Origins of hydrogen peroxide selectivity during oxygen reduction on organic mixed ionic-electronic conducting polymers

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Abstract

Electrochemical reduction of atmospheric oxygen provides carbon emission-free pathways for the generation of electricity from chemical fuels and for the distributed production of green chemical oxidants like hydrogen peroxide. Recently, organic mixed ionic-electronic conducting polymers (OMIECs) have been reported as active electrode materials for the oxygen reduction reaction. This work sets out to identify the operative oxygen reduction mechanism of OMIECs through a multi-faceted experimental and theoretical approach. Using a combination of pH-dependent electrochemical characterization, operando UV-Vis and Raman spectroscopy, ab initio calculations, and steady-state microkinetic simulations, we find that the n-type OMIEC, p(NDI-T2 P75), reduces oxygen selectively to hydrogen peroxide through a non-catalytic, outer-sphere pathway. This pathway serves as a general guide to understand the reactivity of an expanded set of n- and p-type OMIECs investigated in this work and provides a framework to rationalize when (or if) organic compounds function as heterogeneous catalysts for oxygen reduction.

Introduction

Mitigating greenhouse gas emissions in the energy and chemical industries requires a transition from current fossil fuel-based thermochemical processes to carbon emission-free electrochemical processes. Given its abundance, atmospheric molecular oxygen is an attractive oxidant for the generation of electricity from chemical fuels (such as H₂ or methanol in fuel
cells\textsuperscript{1–4} or metals like Zn, Fe, or Al in metal-air batteries\textsuperscript{5–8}) or for the distributed on-site electrochemical production of hydrogen peroxide.\textsuperscript{9,10} In aqueous systems at room temperature, these separate applications require different selectivity in the terminal product of oxygen reduction, where generating hydrogen peroxide terminates at a net 2-electron/2-proton reduction (hydrogen peroxide production reaction, HPPR: \( \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O}_2 \), \( E^0 = 0.695 \text{ V vs. SHE} \)) and fuel cell or metal-air battery applications ideally reduce oxygen to water through a net 4-electron/4-proton process (oxygen reduction reaction, ORR: \( \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O} \), \( E^0 = 1.23 \text{ V vs. SHE} \)).

Although not universal, it is generally assumed that an electrocatalyst is needed to reduce oxygen. Most electrocatalysts that are considered state-of-the-art for the ORR are based on platinum-group metals, which, while being scarce and expensive, are highly active and predominantly selective for the 4-electron reaction.\textsuperscript{11} Alternative directions include the development of non-precious transition metal-based electrocatalysts such as metal complexes,\textsuperscript{12,13} metal oxides,\textsuperscript{14–18} metal sulfides,\textsuperscript{19} and single atom catalysts,\textsuperscript{20,21} which may be selective for the 4-electron or the 2-electron reaction depending on their chemical composition and structure.\textsuperscript{22} Understanding the energetic pathways as well as the structure-property relationships that govern activity and selectivity is crucial to enabling targeted applications. For the HPPR, the most efficient heterogeneous electrocatalysts avoid metal sites entirely and include carbon nitrides, graphene derivatives, and other heteroatom-doped carbons capable of producing \( \text{H}_2\text{O}_2 \) at overvoltages as low as 10 mV.\textsuperscript{23–26} Still, these materials present their own challenges towards improving electrocatalyst design, including conclusive identification of catalytic binding sites and reaction mechanisms due to their variability in chemical structure.\textsuperscript{27,28}

Recently, organic mixed ionic-electronic conducting polymers (OMIECs) have been reported to exhibit catalytic behavior for electrochemical reactions.\textsuperscript{29–33} OMIECs are semiconducting conjugated polymers with synthetically tunable structures and transport properties enabled by electrochemical ion-insertion redox reactions.\textsuperscript{34} These electrochemical doping reactions drive the insertion of mobile ions and electrons (or holes), providing functionality for a range of electrochemical devices.\textsuperscript{34–39} For electrocatalysis, hole/anion transporting OMIECs (p-type), including PEDOT (poly(3,4-ethylenedioxythiophene)) variations, have been studied for oxygen reduction and display selectivity for the 2-electron reaction.\textsuperscript{31,32,40} BBL (poly(benzimidazobenzophenanthroline)), an electron/cation transporting (n-type) OMIEC, has also been shown to be active for the ORR, with pH-dependent selectivity for the 4-electron versus the 2-electron product.\textsuperscript{33} These studies highlight the potential of OMIECs as electrodes
for oxygen reduction, but do not provide proof of inner-sphere electron transfer (i.e., electrocatalysis) and provide limited insight into the design principles that engender their catalytic properties (if any).

Our work sets out to identify the operative oxygen reduction mechanism of OMIECs through a multi-faceted experimental and theoretical approach. We primarily focus our efforts on p(NDI-T2 P75), a naphthalene-1,4,5,8-tetracarboxylic-diimide-bithiophene copolymer with 75% polar side chains (Figure 1).\textsuperscript{41} NDI-T2 copolymers are acceptor-donor copolymers and are known to have good charge transport properties relative to other n-type OMIECs. Notably, this OMIEC is stable in a broad pH range and has heteroatoms and functional groups reported to be vital for electrocatalysis on carbon-based materials, including N, carbonyl groups (C=O), and S.\textsuperscript{28,42–44}

![Figure 1. Structure of p(NDI-T2 P75), an acceptor-donor random copolymer with a backbone composed of an electron-deficient naphthalene diimide (NDI) unit and an electron-rich bithiophene (T2) unit. The hydrophilic side chains based on ethylene glycol, R\textsuperscript{1}, attached to 75% of monomer units (P75) facilitate solvated ion-insertion, and the hydrophobic side chains based on alkyl chains, R\textsuperscript{2}, provide improved electrochemical stability.\textsuperscript{45}](image)

We combine rotating ring-disk electrochemistry, \textit{operando} spectroscopy techniques, and \textit{ab initio} and steady-state microkinetic simulations to evaluate the performance and mechanism of p(NDI-T2 P75) for oxygen reduction. We validate the generality of our mechanistic conclusions by benchmarking the performance of select p- and n-type OMIECs.

In p(NDI-T2 P75), bulk ion-insertion redox reactions and oxygen reduction are found to be decoupled from proton transfer, which enables the decrease of overvoltage for the ORR by increasing pH. We find the singly-reduced, electron polaron state, which forms through bulk ion-insertion redox, controls the activity of this material for the ORR. However, based on the results from \textit{operando} experiments and simulations, as well as the performance of the other
investigated OMIECs, we conclude that these materials do not generally function as electrocatalysts because they operate through an outer-sphere mechanism. The rigorous approach to studying electrochemical H\textsubscript{2}O\textsubscript{2} production presented in this paper can be extended to materials beyond OMIECs and facilitates a guided exploration of to oxygen reducing electrodes.

**Results and discussion**

*Understanding the Electrochemistry of p(NDI-T2 P75)*

Prior to all electrochemical experiments, p(NDI-T2 P75) was purified to remove residual Pd contamination from polymer synthesis (Figure S1, Table S1), resulting in low Pd concentrations of 2 – 5 ppm. While it has been reported that a polymer much like p(NDI-T2 P75) primarily produces H\textsubscript{2}O upon reducing O\textsubscript{2} in a 4-electron reaction,\textsuperscript{46} we demonstrate that the removal of residual Pd is crucial for evaluating the performance of the polymer itself without Pd contributing to ORR performance. Higher concentrations of Pd shift the measured halfwave voltage, \( E_{1/2} \), for oxygen reduction and change whether H\textsubscript{2}O or H\textsubscript{2}O\textsubscript{2} is the majority product (Figure S2).\textsuperscript{47}

We use rotating ring-disk electrochemistry (RRDE) to investigate the behavior of p(NDI-T2 P75) in [K\textsuperscript{+}] = 1 M aqueous electrolytes with pH varied between 7.0 and 13.7. Using a single-component thin film of purified p(NDI-T2 P75) supported on a glassy carbon disk electrode, we perform cyclic voltammetry between 0.2 and –1.0 V vs. Ag/AgCl in Ar-saturated and O\textsubscript{2}-saturated electrolytes to investigate bulk redox behavior and oxygen reduction activity, respectively.

Characteristic voltammograms at a scan rate of 5 mV s\textsuperscript{-1} for p(NDI-T2 P75) in Ar-saturated electrolytes are shown in Figure 2a. For all tested pH values, three reversible redox peaks are observed. The first two peaks, which appear at more positive voltages, correspond to electron polaron formation and the third peak corresponds to the formation of the electron bipolaron.\textsuperscript{48} We confirm the n-type nature of these electron polaron formation reactions through conductivity measurements using an interdigitated electrode array in an organic electrochemical transistor (OECT) architecture (Figure S3). The formation of the electron polaronic state is associated with electron/cation doping of the polymer film resulting in an electronic conductivity enhancement by a factor of >10\textsuperscript{4}. We hypothesize that the voltage offset for the first two electron polaron peaks arises from mixed side chain composition and the resulting domains of ordered (crystalline) and disordered (amorphous) aggregates in the polymer film.\textsuperscript{48,49} It has been demonstrated that inter-
chain electronic state hybridization can occur in ordered domains, which stabilizes the LUMO state (most positive reduction voltage) similar to the effect of charge-transfer hybridization, potentially resulting in a shift of the observed reduction voltage.\textsuperscript{50} Integration of the reduction current suggests \textasciitilde50\% of the film can be reduced to the bipolaronic state at 5 mV s\textsuperscript{-1} (corresponding to a charging time of 4 minutes), confirming that these redox peaks are associated with volumetric charging of the bulk of the polymer.\textsuperscript{51}

Figure 2. a) Ar-saturated reduction/oxidation voltammograms at a scan rate of 5 mV s\textsuperscript{-1}. b) O\textsubscript{2}-saturated RRDE measurement at 1600 r.p.m. with a scan rate of 0.5 mV s\textsuperscript{-1}, showing a high ring current (\(E_{\text{ring}} = 1.20\) V vs. RHE). c) Percent H\textsubscript{2}O\textsubscript{2} produced calculated using the ring current from (b) and the electrode collection efficiency (\(N = 0.25\)). d) Number of electrons transferred during the ORR as calculated through Koutecký-Levich analysis. e) Quantification of Faradaic efficiency obtained from constant current electrolysis (~2 mA cm\textsuperscript{-2}) in an H-cell performed on a carbon fiber paper supported p(NDI-T2 P75) film in 0.1 M KOH.
The oxygen reduction performance of p(NDI-T2 P75) as a function of electrolyte pH is presented in Figure 2b-d. In O$_2$-saturated electrolytes, we observe a large increase in current density at voltages correlated to the electron polaron redox reactions.

The limiting current density for oxygen reduction on p(NDI-T2 P75) is observed to be half the limiting current of a polycrystalline platinum electrode (Figures S4-S6) tested in identical conditions. This result suggests that p(NDI-T2 P75) is highly selective for the 2-electron H$_2$O$_2$ product, rather than the 4-electron H$_2$O product generated on the precious metal counterpart.

High Faradaic efficiencies for H$_2$O$_2$ were additionally observed through collection on the ring electrode (Figures 2b, 2c), Koutecký-Levich analysis (Figures 2d, S4), and constant current electrolysis performed in an H-cell (Figure 2e). The observed variation in limiting current densities and ring currents across the electrodes tested at different pH likely arises from variations in electrode morphology that influence the electrochemically active surface area and RRDE collection efficiency. It is well known that this polymer system becomes hydrated in aqueous electrolytes, and we expect the degree of swelling to also be influenced by pH. Additionally, the polymer exhibited stable performance at ~2 mA cm$^{-2}$ for two hours in the H-cell measurements (Figure 2e). We found negligible changes in chemical structure through post-mortem $^1$H NMR analysis (Figure S7).

Comparing the trends in bulk redox and oxygen reduction, we observe an ~59 mV/pH positive shift in voltage versus RHE for both the electron polaron/bipolaron reactions and oxygen reduction (Figure S8). Although the overall ORR is proton-coupled, the observed pH-dependence reflects that both the bulk ion-insertion reactions and the rate-limiting step of oxygen reduction do not involve proton transfer. Instead, charge compensation for the electron polaron/bipolaron reaction is provided by K$^+$ cations.

$O_2$ Suppresses Electron Polaron Formation

To further study the reduction of oxygen to hydroperoxide on p(NDI-T2 P75), we monitor the electronic and chemical structure evolution of p(NDI-T2 P75) during operation through UV-Vis spectroelectrochemistry and operando Raman spectroscopy measurements.

The UV-Vis spectra of p(NDI-T2 P75) collected as it is reduced from its neutral to its bipolaron state in Ar-saturated 0.1 M KOH is presented in Figure 3a. The increase in optical density at around 500 nm and the respective decrease near 720 nm correspond to electron polaron formation, and the increase in optical density near 630 nm is indicative of the electron bipolaron
Figure 3b presents the differential optical density of the electron polaron feature at 500 nm with respect to time and voltage. The appearance and disappearance of the electron polaron feature in Ar-saturated electrolyte correspond well with the voltages observed in cyclic voltammetry. Notably, however, the intensity of the electron polaron feature was suppressed in O$_2$-saturated electrolyte and shifted to more cathodic voltages. These results suggest the rate of O$_2$ reduction exceeds the rate of electron polaron formation in the film, where O$_2$ present in the electrolyte can rapidly consume the energetic electrons of the electron polaronic state of p(NDI-T2 P75) to generate HO$_2^-$.

Figure 3. a) UV-Vis spectra of a thin p(NDI-T2 P75) film on indium tin oxide (ITO) glass as it is reduced in Ar-saturated 0.1 M KOH to its doubly-reduced, bipolaron state. Throughout the figure, yellow (N), red (P), and purple (BP) labels are indicative of the neutral, electron polaron, and electron bipolaron state of the polymer. b) Negative change in optical density at 500 nm with respect to time for Ar-saturated and O$_2$-saturated 0.1 M KOH as the polymer is reduced to its electrón bipolaron state. The CV was collected in 0.1 M KOH at 5 mV s$^{-1}$. Operando Raman spectra for a thin p(NDI-T2 P75) film on ITO glass as it is reduced and oxidized in c) Ar-saturated 0.1 M KOH and d) O$_2$-saturated 0.1 M KOH.

Further confirmation that O$_2$ suppresses electron polaron formation in p(NDI-T2 P75) was obtained via operando Raman spectroscopy. We first describe the vibrational features of the neutral, polaronic, and bipolaronic states of the polymer measured at characteristic voltages in Ar-saturated electrolyte, shown in Figure 3c.
Starting with the initial reference spectrum obtained at the open-circuit voltage, the symmetric C=O stretching band at 1708 cm\(^{-1}\) can be used as an indicator for neutral repeat units as it has been shown to disappear as NDI-T2 becomes highly reduced.\(^{52}\) As the applied voltage reaches 0.4 V vs RHE and the material is reduced to its singly-reduced, electron polaron state, two new bands at 1538 and 1370 cm\(^{-1}\) arise. These bands can be ascribed to a shift of the pristine bands at 1610 and 1572 cm\(^{-1}\), associated with the C-C stretching in the NDI unit. The intensities of these vibrations increase with applied voltage and are assigned to electron polaron formation.\(^{52}\) Moreover, the intensity ratio of the triplet bands between 1496 and 1400 cm\(^{-1}\) undergoes a few changes, with a substantial drop of intensity of the bands at 1434 and 1406 cm\(^{-1}\), assigned to collective vibrational displacements of the C-C stretching of the NDI and the T2 units. When the applied voltage reaches 0.2 V vs RHE, the bands assigned to the electron polaron at 1583 cm\(^{-1}\) and 1370 cm\(^{-1}\) gain further intensity, while the triplet between 1496 and 1400 cm\(^{-1}\) broadens and loses intensity. Additionally, at this voltage, the band at 1708 cm\(^{-1}\), which can be used to indicate the presence of neutral NDI-T2 repeat units, disappears. Once –0.1 V vs RHE is applied, new vibrational features arise that have not previously been reported, namely the bands at 1344 and 1137 cm\(^{-1}\), which, based on the associated electrochemical features, are likely associated with the formation of the electron bipolaron.

When similar measurements are performed in O\(_2\)-saturated electrolyte, we observe a suppression of the electron polaron features until the applied voltage reaches –0.1 V vs RHE (in comparison to 0.4 and 0.2 V vs RHE in Ar-saturated electrolyte). Additionally, bipolaronic vibrational bands are not observed in the presence of oxygen, and the neutral band in the Raman spectra does not disappear. These results confirm that electron polaron formation is suppressed through rapid consumption by O\(_2\). Similar operando spectroscopic results can be observed in 0.1 M KCl (Figure S9).

**Oxygen Reduction: Is It Catalytic?**

While our results reveal p(NDI-T2 P75) reacts directly with oxygen to form hydro(gen) peroxide, they do not definitively demonstrate this process proceeds through a catalytic, or “inner-sphere,” pathway. Indeed, oxygen reduction may also proceed through non-catalytic outer-sphere pathways, especially at high pH. Understanding the energetics that control these pathways and differentiating between them helps not only to interpret our experimental results, but also recent results on other OMIEC and non-precious metal electrodes for oxygen reduction. Figure 4 presents a general, though not necessarily universal, framework to understand oxygen
reduction in alkaline electrolytes (pH > 11.7) involving the commonly hypothesized surface adsorbate and solvated intermediates.\textsuperscript{53–56} We emphasize that other mechanistic pathways and intermediates may exist and, as yet, no conclusive pathway with direct observation of each 1-electron intermediate has been reported.

(Electro)catalysis necessitates adsorption of reaction intermediates (chemisorption/surface bond formation), which modulates their reduction voltages by $-\Delta G_{\text{ads}}/F$, where $\Delta G_{\text{ads}}$ is the Gibbs energy of adsorption and $F$ is Faraday’s constant. On precious metal surfaces, such as Pt, oxygen is hypothesized to dissociatively adsorb, breaking the O=O double bond to form two $^*\text{O}$ sites in the initial step (where $^*i$ represents a surface site covered with an adsorbed species, $\text{H}^+$). This “direct” pathway bypasses the hydro(gen) peroxide intermediate and is believed to be the origin of the exemplary activity of Pt-based catalysts towards the 4-electron ORR to water (Figure 4).\textsuperscript{57} However, this pathway requires two neighboring adsorption sites to directly bind each O atom. Because no hydrogen peroxide intermediate is believed to be involved in the direct pathway, the activity of precious metal electrocatalysts is hypothesized to be controlled by the adsorption strength of $^*\text{O}$ relative to its successive 1-electron/1-proton coupled reduction product $^*\text{OH}$, $\Delta G_{\text{^*O}} - \Delta G_{\text{^*OH}}$.

On catalysts with single adsorption sites such as heteroatom-doped carbons or non-precious transition metal-based catalysts, the “serial” pathway is hypothesized to dominate. Here, the two O atoms remain bonded upon adsorption which can theoretically yield $^*\text{OOH}$ through a net 2-electron/1-proton reduction. The adsorbed $^*\text{OOH}$ can then desorb to yield hydro(gen) peroxide or be further reduced through a net 2-electron/3-proton reaction to yield 2 molecules of H$_2$O or OH$^-$, depending on pH (Figure 4). Here the adsorption energy of $^*\text{OOH}$ largely determines whether the oxygen reduction terminates at H$_2$O$_2$ (HO$_2^-$) or H$_2$O (OH$^-$). Interestingly, a large body of theoretical work has demonstrated a linear scaling relationship between $\Delta G_{\text{^*OOH}}$ and $\Delta G_{\text{^*OH}}$\textsuperscript{58} (and likewise $\Delta G_{\text{^*O}}$ and $\Delta G_{\text{^*OO}}$) meaning that, like the precious metal case, $\Delta G_{\text{^*O}} - \Delta G_{\text{^*OH}}$ can be used as a proxy to predict the activity and selectivity of catalysts operating through the serial oxygen reduction pathway.
Figure 4. Reaction scheme for oxygen reduction in alkaline electrolytes. The * alone denotes a bare surface site, and \( *i \) represents a surface site with an adsorbed species \( i \). The serial and direct pathways are inner-sphere reaction mechanisms.

In principle, the adsorption energies of \( *\text{OH} \) and \( *\text{O} \) are all that is needed to rationalize the reactivity of electrode materials for the HPPR/ORR. However, these adsorption energies are challenging to measure and, so, are primarily derived through density functional theory calculations using the computational hydrogen electrode ("CHE") formalism.\(^{59}\) Unfortunately, the energetics and selectivity of the net HPPR/ORR depend strongly on pH, as do the intermediate adsorption energies, but most approaches utilizing the CHE formalism fail to consider or demonstrate this.\(^{60}\) Additionally, using \( \Delta G^{\text{O}} - \Delta G^{\text{OH}} \) as a proxy for ORR reactivity may lead to erroneous predictions if the reaction terminates at the 2-electron \( \text{H}_2\text{O}_2 \) product, e.g. the HPPR, as the O-O bond is never broken to yield an \( *\text{OH} \) or \( *\text{O} \) adsorbate (Figure 4). Finally, many recent efforts assume a catalyst is required to reduce oxygen, especially to produce \( \text{H}_2\text{O}_2 (\text{HO}_2^-) \), but as is expanded upon in the following text, this is not necessarily the case, and the HPPR can operate at low overvoltages through an outer-sphere process in alkaline electrolytes.

While the previous discussion framed oxygen reduction through the perspective of electrocatalysis, we now consider the energetics involved for the outer-sphere process where the intermediates remain solvated and do not interact strongly with the electrode. The first electron transfer reaction to oxygen is generally considered the rate-limiting step (RLS) in the outer-sphere ORR due to its very negative standard reduction voltage.\(^{1,61,62}\) Depending on pH,
this step may yield the superoxide radical, O$_2^-$ at pH > pK$_a$ = 4.88, as shown in Reaction [1], or its protonated hydroperoxyl counterpart, HO$_2$, when pH ≤ pK$_a$, shown in Reaction [2].

$$\text{O}_2 + e^- \rightleftharpoons \text{O}_2^-$$ \[1\]

$$\text{O}_2 + e^- + \text{H}^+ \rightleftharpoons \text{HO}_2$$ \[2\]

The standard reduction voltages for these reactions are $E_{\text{O}_2/\text{O}_2^-}^0 = -0.33$ V vs. SHE and $E_{\text{O}_2/\text{HO}_2}^0 = -0.022$ V vs. SHE, respectively. Their formal reduction voltages, $E^0r$, can be calculated as follows, where $R$ is the ideal gas constant, $T$ is the absolute temperature, $p_{\text{O}_2}$ is the partial pressure of O$_2$, and $a_j$ is the activity of species $j$ in the aqueous solution:

$$E_{\text{O}_2/\text{O}_2^-}^0(V \text{ vs. SHE}) = E_{\text{O}_2/\text{O}_2^-}^0 + \frac{RT}{F} \ln \frac{p_{\text{O}_2}}{a_{\text{O}_2^-}}$$ \[3\]

$$E_{\text{O}_2/\text{HO}_2}^0(V \text{ vs. SHE}) = E_{\text{O}_2/\text{HO}_2}^0 + \frac{RT}{F} \ln \frac{p_{\text{O}_2} a_{\text{H}^+}}{a_{\text{HO}_2}}$$ \[4\]

Equations [3] and [4] suggest a reversible voltage for superoxide formation of $E_{\text{O}_2/\text{O}_2^-}^0r = -0.33$ V vs. SHE, which is a common value cited in the literature.\(^{57}\) However, this formal reduction voltage corresponds to an activity of superoxide equal to 1. The low stability of superoxide suggests that its concentration is unlikely to exceed the concentration of dissolved O$_2$ in the electrolyte from which it is produced. Although O$_2$ solubility is pH-dependent,\(^{63}\) we can estimate the superoxide and oxygen activity through Henry’s Law where the Henry’s Law Constant for O$_2$ in water is $H_{\text{O}_2}^{aq} = 1.3 \times 10^{-3}$ M atm$^{-1}$:

$$a_{\text{O}_2^-} \approx a_{\text{O}_2} = H_{\text{O}_2}^{aq} p_{\text{O}_2}$$ \[5\]

Using this value for $a_{\text{O}_2^-}$ we obtain a more reasonable, and commonly observed, halfwave voltage ($E_{1/2}$) $E_{\text{O}_2/\text{O}_2^-}^0r = -0.16$ V vs. SHE, which defines the reversible voltage of dissolved oxygen reduction to superoxide in aqueous electrolytes.\(^{56,64}\) A similar analysis can be performed for hydroperoxyl production, which requires additional knowledge of the electrolyte pH to define $E_{\text{O}_2/\text{HO}_2}^0r$.

The second outer-sphere electron reduction yields hydrogen peroxide, H$_2$O$_2$, at pH ≤ pK$_a$ = 11.7, or hydroperoxide, HO$_2^-$, at pH > pK$_a$ and may proceed through the following reactions depending on pH:
Due to the large O-O bond dissociation enthalpy of H₂O₂ (~2.2 eV/mol), it is hypothesized that further reduction of H₂O₂ requires catalytic adsorption, i.e. an inner-sphere mechanism. This is additionally supported by the observation in our work and others where high Faradaic efficiencies for hydro(gen) peroxide production is observed despite operational overvoltages larger than -1 V for Reaction 1:

\[ \text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O} \quad E^0_{\text{H}_2\text{O}_2/\text{H}_2\text{O}} = 1.77 \text{ V vs. SHE} \]  

We summarize the energetics involved in the catalytic (inner-sphere) and non-catalytic (outer-sphere) pathways through a Pourbaix diagram (modified for the RHE scale) for the reactive oxygen species in Figure 5. When the \( E_{1/2} \) for oxygen reduction is above \( E_{0'_2/\text{H}_2\text{O}_2}^0 \) (or \( E_{0'_2/\text{H}_2\text{O}_2}^0 \)), it can be assumed the reaction proceeds through an inner-sphere catalytic pathway with at least partial selectivity for H₂O production. This means that the electron transfer number (n) in this regime will be greater than two because reducing \( \text{O}_2 \) to \( \text{H}_2\text{O} \) requires four electrons. When the \( E_{1/2} \) for oxygen reduction is below \( E_{0'_2/\text{H}_2\text{O}_2}^0 \) (or \( E_{0'_2/\text{H}_2\text{O}_2}^0 \)) but above \( E_{0'_2/\text{O}_2}^- \) (or \( E_{0'_2/\text{H}_2\text{O}_2}^0 \)), the reduction of oxygen remains electrocatalytic but primarily results in \( \text{H}_2\text{O}_2 \). This is due to favorable adsorption of \( \text{O}_2 \), likely as *OO, which reduces the energy required to reduce \( \text{O}_2 \) to \( \text{O}_2^- \) (Figure 5b). Conversely, if the \( E_{1/2} \) for oxygen reduction is at \( E_{0'_2/\text{O}_2}^- \) (or \( E_{0'_2/\text{H}_2\text{O}_2}^0 \)), the reduction of oxygen is driven by an outer-sphere mechanism and is no longer electrocatalytic (see p(NDI-T2 P75) performance in Figure 5a). At \( E_{1/2} < E_{0'_2/\text{O}_2}^- \) (or \( E_{0'_2/\text{H}_2\text{O}_2}^0 \)), there are other factors limiting oxygen reduction, likely conductivity. Still, in this case there is no requirement for catalytic adsorption and oxygen reduction may proceed through the outer-sphere mechanism.
Figure 5. **a**) This modified Pourbaix diagram for the oxygen reduction reaction exhibits the pH-dependence of the formal reduction voltages of the single-electron reduction of $\text{O}_2$ ($E_{\text{O}_2/\text{O}_2^-}$) and the two-electron reduction ($E_{\text{O}_2/\text{H}_2\text{O}_2^-}$). The different regions of the diagram indicate roughly the voltages at which electrocatalysis occurs, depending on the observed $E_{1/2}$ of the ORR at different pH. The orange circles highlight the observed $E_{1/2}$ for oxygen reduction on p(NDI-T2 P75). **b**) A qualitative comparison between the outer-sphere and inner-sphere reaction pathways. The adsorption energies are arbitrary but demonstrate how the formal reduction voltages are modified in a catalytic pathway.

A critical takeaway from this analysis is to recognize the voltage window for electrocatalytic hydro(gen) peroxide production is the smallest in the basic pH range (Figure 5), meaning that no specific adsorption event is necessary to start to reduce $\text{O}_2$ at low overvoltages. This makes evaluating whether a material functions as an electrocatalyst for the 2-electron reduction in alkaline electrolytes difficult, especially when relying on standard electrochemical characterization (e.g. rotating ring disk electrode, constant current/voltage measurements, etc.), which does not provide direct proof of a binding event and cannot differentiate between hydro(gen) peroxide produced via the electrocatalytic versus outer-sphere pathway. Unfortunately, this is also the pH regime of stability for many transition metal-based electrodes used in these reactions. Indeed, it is difficult to compare results for different materials reported in literature because they are often evaluated in the high pH regime, where the change in performance (i.e. the difference between the observed $E_{1/2}$ for oxygen reduction and $E_{\text{O}_2/\text{H}_2\text{O}_2^-}$) between an electrocatalyst and a non-catalytic electrode is narrow and often within the window of reasonable experimental error. We thus emphasize that extra diligence be used in determining if a material is “catalytic” when working at high pH—specifically through a
combination of pH-dependent electrochemical measurements and, ideally, observation of a surface bound intermediate.

**Oxygen Reduction as an Outer-sphere Electron Transfer Process**

The *operando* Raman and UV-Vis spectroscopy reveal that, when $\text{O}_2$ is dissolved in the electrolyte and is electrochemically reduced at the p(NDI-T2 P75) electrode, both polaron and bipolaron formation are suppressed. However, we did not observe direct spectroscopic evidence of a surface bound intermediate species. These observations are consistent with a chemical reaction in which an electron is transferred between the polaronic state of the polymer and oxygen, forming a reduced oxygen species and re-oxidizing the polymer to the neutral state in the process (mediated electron transfer). As described previously, the outer-sphere reduction of oxygen should be thermodynamically limited by the first electron transfer to dissolved $\text{O}_2$ to form superoxide, $\text{O}_2^{-}$, which occurs at reversible conditions at $E^\text{0r}_{\text{O}_2(\text{aq})/\text{O}_2^{-}} = -0.16 \text{ V vs. SHE}$. The RRDE electrochemistry shows that oxygen reduction on p(NDI-T2 P75) occurs at the same voltage as this RLS and shows the same pH dependence (Figures S8, S11), strongly suggesting the outer-sphere nature of this process.

To test the validity of this outer-sphere hypothesis, we used density functional theory (DFT) to investigate the $\text{O}_2$ adsorption properties of p(NDI-T2 P75) at different redox states and voltage binding sites (Figure S10). The neutral state of the polymer showed no affinity for binding $\text{O}_2$ (Figure S11). For the reduced states, the reduced complex (NDI-T2 + $\text{O}_2$)$^-$ and the case where isolated $\text{O}_2$ bears the entire charge are energetically identical and favorable relative to the case where the NDI-T2 alone bears the charge (Figure S11). Inspection of the partial charge distribution for the reduced complex (Figure 6a) shows that the extra $-1 \text{ e}^-$ charge is mainly localized on the $\text{O}_2$ molecule, leaving the NDI-T2 monomer almost neutral, irrespective of the $\text{O}_2$ location in the complex (Figure 6b). A full description of the DFT calculation methods is provided in the Supplementary Information. These results suggest that the lowest energy configuration is similar to the case where the electron is fully transferred to an isolated $\text{O}_2$ and that $\text{O}_2$ is not strongly bound to NDI-T2, which supports the outer-sphere oxygen reduction mechanism.
Figure 6. a) The partial charges borne by the NDI-T2 monomer and O_2 for all four reduced (NDI-T2 + O_2)^- complexes in the singly reduced case. b) The additional charge ($Q_{add} = Q_{red} - Q_{neu}$) distribution of the complexes with O_2 initiated at C4a1, C4a2, N, and S. c) Experimental and simulated (from microkinetic model) mass transfer corrected current density Tafel plot. d) Electron polaron coverage, $\theta_P$, in O_2-saturated and O_2-free electrolytes.

To better understand how the ORR proceeds through an outer-sphere mechanism on p(NDI-T2 P75) and to identify which elementary step is rate-limiting, we next simulated the atomistic processes through a microkinetic model. We considered the following EC'EC' mechanism to explain the observed electrochemistry.

$$E: \quad N + e^- \rightleftharpoons P \quad E_1^{II}$$  \[10\]

$$C': \quad P + O_2 \rightleftharpoons N + O_2^- \quad K_2$$  \[11\]
C*: \[ P + O_2^- + xH_2O \rightleftharpoons N + H_2O_2^{(x-2)} + xOH^- \] \[ K_3 \quad [12] \]

In this mechanism, the first electron transfer (E) converts the neutral polymer, \( N \), into its reduced electron polaron state, \( P \). The now electronically conductive polaronic state of the polymer can chemically reduce oxygen generating superoxide, \( O_2^- \), while regenerating the neutral state of the polymer (C'). In the next step, superoxide can similarly oxidize the polaron resulting in a chemical step that produces hydro(gen) peroxide and the neutral state of the polymer (C'). Note, because the polaron is always the electron donor to oxygen and superoxide, there is only one electrochemical step (Figure S12). We note that Step [11] corresponds to the elementary reaction considered in the DFT calculations.

A full description of the microkinetic model, solution procedure, and error analysis is included in the Supplementary Information. In short, reactions [10-12] are cast into a set of rate expressions and the fraction of the neutral and electron polaron states of the polymer as a function of applied voltage are determined using Butler-Volmer kinetics and the steady state approximation.\(^{66,67}\) The steady state solutions are simultaneously fit to both the experimental log current density – voltage (or Tafel) data and the linear current density – voltage RDE data at all pH's to extract a self-consistent set of fitting parameters describing the thermodynamics and kinetics of each elementary reaction step. These fitting parameters are the formal reduction voltage of reaction [10]: \( E_{1,0}^{0'} \); and the associated chemical and electrochemical reaction rate constants and symmetry coefficients: \( k_1^0, \beta_1, k_{f,2}, \) and \( k_{f,3} \). Note that the equilibrium constants for reactions [11,12], \( K_2 \) and \( K_3 \), are defined through the outer-sphere formal reduction voltages of reactions [1,2,6-8] relative to \( E_{1,0}^{0'} \).

The results of the simulation are shown in Figure 6c and 6d, and the values of the fitting parameters are presented in Table 1. As is evident in Figure 6c and S13a, the simulation provides excellent fits of the experimental data at all pH using a self-consistent set of pH-independent fitting parameters and can explain the observed Tafel behavior across 4-orders of magnitude in kinetic current.

**Table 1. Fitted parameters with their 95% confidence intervals for the simulated oxygen reduction reaction.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (± 95% Confidence Interval)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_{1,0}^{0'} ) (V vs. SHE)</td>
<td>(-0.190 ± 0.001)</td>
</tr>
<tr>
<td>( \log k_1^0 ) (mol cm(^2) s(^{-1}))</td>
<td>(-7.13 ± 0.02)</td>
</tr>
<tr>
<td>β₁</td>
<td>0.24 ± 0.01</td>
</tr>
<tr>
<td>----------</td>
<td>-------------</td>
</tr>
<tr>
<td>log $k_{f,2}$ (cm s$^{-1}$)</td>
<td>– 1.38 ± 0.02</td>
</tr>
<tr>
<td>log $k_{f,3}$ (cm s$^{-1}$)</td>
<td>1.06 ± 0.03</td>
</tr>
</tbody>
</table>

The formation of the electron polaron in Step 1 of the reaction mechanism is identified as the RLS. Note that Step 3 always has $K_3 > K_2$ and $k_{f,3} > k_{f,2}$ at all pH's in this study and is, therefore, the fastest reaction of the series. Because the polaron formation is the RLS, the polaron is rapidly consumed by dissolved oxygen in the electrolyte. This effect can be seen in the simulated polaron concentration in the presence and absence of O$_2$ (Figure 6d), which qualitatively reproduces the experimental *operando* spectroscopic observations of the suppression (or consumption) of the polaron when O$_2$ is present.

In Figure S15b, the fitted $E_{1/2}^I$ values are shown as dotted lines overlaying the experiment cyclic voltammograms of p(NDI-T2 P75) in Ar-saturated electrolytes. We find that the fitted $E_{1/2}^I$ values show excellent agreement with the observed $E_{1/2}$ of the first polaron peak, which supports the hypothesized reaction mechanism.

**Testing the Outer-sphere Hypothesis Using Other OMIECs**

We further examine our proposed EC’EC’ mechanism by benchmarking the oxygen reduction performance of select metal-free OMIECs as well as glassy carbon, which is the underlying substrate for these measurements and similarly reduces oxygen through an outer-sphere pathway (Figure 7). The polymers chosen were p(NDI-T)$^{68}$, p(gPyDPP-MeOT2)$^{69}$, and p(g3T2)$^{37}$ (Figure 7a).

First, we employ p(NDI-T)$^{68}$, which can be reduced to its electron polaronic state at voltages more positive than $E_{0_{2}/O_2^-}^{0I}$ (Figure 7b), to demonstrate that positively shifting the ion-insertion redox voltage does not shift the $E_{1/2}$ of oxygen reduction more positive than $E_{0_{2}/O_2^-}^{0I}$. In the EC’EC’ process, when the voltage for the first electrochemical step (electron polaron formation) is positive of $E_{0_{2}/O_2^-}^{0I}$, the ORR will be thermodynamically limited by $E_{0_{2}/O_2^-}^{0I}$. Following this rationale, it is not surprising that p(NDI-T) and p(NDI-T2 P75) exhibit comparable HPPR activity (Figure 7c). Here, however, it is unclear whether polaron formation remains rate-limiting and the observed increase in current relative to p(NDI-T2 P75) may be due to a larger capacity of reactive electrons in the film or from a difference in electrochemically active surface area.
Figure 7. a) Chemical structures of the OMIECs tested, including p(NDI-T2 P75), p(NDI-T), p(PyDPP-MeOT2) and p(g3T2). b) RDE measurements in Ar-saturated 0.1 M KOH at a scan rate of 5 mV s$^{-1}$. Current densities were scaled to highlight redox features. The voltammograms were scaled by a factor of 1, 1, 2, 2, and 50 for p(NDI-T2 P75), p(NDI-T), p(PyDPP-MeOT2), p(g3T2), and glassy carbon, respectively. c) RRDE measurements in O$_2$-saturated 0.1 M KOH at 1600 r.p.m. at a scan rate of 0.5 mV s$^{-1}$.

Next, we evaluate p(PyDPP-MeOT2), which undergoes its first electrochemical step at voltages less than $E'_0$ (Figure 7b), to assess the hypothesis that OMIECs first need to form the electron polaron and become electronically conductive before they can reduce oxygen.
When the voltage for the electrochemical step is less than $E^{0r}_{O_2/O_2^2}$, the $E_{1/2}$ for oxygen reduction will correspond to the voltage of this first redox reaction, which is consistent with the proposed outer-sphere mechanism. Here, we take the $E_{1/2}$ for oxygen reduction to correspond to the largest increase in reduction current (~0.17 V vs. RHE), though we note the initial activity in p(gPyDPP-MeOT2) is likely caused by residual Pd (Table S1) or exposure of the underlying glassy carbon substrate. In agreement with this finding regarding the crucial nature of the first electrochemical step, p(g3T2), a p-type OMIEC, does not effectively reduce oxygen through the EC’EC’ mechanism with high activity because of the lack of ion-insertion redox at appropriate reduction voltages (Figure 7)—although here too there is likely some exposure of the underlying glassy carbon substrate.

While the side chains for these OMIECs are not identical, they all contain a polar (hydrophilic) portion, which is essential for bulk ion-insertion redox. An NDI-T2 polymer with entirely nonpolar side chains was tested and proved to be inoperative in aqueous electrolytes (Figure S14). The OMIECs studied here span polymers with variations in backbone chemistry (homop- and copolymers) and side chain chemistry, suggesting that the reactivity of many polymers within this class of materials may be rationalized through this outer-sphere and EC’EC' mechanism. However, we note our sample set of materials is still too narrow to make general claims for the whole range of OMIECs.

**Conclusions**

In this work, we investigated a set of organic mixed ionic-electronic conducting polymers as single-phase electrodes for the oxygen reduction reaction, focusing on p(NDI-T2 P75) as a model system. In p(NDI-T2 P75), the halfwave voltages for the bulk ion-insertion redox reactions (electron polaron formation) and oxygen reduction were found to be independent of pH, and the dominant product was found to be hydro(gen) peroxide ($n = 2$) across the pH range investigated. Despite suppression of the polaronic state during oxygen reduction, no evidence for a surface bound intermediate was observed through operando UV-Vis and Raman spectroscopy, pH-dependent electrochemistry, and DFT calculations. The reactivity was thus rationalized through an outer-sphere EC’EC' kinetic model which extracted the polaron formation reaction as the rate-limiting step.

Importantly, this interpretation explains oxygen reduction reactivity trends of other electron/cation and hole/anion transporting polymers through the relationship between their electron polaron formation voltage relative to the outer-sphere oxygen to superoxide formal
reduction voltage \( E_{O_2/O_2^-}^{0r} \). Importantly, we find that shifting the ion-insertion redox voltage above \( E_{O_2/O_2^-}^{0r} \) does not shift the \( E_{1/2} \) of oxygen reduction more positive than \( E_{O_2/O_2^-}^{0r} \). While our results do not preclude the opportunities for polymers to serve as electrocatalysts for oxygen reduction, they demonstrate that electronic conductivity, redox-functionality, and even the presence of heteroatom N, O, and S-functionalities in organic structures are not sufficiently general as catalytic design principles. In addition, our work provides a framework to rationalize the energetic contributions to oxygen reduction across pH and understand when (and if) electrode materials are serving as true “catalysts.”
Experimental Methods/Materials

Materials

Polymers ActivInk® N2200 (P-0) was purchased from Flexterra and used without further purification. P75 was synthesized according to procedures previously described in the literature. The polymers P75, p(NDI-T), p(gPyDPP-MeOT2), and p(g3T2) were purified by preparative Gel Permeation Chromatography (GPC, Japan Analytical Industry), using chloroform as the solvent. Paper electrodes (AvCarb P50T) were purchased from the FuelCellStore. 99.9 % potassium chloride (KCl) and 99.99% potassium hydroxide (KOH, semiconductor grade) were purchased from Sigma Aldrich. Argon (99.999%) and Oxygen (99.999%) gas were purchased from Praxair. Anhydrous chloroform was purchased from Sigma Aldrich. Potassium bicarbonate KHCO₃ (>99%) was purchased from Sigma Aldrich. Indium coated tin oxide (ITO) was purchased from Ossila.

Electrochemical characterization and RRDE measurements

Polymer solutions of p(NDI-T2 P75) were prepared by dissolving the polymer in chloroform at a mass concentration of 11.7 mg/mL. Prior to deposition, the RRDE was cleaned and polished with Al₂O₃ (particle size 0.05 μm) to a mirror finish. To create thick polymer films (estimated thickness = 1 μm), 10 μL of this solution was dropcast onto the glassy carbon disk of a rotating ring disk electrode (RRDE) (E6R1, Pt ring, polyether ether ketone (PEEK) shrouded, Pine Research) and the electrode was rotated at 400 r.p.m. for 2 min.

Three-electrode electrochemical measurements were conducted in an alkaline-resistant PTFE cell (AF01CKT1001, Pine Research Instrumentation) using a VSP-300 potentiostat (Biologic), with a leakless Ag/AgCl reference electrode (ET069, eDAQ), a coiled Pt wire counter electrode, and the RRDE with the dropcast or spin cast films p(NDI-T2 P75) film. All voltages are referenced versus the reversible hydrogen electrode (RHE), where the RHE voltage of the Ag/AgCl reference for each experiment was standardized against a bulk RHE electrode (Hydroflex Hydrogen Reference Electrode, eDAQ) in each electrolyte prior to testing. The 0.1 M KOH electrolytes were prepared using KOH and ultrapure de-ionized water. For each experiment, the uncompensated resistance, R, was measured at open circuit voltage (polymer is in the pristine, neutral state) through electrochemical impedance spectroscopy (EIS) at the high frequency intercept and iR correction was completed manually during the data analysis phase. In Ar-saturated solution, the Pt ring was electrochemically cleaned according to the procedure outlined by Chen et al. The p(NDI-T2 P75) film was then cycled five times between 0.2 V and –0.5 V vs. Ag/AgCl and another five times between 0.2 V and –1.0 V vs. Ag/AgCl at 5 mV s⁻¹ scan rate. O₂ gas was then bubbled through solution for at least 30 minutes to saturate the electrolyte. In O₂-saturated solution, RRDE measurements were completed at different rotation rates (400, 900, 1200, and 1600 r.p.m., MSR Rotator, Pine Research) while the p(NDI-T2 P75) was cycled between 0.2 V and –1.0 V at 5 mV s⁻¹ and the ring was held constantly at 1.2 V vs RHE. At 1600 r.p.m., an extra RRDE measurement was completed following the same procedure as before, with a changed scan rate of 0.5 mV s⁻¹.
**H-cell measurements**

Electrolysis was performed in a 2-compartment glass H-cell with a ceramic separator. The cathode compartment housed a 0.25 cm$^2$ Teflon-coated carbon paper (AVCarb P50T) electrode loaded with ~4 mg cm$^{-2}$ polymer, and a leakless Ag/AgCl reference electrode (eDAQ). In the anode compartment, Ni foam (MTI) was used as the counter electrode, and each compartment was filled with 5 mL 0.1 M KOH. Electrolytes were stirred and O$_2$ was bubbled into the cathode test compartment throughout the experiment. At 20-minute intervals 600 μL aliquots of sample were collected from the cathode compartment and replaced with fresh electrolyte.

Peroxide concentration was measured using a Cerium(IV) sulfate colorimetric assay.$^{44}$ Samples were prepared by mixing 175 μL of analyte, 700 μL of 1 mM Ce(IV) solution (in 0.5 M H$_2$SO$_4$), and 875 μL of 0.5 M H$_2$SO$_4$. The UV-visible spectrum (Cary 6000i UV-Vis Spectrometer) was recorded in transmission mode, and the intensity at 318 nm was used to quantify the Ce(IV) concentration in the sample, from which the H$_2$O$_2$ concentration was determined. A linear calibration curve was constructed by measuring analytes of known H$_2$O$_2$ concentration. When necessary, analytes were diluted in 0.5 M sulfuric acid to be within the measurement range of the assay.

**Spectroelectrochemical measurements**

Thin films on ITO coated glass substrates were prepared by spin coating. 65 μL of a p(NDI-T2 P75) solution (10 mg/mL) were spin coated onto a cleaned ITO coated glass substrates at 1000 r.p.m.. A thin layer of epoxy glue was applied at the edges of the film to prevent delamination (5 minute setting, Loctite Epoxy). The p(NDI-T2 P75) film was then placed into a quartz cuvette (DLC-300-Q-20, Starna Cells) filled with 0.1 M KOH. The electrochemical measurements were completed in a three-electrode set-up with a PEEK-shrouded leakless Ag/AgCl reference (eDAQ) and a coiled Pt wire as the counter. The UV-vis measurements were completed with a Tungsten light source (HL-2000-LL, Ocean Optics) and a spectrometer (QE Pro, Ocean Optics) and the instruments were synchronized using a Matlab code.$^{37}$

**Raman measurements**

In-situ Raman spectra were acquired by a self-design electrochemical cell. (3D-printed by Protolabs, UK) with a miniature leakless Ag/AgCl reference electrode (eDAQ), and platinum sheet counter electrode (Sigma-Aldrich, USA). The samples were spin coated at 1000 r.p.m. for 60 s on an ITO slide (Kintec Inc, Hong Kong). Spectra were acquired in the Raman Stokes region using 532 nm excitation wavelength, in the range 150-2200 cm$^{-1}$ (Horiba Xplora Confocal Raman). A 10x Olympus objective was used to perform measurements with laser power set at < 0.963 mW to avoid sample degradation. For a good signal-to-noise ratio, each spectrum was taken over an integration time of 20-30 s and averaged over three measurements. The spectrometer was calibrated through a Si sample using the spectral line 520.7 cm$^{-1}$. Spectra were analyzed using OMNIC software. Electrochemical signals were applied through a Bio-Logic potentiostat. A constant voltage was held for at least 30 seconds before each Raman measurement.

**Microkinetic modeling**

We use MATLAB R2019b to fit the model to the experimental data using the lsqcurvefit algorithm with MultiStart for 50,000 iterations.
The fitting parameters are the formal reduction voltage to form the polaron (in the absence of O\(_2\)) in Step 1, \(E_1^{0'}\), the polaron reaction’s standard rate coefficient, \(k_1^0\), and associated symmetry coefficient, \(\beta_1\), as well as the forward chemical rate coefficients of Steps 2 and 3, \(k_{f,2}, k_{f,3}\).

The 95% confidence interval for each variable is calculated as (\(q = 10534\) data points):

\[
CI = \pm t_{\alpha=0.025,DOF=q-5} \text{diag}(\sqrt{S})
\]  \[13\]

The covariance matrix, \(S\), is defined as:

\[
S = R^2 (A^T A)^{-1}
\]  \[14\]

Where \(A\) is the Jacobian matrix of the fitted values with regards to the fitted coefficients, \(A^T\) is the transpose matrix of \(A\), and \(R^2\) is the mean square log error.

\[
R = \frac{1}{q^{0.5}} \sqrt{\sum (\log j_{\text{model}} - \log j_{\text{exp}})^2 + \sum (j_{RDE,\text{norm}} - j_{RDE,\text{exp}})^2}
\]  \[15\]

The Jacobian matrix, \(A\), is the partial derivative matrix of \(j\) with respect to the rate constants, i.e.:

\[
A = \begin{bmatrix}
\frac{\partial j_1}{\partial E_1^{0'}} & \ldots & \frac{\partial j_1}{\partial k_{f,3}} \\
\vdots & \ddots & \vdots \\
\frac{\partial j_q}{\partial E_1^{0'}} & \ldots & \frac{\partial j_q}{\partial k_{f,3}}
\end{bmatrix}
\]  \[16\]
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Author contributions:

A.G. and J.T.M. conceived the idea. A.G., J.T.M, A.S., and W.C.C. supervised the work. A.F.D. performed the RRDE and UV-Vis spectroelectrochemistry characterization. A.F.D. performed the OECT measurements. A.Y.L. and I.D. performed the operando Raman measurements. H.Y., D.P., and J.N. performed the DFT calculations. E.P. performed the H-cell peroxide quantification measurements. L.T. performed the stability measurements. K.W. and A.M. performed the ICP-MS measurements. I.P.M., X.C., S.G., A.M., and A.G. performed the syntheses. J.T.M. developed the microkinetic simulation. All authors discussed the results and contributed to preparing the final draft of the manuscript.

Data availability

The experimental data that support the findings of this study are available via [Placeholder for data repository] (Ref. XX) (To be published simultaneously with the manuscript)

Competing Interests:

The authors declare no competing interests.

Supplementary Information is available for this paper: Methods, Tables S1-S2, Figures S1-S15, Supplementary Discussion, and Supplementary References

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