetric behavior of 1-Ni, but the catalytic peak potential is very sensitive to $k_{CPET}$. Since we do not observe a significant isotope effect (Figure 8.9), we consider a rate-limiting concerted pathway to be unlikely. Instead, these data are consistent with the occurrence of a stepwise PTET from [1-Ni]$^-$ to form the formally Ni(II)H intermediate (top route of Figure 8.12). We note that we cannot entirely rule out the possibility of a rapid, reversible non-rate-limiting CPET at this time. In this case, isotopic substitution and consequent alteration of the heterogeneous rate constant would not give rise to a change in peak potential at these relatively slow scan rates. Additional computational studies are

<table>
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<th>Oxidized Species</th>
<th>Reduced Species</th>
<th>$E^\circ_{sim}$</th>
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<tr>
<td>HOOC--NiP</td>
<td>[HOOC--NiP]$^-$</td>
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<td>0.025(^b)</td>
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<td>[HOOC--NiP]$^-$</td>
<td>[HOOC--NiP]$^{2-}$</td>
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<td>0.06(^c)</td>
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<td>[HOOC--NiP]$^-$</td>
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<td>[OOC--Ni(H)P]$^{2-}$</td>
<td>[OOC--Ni(H)P]$^{3-}$</td>
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<td>0.05(^b)</td>
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<table>
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<tr>
<th>Reactants</th>
<th>Products</th>
<th>$K_q$</th>
<th>$k_{forward}$</th>
</tr>
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<tr>
<td>[OOC--NiP(H)]$^{2-}$ + [OOC--NiP]$^{3-}$</td>
<td>[OOC--NiP(H)]$^{3-}$ + [OOC--NiP]$^{2-}$</td>
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<td>$k_{diff}$(^g)</td>
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<td>$&gt; 10^5$</td>
<td>$k_{diff}$(^g)</td>
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</table>

\(^a\) Reduction potentials are relative to the reduction potential of Fc'/Fc. \(^b\) Obtained from simulating experimental CV data. \(^c\) Values estimated from that of non-hangman compound 2-Ni. \(^d\) Value determined from treatment of 1-Ni with potassium carbonate, and further refined by simulating shoulder near anodic return peak of 1-Ni/1-Ni$^-$ wave. \(^e\) Value set equal to that obtained from trumpet plots of the corresponding protonated species. \(^f\) These equilibrium constants are governed by the difference in reduction potentials of the two sets of species. \(^g\) The forward rate constants of these downhill reactions are assumed to be the diffusion limited rate constant: $10^{10}$ M$^{-1}$ s$^{-1}$. \(^h\) All nickel porphyrins with protonated hanging groups are permitted as acid sources in the mechanism.
required to explore this possibility while considering the various potential proton-acceptor sites of the molecule.

Simulations of the PTET pathway are successful in replicating the experimental data with good fidelity as shown in Figure 8.15. Simulation parameters are provided in Table 8.7, and these values provide estimates of the thermodynamic and kinetic parameters that govern catalysis. According to these CV simulations, an intramolecular PT from the

![Figure 8.15](image)

**Figure 8.15.** Experimental (thick light-brown curves) and simulated (thin blue curves) cyclic voltammograms of a 0.4 mM solution of 1-Ni at a scan rate of (a) 30 mV/s, (b) 300 mV/s and (c) 10 V/s. Voltammograms were simulated according to a mechanistic framework consisting of an PTET pathway (Figure 8.11) from [1-Ni] to [1-NiH]2-, followed by reduction to [1-NiH]3-, which is subsequently protonated by the pendant acid group of another porphyrin molecule to liberate H2. Parameters used in simulation are tabulated in Table 8.7. (d) Variation of the experimental peak potential of the irreversible catalytic wave of 1-Ni as a function of scan rate (green circles) compared to the variation observed from simulated CVs (blue trace).
Ni$^+I$ resting state leads to a formal Ni$^{III}H$ species, which exists in minor equilibrium. Subsequent ET furnishes Ni$^{II}H$, followed by another reduction to Ni$IH$. Protonation of the hydride by an acid source produces H$_2$ in a facile step.

The only ET step for which there is poor agreement between the computed equilibrium potential (-0.81 V) and experiment/simulation (ca. -1.57 V) is for the Ni$^{III}H$ to Ni$^{II}H$ reduction. The DFT calculations only considered cases where the proton acceptor is transferred to the metal center; the disparity between CV simulation (Table 8.7) and computation (Table 8.3) in this single reduction potential value thus suggests that the proton may not transfer directly to the metal center but rather to the macrocycle. In this

<table>
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<th>Parameters used in simulating PTET-based pathway</th>
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**Heterogeneous/Electrochemical Reactions:**

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<td>HOOC--NiP</td>
<td>[HOOC--NiP]$^-$</td>
<td>-1.37</td>
<td>0.025$^b$</td>
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<td>[HOOC--NiP]$^-$</td>
<td>[HOOC--NiP]$^{2-}$</td>
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<td>0.06$^c$</td>
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<td>0.025$^e$</td>
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**Homogeneous/Chemical Reactions:**

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<td>$&gt; 10^5$ $^b$</td>
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<td>[OOC--NiP(H)]$^{+}$ + [OOC--NiP]$^{3-}$</td>
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<td>$1.25 \times 10^{7}$ $^f$</td>
<td>$k_{\text{diff}}$ $^g$</td>
</tr>
<tr>
<td>[OOC--NiP(H)]$^{2-}$ + [OOC--NiP]$^{3-}$</td>
<td>[OOC--NiP(H)]$^{3-}$ + [OOC--NiP]$^{2-}$</td>
<td>$4.74$ $^f$</td>
<td>$k_{\text{diff}}$ $^g$</td>
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<td>[OOC--NiP(H)]$^{3-}$ + acid $^h$</td>
<td>H$_2$ + [OOC-NiP]$^{2-}$ conjugate base</td>
<td>$&gt; 10^5$</td>
<td>$k_{\text{diff}}$ $^g$</td>
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</tbody>
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$a$ Reduction potentials are relative to the reduction potential of Fe/Fe$^+$. $^b$ Obtained from simulating experimental CV data. $^c$ Values estimated from that of non-hangman compound 2-Ni. $^d$ Value determined from treatment of 1-Ni with potassium carbonate, and further refined by simulating shoulder near anodic return peak of 1-Ni/1-Ni$^{-1}$ wave. $^e$ Value set equal to that obtained from trumpet plots of the corresponding protonated species. $^f$ These equilibrium constants are governed by the difference in reduction potentials of the two sets of species. $^g$ The forward rate constants of these downhill reactions are assumed to be the diffusion limited rate constant: $10^{10}$ M$^{-1}$ s$^{-1}$. $^h$ All nickel porphyrins with protonated hanging groups are permitted as acid sources in the mechanism.
vein, one might envision a possible initial PT to the macrocycle, followed by ET reduction along with a concerted intramolecular PT (a net PT-CPET process) to the metal center. Our CV data would be consistent with this pathway as well. Efforts to explore such alternative proton accepting sites and alternative mechanisms they might give access to are underway. Nevertheless, at this stage, the PTET pathway described above is the most compelling pathway for H₂ evolution by Ni hangman complexes.

8.4. Conclusion

Co and Ni porphyrins are capable of mediating the HER in non-aqueous electrolytes. A comparison between the PCET kinetics of Co hangman porphyrin 1-Co and non-hangman systems 2-Co and 3-Co forms the basis for establishing the hangman effect. We find that the pendant proton relay in Co hangman porphyrins serves to facilitate a rapid intramolecular proton transfer with a rate constant on the order of 8.5 × 10⁶ s⁻¹ in a stepwise ETPT process. The rapid intramolecular proton transfer provides a facile pathway for the formation of a Co(II)H intermediate. By comparison to the intermolecular PT kinetics of non-hangman porphyrins (kₚₜ ~1000 M⁻¹s⁻¹), our results indicate that the presence of a pendant proton relay proximate to the metal center gives rise to a rate enhancement that is equivalent to an effective benzoic acid concentration >3000 M.

Interrogating the PCET kinetics of Ni hangman porphyrins reveals that substitution of Ni for Co leads to a change in mechanism, involving a stepwise PTET pathway for the formation of a formally Ni⁰H intermediate by protonation of Ni¹ followed by reduction. In cobalt porphyrins, the Co¹ state is not protonated and only after Co⁰ is formed does the proton transfer to produce Co²H. In previous work, it has been shown that a PTET pathway for 1-Co may be realized but only when strong acids such as p-toluenesulfonic (tosic) acid are employed²⁹ The hangman effect in Ni porphyrins is associated with the facilitation of this PTET mechanism. Indeed since Ni-based catalysis avoids generation of the formally metal(0) species, the nickel porphyrin offers an improvement in catalytic activity over the
cobalt analogue. Computational and spectroelectrochemical results are consistent with the reduction of NiI involving porphyrin ligand-based orbitals, such that the NiI species is truly a NiI-porphyrin radical. Future studies might shed more light on the nature of the “hydrides” formed during these PCET reactions and the possible role of the ligand as the primary proton acceptor. Such studies could shed more light on the requirements for facile H2 evolution through PCET.

8.5. Experimental Methods

8.5.1. Co metalloporphyrin studies

**Materials.** Catalysts 1-Co, 2-Co, and 3-Co were prepared following already published procedures. Benzoic acid (≥99.5%) and tetrabutylammonium hexafluorophosphate (TBAPF6, ≥99.0%) were purchased from Aldrich and used as received.

**Electrochemical Studies.** Electrochemical measurements were performed on a CH Instruments (Austin, Texas) 760C Electrochemical Workstation using CHI Version 10.03 software. Cyclic voltammetry (CV) experiments were conducted in a nitrogen-filled glovebox at 295 K using a CH Instruments glassy carbon button working electrode (area = 0.071 cm²), BASi Ag/AgCl reference electrode, and Pt mesh counter electrode in 0.2 M TBAPF6 acetonitrile solutions 4 mL total volume. Acetonitrile was previously dried by passage through an alumina column under argon. Peak potential values were compensated for solution resistance and were referenced to ferrocenium/ferroene (Fc+/Fc) couple by recording the CVs of the complexes in the presence of a small amount of ferrocene. Appropriate background scans were subtracted from all CVs. Solutions were stirred between acquisition of individual CVs and the working electrode was polished before each measurement.
For the concentration dependence experiment of the 1-Co irreversible EC wave (Figure 8.3a), a 1 mM solution of porphyrin 1-Co in 0.2 M TBAPF$_6$ was prepared and was successively diluted with electrolyte solution to afford 0.75, 0.5, and 0.25 mM solutions. The CV of the solution was recorded at each concentration using the three different scan rates shown in Figure 8.3a.

For the acid titration of 3-Co (Figure 8.4a), to a 0.1 mM 3-Co solution in 0.2 M TBAPF$_6$ electrolyte, 2, 10, and 12 $\mu$l of a 100 mM benzoic acid solution in 0.2 M TBAPF$_6$ were successively added to give 0.05, 0.3, and 0.6 mM benzoic acid concentrations. The change in the total volume of the sample, and thus, in the 3-Co concentration, was negligible. The CV of the solution was recorded after each addition.

For the titration experiment of a 1 mM 3-Co solution with benzoic acid that was used in Figure 8.6b, stock solutions of 2 mM 3-Co in 0.2 M TBAPF$_6$ and 100 mM benzoic acid in 0.2 M TBAPF$_6$ were prepared and appropriate volumes from these two were mixed with electrolyte solution to give a final volume of 4 mL and solutions consisting of 1 mM 3-Co with 0.5, 1, 3, 6, and 20 mM benzoic acid. The CV of the solution was recorded at the beginning for the acid free sample to get the $i_0$ value, and after the benzoic acid addition to get the associated $i_{cat}$ value. A similar procedure was followed for 3-Co concentrations of 0.3 and 1.0 mM.

For the titration experiment of a 1 mM 3-Co solution with benzoic acid that was used in Figure 8.6b, stock solutions of 2 mM 3-Co in 0.2 M TBAPF$_6$ and 100 mM benzoic acid in 0.2 M TBAPF$_6$ were initially prepared. 2 mL of the 2 mM 3-Co solution were diluted with electrolyte until final volume 4 mL to give a 1 mM 3-Co sample. The CV of this acid free solution was recorded to obtain the $i_0$ value. Appropriate volumes from the two stock solutions were mixed with electrolyte until final volume 4 mL to give the corresponding 1 mM 3-Co solutions with 0.5, 1, and 3 mM benzoic acid. To the latter (i.e. 3 mM) solution, 1.5 and 6.8 mg of benzoic acid was successively added to afford solutions
comprising 6 and 20 mM acid concentrations. The CVs of all the above acidic solutions were recorded to get the corresponding $i_{\text{cat}}$ values.

**CV simulation and generation of working curves.** All simulated CVs were calculated using the DigiElch software package. Diffusion coefficients of compounds were determined straightforwardly from the peak currents of reversible waves, and these values were used in the applicable simulations. Symmetry factors ($\alpha$ values) were set as 0.5 for all ET steps. The working curves shown in Fig. 8.6a were generated as follows: using the experimentally determined heterogeneous ET rate constants, a CV was simulated for the case of a catalyst at a specified concentration in the absence of substrate (PhCOOH). The peak current associated with the Co$^{+0}$ couple was recorded as $i_{\text{cat}}$. Next, a CV was simulated for the same catalyst concentration, but with substrate added at an excess factor, $\gamma$, of 0.5 for a reaction scheme in which $k_{\text{PT2}}$ is 100 times a specified value of $k_{\text{PT1}}$ ($\rho = 100$). The peak current associated with this voltammogram was recorded as $i_{\text{cat}}$. The normalized current value $i_{\text{cat}}/i_{\text{cat}}\gamma$ was calculated. Varying $k_{\text{PT1}}$ (and thus, according to Eq. 7, log $\lambda_{\text{PT1}}$) and determining the corresponding $i_{\text{cat}}$ (and therefore $i_{\text{cat}}/i_{\text{cat}}\gamma$) values, furnished the black curve in Fig. 8.6a. Although this may also be achieved by modulating other variables (i.e. T, v, or [3-Co]bulk) as described by equation 8.7 in the text, alteration of any other variable would also require simulation of a new CV in the absence of substrate to acquire a new $i_0$. As $k_{\text{PT1}}$ was altered, $k_{\text{PT2}}$ was set to the appropriate value fixed by the desired ratio of $k_{\text{PT2}}$ to $k_{\text{PT1}}$, $\rho$ (Equation 8.8). This was repeated for $\rho = 10$, 1, 0.1, 0.01, and 0.001 to generate the remaining plots in Figure 8.6a.

The working curves shown in Fig. 8.6b were generated as follows: using the experimentally-determined heterogeneous rate constants a CV was simulated for the case of a catalyst at a specified concentration in the absence of substrate (PhCOOH). The peak current associated with the Co$^{+0}$ couple was recorded as $i_0$. Next, a CV was simulated for the same catalyst concentration, but with substrate added at an excess factor, $\gamma$, of 0.5 for a reaction scheme in which $k_{\text{PT2}}$ is 10 times a specified value of $k_{\text{PT1}}$ ($\rho = 10$). The peak current associated
with this voltammogram was recorded as $i_{\text{cat}}$. Thus, the normalized current value $i_{\text{cat}} / i_{\text{cat}'}$ was calculated. Varying $k_{PT1}$ (and thus, according to Equation 8.7, $\log \lambda_{PT1}$), and determining the corresponding $i_{\text{cat}}$ (and therefore $i_{\text{cat}} / i_{\text{cat}'}$) values, furnished the black curve in Fig. 8.6b. As $k_{PT1}$ was altered, $k_{PT2}$ was set to the appropriate value fixed by the desired ratio of $k_{PT2}$ to $k_{PT1}$, $\rho = 10$ (Equation 8.8). This was repeated for $\gamma = 1, 2, 3, 6, 20$ and 100 to generate the remaining plots in Fig. 8.6b

### 8.5.2. Ni metalloporphyrin studies

**General Experimental Details.** $^1$H NMR spectra (500 MHz) were recorded on samples in CDCl$_3$ at room temperature unless noted otherwise. Silica gel (60 µm average particle size) was used for column chromatography. 4-Formyl-5-bromo-2,7-di-tert-butyl-9,9-dimethylxanthene, 5-pentafluorophenylpyrromethane, were prepared as described in the literature. THF (anhdyrous), methanol (anhydrous), CH$_2$Cl$_2$ (anhydrous), benzoic acid (≥99.5%), and tetrabutylammonium hexafluoro-phosphate (TBAPF$_6$, ≥99.0%), and all other chemicals were used as received. LD-MS data was measured on porphyrins in the absence of matrix.

The microwave-assisted reactions were performed inside the cavity of a CEM Discover microwave synthesis system equipped with infrared, pressure and temperature sensors for monitoring the synthesis. The reaction vessels were 10 mL crimp-sealed thick-wall glass tubes. The contents of each vessel were stirred with a magnetic stirrer.

UV-vis spectra were recorded at room temperature in quartz cuvettes in CH$_2$Cl$_2$ on a Varian Cary 5000 UV-vis-NIR spectrophotometer. UV-vis spectroelectrochemical measurements were made using a quartz thin layer cell (0.5 mm path length) at room temperature in a N$_2$-filled glovebox with an Ocean Optics USB4000 spectrophotometer and DT-Mini-2GS UV-vis-NIR light source.

Electrochemical measurements were performed on a CH Instruments (Austin, Texas) 760D Electrochemical Workstation using CHI Version 10.03 software. Cyclic
voltammetry (CV) experiments were conducted in a nitrogen-filled glovebox at 295 K using a CH Instruments glassy carbon button working electrode (area = 0.071 cm$^2$), BASi Ag/AgNO$_3$ (0.1 M) reference electrode in 0.1 M TBAPF$_6$ acetonitrile solution at room temperature, and Pt mesh counter electrode in 0.2 M TBAPF$_6$ acetonitrile solutions 2 or 4 mL total volume. Acetonitrile was previously dried by passage through a neutral alumina column under argon. TBAPF$_6$ was dried prior to CV measurements. All CVs were recorded with compensation for solution resistance, and potentials were referenced to the ferrocenium/ferrocene (Fc$^+$/Fc) couple. Appropriate background scans were subtracted from all CVs. Solutions were stirred between acquisition of individual CVs and the working electrode was polished before each measurement.

Bulk electrolysis was performed using a glassy carbon rod (7 mm × 5 cm) working electrode and a platinum mesh auxiliary electrode in a gas-tight electrochemical cell. The amount of H$_2$ gas produced in the headspace was analyzed by an Agilent 7890A GC. The potentials for electrolysis were −1.77 V for 1-Ni, −1.85 V for 2-Ni, and −1.75 V for 3-Ni (all potentials are referenced to Fc$^+$/Fc).

1-Ni X-ray Data. Crystals of 1-Ni were obtained by slow evaporation from a CH$_2$Cl$_2$/hexanes solution of 1-Ni. The X-ray structure of 1-Ni is shown in main text Figure 1. The central nickel atom is found in a square planar coordination environment with sum of $\angle$N–Ni–N equaling 360°, indicating that the Ni is not appreciably displaced from the N4 plane of the pyrrolic nitrogen atoms. The Ni–N distances are not perfectly equivalent as three Ni–N distances are 1.951(3) Å with the remaining Ni–N distance found to be slightly shorter at 1.940(3) Å. The macrocycle distorts only slightly from perfectly square planar with the two pairs of trans meso-carbon atoms bending ~10° out of the N4 plane in opposing directions. These solid state metrics are comparable to those of the previous reported cobalt porphyrin (CoHPX3CO$_2$H)$_{26}$ This cobalt analog possessing mesityl substituents is similarly planar with the Co atom not appreciably displaced from N4 plane.
of pyrrolic nitrogen atoms. As mentioned in section 8.2.1, one notable difference in the crystallographic structures of 1-Ni and CoHPX3CO2H is the apically coordinated solvent molecule found in the structure of CoHPX3CO2H.

**Synthetic Details.** 5-[4-(5-Bromo-2,7-di-tert-butyl-9,9-dimethylxanthene)]-10,15,20-tris(pentafluoro-phenyl)porphyrinatonickel (II) (2-Ni). A microwave glass tube (10 mL) containing a magnetic stir bar was charged with 8 mL of CHCl3:MeOH (7 mL:1 mL) and sample of HPXBr (2) (0.0500 g, 0.0414 mmol). The solution was stirred at room temperature for 10 min to obtain a homogenous mixture. A sample of NiBr2 (0.226 g, 1.035 mmol, 25 mol equiv to 2) was added. The resulting mixture was stirred at room temperature for 5 min. The reaction vessel was sealed with a septum and subjected to microwave irradiation at 65 °C. The protocol was as follows: (1) heat the reaction vessel from room temperature to 65 °C, (2) hold at 65 °C and irradiate for 20 min (temperature overshoots of 67 - 70 °C were permitted; temperature was re-established at 65 °C by using open flow valve option), (3) allow the reaction mixture to cool to room temperature, (4) check the reaction mixture by silica TLC analysis (Hexanes:CH2Cl2 4:1), (5) repeat steps 1 - 4 until all of the free base starting material, 2, was consumed (6 - 8 h). Upon complete reaction, triethylamine (10 mole equiv to metal salt) was added to the solution, which was washed with water and brine, dried over Na2SO4, and concentrated to dryness. The resulting crude product was chromatographed [silica, Hexanes:CH2Cl2 1:1 → 1:4] to afford dark purple solid (48 mg, 91%). 1H NMR (500 MHz, CDCl3) δ / ppm: 1.25 (s, 9H), 1.53 (s, 9H), 1.88 (s, 6H), 7.08 (d, J = 2.0 Hz, 1H ), 7.40 (d, J = 2.0 Hz, 1H), 7.87 (d, J = 2.5 Hz, 1H), 7.94 (d, J = 2.5 Hz, 1H), 8.72 (d, J = 5.0 Hz, 2H), 8.83 (s, 4H), 8.92 (d, J = 5.0 Hz, 2H);. Anal. Calcd. for M = C61H36BrNiF15N4O: Cald. 1264.5382. Found for HR(ESI)-MS: 1265.12λ7; LD-MS. 1264.15. λmax,abs /nm (CH2Cl2) = 407, 525, 55λ.

5-[4-(2,7-Di-tert-butyl-5-methoxycarbonyl-9,9-dimethylxanthene)]-10,15,20-tris-(pentafluorophenyl)-porphyrinatonickel(II) (NiHPX-CO2Me, 4-Ni). A microwave
glass tube (10 mL) containing a magnetic stir bar was charged with 5.5 mL of CHCl₃:MeOH (4.4 mL:1.1 mL) and sample of HPXCO₂Me (4) (0.0300 g, 0.025 mmol). The solution was stirred at room temperature for 10 min to obtain a homogenous mixture. A sample of NiBr₂ (0.138 g, 0.632 mmol, 25 mol equiv to 4) was added. The resulting mixture was stirred at room temperature for 5 min. The reaction vessel was sealed with a septum and subjected to microwave irradiation at 65 °C. The protocol was as follows: (1) heat the reaction vessel from room temperature to 65 °C, (2) hold at 65 °C and irradiate for 20 min (temperature overshoots of 67 - 70 °C were permitted; temperature was re-established at 65 °C by using open flow valve option), (3) allow the reaction mixture to cool to room temperature, (4) check the reaction mixture by silica TLC analysis (Hexanes:CH₂Cl₂ 4:1), (5) repeat steps 1 - 4 until all of the free base HPXCO₂Me starting material was consumed (8 - 10 h). Upon complete reaction, triethylamine (10 mol equiv to metal salt) was added to the solution, which was washed with water and brine, dried over Na₂SO₄, and concentrated to dryness. The resulting crude product was chromatographed [silica, hexanes:CH₂Cl₂ silica, hexanes:CH₂Cl₂ 1:1 → 1:6] to afford dark purple solid (28 mg, 90%). ¹H NMR (500 MHz, CDCl₃) δ / ppm: 0.69 (s, 3H), 1.27 (s, 9H), 1.41 (s, 9H), 1.91 (s, 6H), 7.37 (d, J = 2.0 Hz, 1H ), 7.55 (d, J = 2.0 Hz, 1H), 7.64 (d, J = 2.5 Hz, 1H), 7.83 (d, J = 2.5 Hz, 1H), 8.66 (d, J = 5.0 Hz, 2H), 8.77 (s, 4H), 8.84 (d, J = 5.0 Hz, 2H);


5-[4-(2,7-Di-tert-butyl-5-hydroxycarbonyl-9,9-dimethylxanthene)]-10,15,20-tris-(pentafluorophenyl)-porphyrinatonickeII (I-Ni). A microwave glass tube (10 mL) containing a magnetic stir bar was charged with 5.5 mL of CHCl₃:MeOH (4.4 mL:1.1 mL) and sample of 1 (0.0520 g, 0.044 mmol). The solution was stirred at room temperature for 10 min to obtain a homogenous mixture. A sample of NiBr₂ (0.240 g, 1.10 mmol, 25 mol equiv to 1) was added. The resulting mixture was stirred at room temperature for 5
min. The reaction vessel was sealed with a septum and subjected to microwave irradiation at 65 °C. The protocol was as follows: (1) heat the reaction vessel from room temperature to 65 °C, (2) hold at 65 °C and irradiate for 20 min (temperature overshoots of 67 - 70 °C were permitted; temperature was re-established at 65 °C by using open flow valve option), (3) allow the reaction mixture to cool to room temperature, (4) check the reaction mixture by silica TLC analysis (hexanes:CH₂Cl₂ 4:1), (5) repeat steps 1 - 4 until all of the free base HPXCO₂H starting material was consumed (8 – 10 h). Upon complete reaction, triethylamine (10 mol equiv to metal salt) was added to the solution, which was washed with water and brine, dried over Na₂SO₄, and concentrated to dryness. The resulting crude product was chromatographed [silica, hexanes:CH₂Cl₂ silica, hexanes:CH₂Cl₂ 1:1 → 1:9] to afford dark purple solid (51 mg, 94%). ¹H NMR (500 MHz, CDCl₃) δ / ppm: 1.26 (s, 9H), 1.49 (s, 9H), 1.93 (s, 6H), 7.32-7.46 (brs, 1H), 7.71 (dd, J = 2.5 Hz, 2H ), 7.91 (dd, J = 8.5 Hz, 2H), 8.69 (d, J = 5.0 Hz, 2H), 8.78 (s, 4H), 8.81 (d, J = 5.5 Hz, 2H);. Anal. Calcd. for M = C₆₂H₃₇F₁₅N₄NiO₃: Cald. 1229.6516. Found for HR(ESI)-MS: 1251.1866 (M+Na); LD-MS. 1229.18. λmax,abs /nm (CH₂Cl₂) = 406, 524, 558.

Spectroelectrochemical Studies. UV-vis spectroelectrochemical measurements were made using a quartz thin layer cell (0.5 mm path length) at room temperature in a N₂-filled glovebox with an Ocean Optics USB4000 spectrophotometer and DT-Mini-2GS UV-vis-NIR light source using an optically transparent platinum flag working electrode, platinum wire counter electrode, and Ag wire reference electrode (BASi). Cyclic voltammetry and controlled potential electrolysis in the thin layer cell were carried out using a CH Instruments 730C Electrochemical Workstation. Samples were prepared in 0.1 M TBAPF₆ acetonitrile at a 0.6 mL total volume.

Computational studies. Structures were optimized with density functional theory (DFT) using a variety of exchange-correlation functionals: B3P86, B3LYP, BP86, BLYP, TPSSh, M06L, and ωB97XD. Optimizations were performed
with the 6-31+G(d,p)\textsuperscript{53} basis set for the transferring proton and the 6-31+G(d) basis set\textsuperscript{54–56} for all other atoms with default options in Gaussian 09.\textsuperscript{57} Optimizations and single point energy calculations in acetonitrile solvent utilized the conductor-like polarizable continuum model (C-PCM)\textsuperscript{58,59} with Bondi radii and included nonelectrostatic interactions resulting from dispersion,\textsuperscript{60,61} repulsion,\textsuperscript{61} and cavity formation.\textsuperscript{62} Entropic and zero-point energy effects were calculated from the vibrational frequencies at $T = 298.15$ K and were included in the calculation of the reaction free energies, which in turn were used to calculate the reduction potentials. When optimized in the gas phase, the free energies of the solvated molecules were calculated with gas phase geometries employing a Born–Haber thermodynamic cycle that combines gas phase free energies with single point solvation free energies of the reduced and oxidized species. The detailed procedure is described in our previous publications.\textsuperscript{63} Tables 8.1 and 8.2 illustrate that the results are qualitatively similar for these two types of geometries. The results in the main paper utilized the geometries optimized in solution. As stated in section 8.2.2, for computation tractability, the tert-butyl groups on the xanthene backbone and pentafluorophenyl meso-substituents of the porphyrin ring were truncated to methyl groups and chlorine atoms, respectively.

These truncations were chosen based on the Hammett constants\textsuperscript{64,65} ($\sigma$) of the substituents, which are similar:

\[
\begin{array}{|c|c|c|}
\hline
\text{Substituent} & \sigma_{m}^* & \sigma_{p}^* \\
\hline
-\text{Cl} & 0.37 & 0.23 \\
-\text{C}_6\text{F}_5 & 0.26 & 0.27 \\
-\text{tBu} & -0.10 & -0.20 \\
-\text{CH}_3 & -0.07 & -0.17 \\
\hline
\end{array}
\]

*Subscripts “m” or “p” refer to the position (“meta” or “para”) of the substituent.

Figures of computational results were created with GaussView 5.0.\textsuperscript{66}

**CV Simulation.** All simulated CVs were calculated using DigiElch 7 software.\textsuperscript{34} Diffusion coefficients of compounds were determined straightforwardly from the peak
currents of reversible waves, and these values were used in the relevant simulations. Symmetry factors/transfer coefficients (α values) were set to 0.5 for all ET steps. Full details of the parameters used in simulation are listed in Tables 8.3–8.7.

For the simulation of trumpet plots, CVs were simulated using the known E_{1/2} values and diffusion coefficient (determined from the peak current) as the fixed input parameter in the model. The CV was then simulated for an initial guess value of the standard heterogeneous rate constant (kₘ) at a particular scan rate, v (say, 10 mV/s). The anodic and cathodic peak potentials were noted. The kₘ value was then maintained and v was changed to 30 mV/s, the CV was simulated again and the new peak potentials were noted. This was repeated for v = 100, 300, 1000, 3000, …, 10000 mV/s. A plot of peak potentials versus log v was constructed and the simulated data was compared to the experimental result. This procedure is then iterated for different kₘ values until a good match is obtained between the experimental points and the simulated values over the entire scan rate range.
8.6 References


