Mechanistic Evidence for Ligand-Centered Electrocatalytic Oxygen Reduction with the Conductive MOF Ni$_3$(hexaiminotriphenylene)$_2$

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Supporting Information

ABSTRACT: Establishing catalytic structure–function relationships introduces the ability to optimize the catalyst structure for enhanced activity, selectivity, and durability against reaction conditions and prolonged catalysis. Here we present experimental and computational data elucidating the mechanism for the O$_2$ reduction reaction with a conductive nickel-based metal–organic framework (MOF). Elucidation of the O$_2$ reduction electrokinetics, understanding the role of the extended MOF structure in providing catalytic activity, observation of how the redox activity and pK$_a$ of the organic ligand influence catalysis, and identification of the catalyst active site yield a detailed O$_2$ reduction mechanism where the ligand, rather than the metal, plays a central role. More generally, familiarization with how the structural and electronic properties of the MOF influence reactivity may provide deeper insight into the mechanisms by which less structurally defined nonplatinum group metal electrocatalysts reduce O$_2$.

KEYWORDS: O$_2$ reduction, electrocatalysis, metal–organic framework, porous catalysts, 2D materials

INTRODUCTION

Understanding catalytic kinetics and thermodynamics to construct a reasonable reaction mechanism is central for both elucidating the behavior of a given catalyst and gaining predictive power over structure–function relationships. This predictive power aids in efficiently optimizing catalyst performance by systematically tuning the structural and electronic properties of the catalyst. One class of materials that could benefit from mechanism-guided optimization is nonplatinum group metal (non-PGM) electrocatalysts for the O$_2$ reduction reaction (ORR) to water (4e$^-$ reduction) and/or hydrogen peroxide (2e$^-$ reduction). Such catalysts typically include abundant transition metals and/or heteroatoms such as N, O, and S doped into a carbonaceous matrix.1–6 Although quite active and stable during ORR, previously reported non-PGM catalysts often consist of amorphous carbon mechanically blended with transition metal macrocycles or other metal and main group heteroatomic sources. These relatively poorly defined materials do not lend themselves to facile mechanistic studies; the inhomogeneous dispersion and irregular orientation of the dopants throughout the carbon matrix engenders structural ambiguity that makes identification, experimental probing, and computational modeling of active sites difficult.

Conversely, highly ordered metal–organic frameworks (MOFs) containing well-defined, spatially isolated active sites present an attractive platform for experimental and computational correlation between the chemical and electronic structure of a given catalyst and the electrocatalytic activity and mechanism, a feat that is traditionally restricted to homoge-

Figure 1. Ni$_3$(HITP)$_2$ structure. Ni, N, and C atoms are shown in yellow, blue, and gray, respectively. H atoms are omitted for clarity.
an active ORR electrocatalyst stable in alkaline medium. The activity of Ni₃(HITP)₂ compares well with those of the most active non-PGM electrocatalysts, with an ORR onset potential (j = −50 μA·cm⁻²) of 0.82 V versus RHE.

Unlike other non-PGM catalysts, Ni₃(HITP)₂ presents a well-defined structure and thus the opportunity to determine whether the ORR activity is associated with the organic building blocks or the metal ions. These results could have implications for understanding the wider class of non-PGM catalysts, whose mechanism for ORR activity remains the subject of numerous studies.

Here, we present experimental and computational evidence for a ligand-based active site in Ni₃(HITP)₂. Our data show no evidence for Ni involvement in the catalytic cycle, but suggest important consequences for changing the electronic structure of the ligand. Establishment of precise structure–function relationships in this material introduces the possibility for tuning the structure with atomic precision such that catalytic ORR activity, selectivity, and stability can be maximized.

**RESULTS AND DISCUSSION**

Having previously shown that Ni₃(HITP)₂ reduces O₂ electrocatalytically in strongly basic medium (0.1 M KOH), we explored its utility over the wider aqueous pH range and found that the material is competent for ORR catalysis under all alkaline conditions (pH 8 and above), but not in acidic medium. Indeed, cyclic voltammograms (CVs) of Ni₃(HITP)₂ above pH 8 showed catalytic waves with no loss in current density over 20 cycles, whereas catalytic current decreased with every cycle in acidic media (Figure 2).

To derive a kinetic rate law for ORR with Ni₃(HITP)₂, we sought to determine the reaction order in [O₂], [H⁺], and the number of electrons transferred prior to or during the rate-limiting step. The reaction order in [O₂] was measured at varying potentials as well as varying concentrations of O₂. At pH 13, in the potential range of 0.667 to 0.787 V versus RHE, O₂ reduction exhibits an [O₂] order of 0.78–0.88, nearing first-order (Figure S1a). At pH 8, in the potential range of 0.320 to 0.520 V vs RHE, O₂ reduction is also first-order in [O₂] (Figure S1b).

To determine the number of electrons involved in the rate law, we collected potentiostatic data under O₂ atmosphere in pH 8, 9.5, and 13.0, and passing a cathodic current of 10 μA in the presence of O₂. These conditions evidenced a sub-Nernstian δE/δpH relationship of −22 mV·dec⁻¹, corresponding to a fractional order of [H⁺]¹/₆. This low fractional order implies that there are no proton-coupled electron transfer (PCET) steps prior to or in the rate-limiting step. Although intriguing, a sub-Nernstian order in a given reactant is not unprecedented, and can be associated with experimental conditions deviating from the ideal standards employed in electrokinetic derivations or from competing reaction kinetics, for instance. Notwithstanding, the fractional order in [H⁺] observed here is not caused by extraneous factors such as uncompensated Ohmic losses caused by ion strength differences in the electrolyte: titrating toward acidic or toward basic pH values produced similar data under both O₂ and N₂ atmosphere (Figures 4 and S3).

Another potential source of the fractional [H⁺] order is the variation of electrical conductivity of the catalyst with pH, which would lead to changes in the Tafel slopes. The Tafel slopes are nearly identical at pH 13 and pH 8, −128 mV·dec⁻¹ and −124 mV·dec⁻¹ (Figure 3), respectively, and are close to −118 mV·dec⁻¹, the value expected for an irreversible 1e⁻ transfer in the rate-limiting step. The linear Tafel slopes and consistent first-order with respect to [O₂] over the activation-controlled ORR potential range suggests that the kinetic rate law does not change over the probed potential range.

Figure 2. Cyclic voltammograms of Ni₃(HITP)₂ under O₂ atmosphere in pH 13, pH 8, and pH 4. Potentials are referenced versus RHE.

To establish whether the 1e⁻ transfer step is coupled to proton transfer, galvanostatic [H⁺] order data was collected while titrating the alkaline electrolyte from pH 13.0 to pH 9.5 and passing a cathodic current of 10 μA in the presence of O₂. These conditions evidenced a sub-Nernstian δE/δpH relationship of −22 mV·dec⁻¹, corresponding to a fractional order of [H⁺]¹/₆. This low fractional order implies that there are no proton-coupled electron transfer (PCET) steps prior to or in the rate-limiting step. Although intriguing, a sub-Nernstian order in a given reactant is not unprecedented, and can be associated with experimental conditions deviating from the ideal standards employed in electrokinetic derivations or from competing reaction kinetics, for instance. Notwithstanding, the fractional order in [H⁺] observed here is not caused by extraneous factors such as uncompensated Ohmic losses caused by ion strength differences in the electrolyte: titrating toward acidic or toward basic pH values produced similar data under both O₂ and N₂ atmosphere (Figures 4 and S3).

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Figure 3. Tafel plots for ORR on Ni₃(HITP)₂ in pH 13 versus pH 8 electrolyte.

Figure 4. Dependence of ORR onset potential on pH, with acid and base titrant to show reversibility of the ORR potential dependence on pH.
to different apparent current density as a function of pH at a fixed potential. However, the electrical conductivity of Ni₃(HITP)₂ films grown onto interdigitated electrodes decreased with decreasing pH, a trend opposite to what would be expected if the conductivity had any effect on the kinetic rate law (Figure S4, Supplementary Note 1).

Altogether, the data above point to the following empirical rate law:

\[ j = k_0[O_2]^\alpha[H^+]^{1/6}e^{\alpha F/R T} \]

where \( j \) is the measured steady state current density, \( k_0 \) is a potential-independent rate constant, \( E \) is the applied potential, \( \alpha \) is the experimental transfer coefficient for the reaction (here, approximated as 0.5), \( \alpha \) is the potential-independent rate constant, \( \alpha \) is the experimental transfer coefficient for the reaction (here, approximated as 0.5), \( F \) is Faraday’s constant, \( R \) is the gas constant, and \( T \) is the absolute temperature.

The first-order in \([O_2]\), partial order in \([H^+]\), and 1e⁻ transfer in the rate-limiting step point to \( O_2 \) binding to the catalyst as the rate-limiting step, with formation of superoxide.

To identify the specific site for \( O_2 \) activation in our catalyst, we subjected films of Ni₃(HITP)₂ grown on indium–tin-oxide (ITO)-coated polyethylene terephthalate (PET) to in situ investigation by X-ray absorption spectroscopy (XAS) at the Ni K-edge. Potentiostatic ORR experiments on the Ni₃(HITP)₂ films evidenced no shift in the Ni K-edge in the X-ray absorption near-edge spectroscopic (XANES) region (Figure 5a). Additionally, the rising edge energy (8343.7 eV, measured at the half-height of the absorption edge) was close to that of a standard Ni(II) complex, nickel(II) phthalocyanine (8344.1 eV). This confirmed that Ni remains in the +2 oxidation state throughout catalysis. Furthermore, R-space extended X-ray absorption fine structure (EXAFS) spectra both before and during ORR indicated no significant change in the coordination environment or nearest neighbor distances with respect to the Ni atoms (Figure 5b). EXAFS spectra both before and during catalysis yielded similar best fit parameters giving identical Ni–N bond distances of 1.84 Å (Table S3), consistent with square-planar divalent Ni atoms.13

The kinetic and XAS data suggest that \( O_2 \) binding and activation in Ni₃(HITP)₂ do not occur on Ni, but on the ligand. To determine which of the ligand atoms present the most favorable binding site for \( O_2 \), we employed density functional theory (DFT) calculations.14,15 Specifically, we considered a neutral fragment consisting of a central HITP³⁻–ligand bound to three Ni atoms and terminated with o-diaminobenzosemiquinonate ligands (Figure 6a, Supplementary Note 2). To identify the most likely active site for catalysis, we considered specific sites where \( O_2 \) would most readily bind: the Ni atom, the imine N atoms, or one of the three unique C atoms. The calculations indicated that chemical binding of \( O_2 \) to the Ni center had an uphill free energy of 1.4 eV, and no energy minimum was found for binding \( O_2 \) to a nitrogen atom, which together point to a carbon-based active site. Of the three unique C atoms, the optimal binding site was calculated to be the \( \beta \)-C relative to the imine group, as shown in Figure 6b. Although the binding energy of \( O_2 \) to this C atom in the absence of electron transfer was found to be uphill by 1.1 eV, no energy minimum was found for the remaining two distinct C sites, which are therefore unfavorable for \( O_2 \) binding.

The potential for this \( \beta \)-C atom to serve as an \( O_2 \) binding site was further supported by Mulliken charge population analysis.16 Whereas all other atoms had Mulliken populations of close to zero, the \( \beta \)-C was found to have a Mulliken population of –1.01 (Figure S5). This larger population indicates a likely site for reactivity, as charge localization can point to the easiest location for breaking aromaticity. Importantly, the orientation of the C-bound \( O_2 \) with respect to the NH group of the HITP ligand raises the possibility of a stabilizing hydrogen bonding interaction between the distal O atom and the imine proton, which indeed were found to lie 1.98 Å apart.

Given that the thermodynamic barrier for \( O_2 \) binding to the optimal carbon site was still higher than would be expected given the observed catalytic activity, we investigated the

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Figure 5. (a) XANES spectrum of Ni₃(HITP)₂ before versus during ORR in pH 13 along with that of Ni(II) phthalocyanine; (b) Fourier transforms of \( k^2 \)-weighted Ni K-edge EXAFS data of as-prepared Ni₃(HITP)₂ and under ORR conditions.

Figure 6. (a) Model fragment of Ni₃(HITP)₂; (b) Calculated binding site of \( O_2 \) onto the Ni₃(HITP)₂ fragment. C, H, N, Ni, and O atoms shown in gray, white, blue, yellow, and red, respectively.
possibility of electron transfer accompanying O_2 binding. Indeed, binding of O_2 to the Ni_3(HITP)_2 fragment in concert with a 1e^- transfer to O_2 to form superoxide was found to be endergonic by only 0.1 eV in the absence of an applied potential. Notably, the barrier for electrochemical binding of O_2 to the Ni sites was found to be considerably higher, at 0.6 eV. The barrier for electrochemical binding of O_2 to the β-C is not prohibitive and is consistent with the experimental observation of first order [O_2] dependence as well as a Tafel slope of approximately −118 mV-dec^-1. In agreement with rate-limiting superoxide formation, subsequent protonation of superoxide was calculated to be exergonic by 0.3 eV. Lastly, our calculations indicate that transfer of a second electron to break the oxygen-catalyst bond and release H_2O^- is favorable by 1.2 eV (Figure 7, Table S4). Although Ni serving as an O_2 binding site here is unlikely, the spin-density plot of the MOF model fragment shows that electrochemical binding of O_2 breaks the spin symmetry, with excess spin distributed across both the metal and ligand (Figure S6). Thus, the Ni sites do not directly participate in O_2 reactivity, but they do contribute to the electronic structure of the ORR-active species.

To obtain a more comprehensive picture of the full catalytic mechanism, potential sources of the fractional order in [H^+] were further investigated. The earlier discussion on this subject notwithstanding, a plausible explanation for the partial proton transfer and therefore is likely responsible for the fractional [H^+] order during ORR. Similar pH-dependent redox activity was reported in a nitrogen-doped graphitic carbon ORR catalyst.

With the discussed experimental and computational data in hand, the following mechanism for the 2e^- reduction of O_2 on Ni_3(HITP)_2 emerges (Scheme 1):

I. Rate-limiting electron transfer and binding of O_2 to the β-C with respect to the ligand imine to form the superoxide adduct
II. Protonation of bound O_2^- by water to form a hydroperoxide
III. Electron transfer to the hydroperoxide and desorption of HO_2^- IV. Regeneration of the catalyst resting state

This proposed mechanism is consistent with our experimental data and the computational studies, but it does not address whether the highly delocalized frontier orbitals of Ni_3(HITP)_2 are necessary for catalysis or whether a smaller fragment of this material is sufficient for competent catalysis. To investigate the possibility of a small-molecule mimic of Ni_3(HITP)_2 acting as a competent ORR catalyst, we focused on the well-known molecular complex Ni(ISQ)_2 (ISQ = o-diiminobenzosemiquinone, Figure 8). Importantly, under conditions mimicking those employed for Ni_3(HITP)_2, Ni(ISQ)_2 showed no ORR activity (Figure S9).

Density functional theory (DFT) provided insight into the dramatic difference in catalytic activity between the MOF and the molecular complex (Figure S10). Specifically, whereas O_2 binding and electron transfer to the MOF is endergonic by only 0.1 eV (see above), calculations suggest that the formation of the superoxide complex with Ni(ISQ)_2 is endergonic by 0.7 eV at pH 13. Although in line with the experimental observation that the molecular complex is not a good ORR catalyst, this difference is surprisingly large and highlights the importance of having a delocalized valence band in the MOF. Indeed, representations of the highest occupied molecular orbitals for Ni(ISQ)_2 and the more extended Ni_3(HITP)_2 model system described earlier show significant redistribution of the π electron density in Ni(ISQ)_2, but very little disruption of the π system in Ni_3(HITP)_2 (Figure S11). In other words, the MOF is able to accommodate a key superoxide complex without significant disruption of its electronic structure, only by virtue of its extended covalent lattice. Thus, even though the metal itself does not play a significant role in ORR catalysis, the conductivity and electron delocalization in the MOF is essential for catalysis.

**CONCLUSIONS**

Electrochemical and spectroscopic techniques supported by computational evidence revealed that the active site for catalytic O_2 reduction with Ni_3(HITP)_2, an electrically conductive MOF, is not metal-based, as proposed for many transition-metal macrocycles, but rather ligand-based. The highly ordered MOF structure and well-defined active sites have enabled precise correlation of the structure and electronic structure of the catalyst with the ORR activity and mechanism, including the identification of a partial proton order related to the pH dependence of the MOF oxidation potentials. This comprehensive model for O_2 binding thermodynamics, electrokinetics, and detailed mechanism of ORR on Ni_3(HITP)_2 should enable...
catalyst design in other conductive MOF systems. Most importantly, these studies show that electron delocalization is critical for accessing key intermediates that become energetically prohibitive for molecular systems bearing only structural resemblance to the MOFs.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.7b02647.

Potentiostatic ORR order in [O2] with corresponding slopes. Koutecky−Levich data at pH 8. Current versus pH data under N2. Dependence of electrical conductivity on pH. Mulliken charge population analysis of the Ni3(HITP)2 model fragment before versus after electrochemical O2 binding. Excess spin density plot of superoxide bound-Ni3(HITP)2 model fragment. Dependence of MOF redox potentials on pH. Pourbaix diagram of Ni3(HITP)2. CV of Ni(ISQ)2 under N2 and O2. Calculated structures for Ni(ISQ)2 and a representative Ni3(HITP)2 fragment. Calculated HOMOs for Ni(ISQ)2 and Ni3(HITP)2 fragment with and without bound superoxide. Best-fit parameters for Ni K-edge EXAFS curve fitting. Calculated thermodynamic data for ORR with the Ni3(HITP)2 fragment and Ni(ISQ)2 (PDF)

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Notes
The authors declare no competing financial interest.
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