

# Thousand-fold increase in O<sub>2</sub> electroreduction rates with conductive MOFs

Ruperto G. Mariano, Oluwasegun J. Wahab,<sup>||</sup> Joshua A. Rabinowitz,<sup>||</sup> Julius Oppenheim, Tianyang Chen, Patrick R. Unwin,<sup>\*</sup> and Mircea Dincă<sup>\*</sup>



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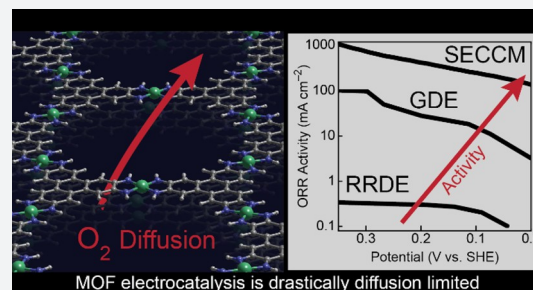


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Supporting Information

**ABSTRACT:** Molecular materials must deliver high current densities to be competitive with traditional heterogeneous catalysts. Despite their high density of active sites, it has been unclear why the reported O<sub>2</sub> reduction reaction (ORR) activity of molecularly defined conductive metal–organic frameworks (MOFs) have been very low: ca.  $-1 \text{ mA cm}^{-2}$ . Here, we use a combination of gas diffusion electrolyses and nanoelectrochemical measurements to lift multiscale O<sub>2</sub> transport limitations and show that the intrinsic electrocatalytic ORR activity of a model 2D conductive MOF, Ni<sub>3</sub>(HITP)<sub>2</sub>, has been underestimated by at least 3 orders of magnitude. When it is supported on a gas diffusion electrode (GDE), Ni<sub>3</sub>(HITP)<sub>2</sub> can deliver ORR activities  $>-150 \text{ mA cm}^{-2}$  and gravimetric H<sub>2</sub>O<sub>2</sub> electrosynthesis rates exceeding or on par with those of prior heterogeneous electrocatalysts. Enforcing the fastest accessible mass transport rates using scanning electrochemical cell microscopy revealed that Ni<sub>3</sub>(HITP)<sub>2</sub> is capable of ORR current densities exceeding  $-1200 \text{ mA cm}^{-2}$  and at least another 130-fold higher ORR mass activity than has been observed in GDEs. Our results directly implicate precise control over multiscale mass transport to achieve high-current-density electrocatalysis in molecular materials.



MOF electrocatalysis is drastically diffusion limited

## INTRODUCTION

Achieving synthetic molecular control over electrocatalytic materials is a longstanding challenge in electrocatalysis. Molecular materials need to deliver high current densities to be competitive with heterogeneous electrocatalysts, but this is rare.<sup>1</sup> Electrically conductive metal–organic frameworks (MOFs) offer a way to bridge this gap, as they are molecularly defined and are both intrinsically porous and conductive.<sup>2</sup> They are fundamentally distinct from electrocatalysts made from sacrificial MOF precursors (such as single-atom catalysts accessed via thermolysis or electrolytic degradation of MOFs), because they retain their molecular definition.<sup>3,4,13,14,5–12</sup> As such, the structure space available to conductive MOFs renders them an ideal platform to tune the atomic structure for performance. We and others have previously shown that a family of 2D MOFs with the general formula M<sub>3</sub>(HITP)<sub>2</sub> (HITP = 2,3,6,7,10,11-hexaiminotriphenylene, M = Co, Cu, Ni) (Figure 1A) are active for the O<sub>2</sub> electroreduction reaction (ORR), a transformation central to H<sub>2</sub>O<sub>2</sub> electrosynthesis, metal/air batteries, and fuel cells.<sup>4,15,16</sup> These and other conductive MOFs typically exhibit intrinsic surface areas ( $\sim 300\text{--}900 \text{ m}^2 \text{ g}^{-1}$ ) at least 10 times larger than that of dense metallic nanoparticles and conductivities comparable to that of graphite, yet their geometric current densities for ORR rarely exceed  $-1 \text{ mA cm}^{-2}$ , implying a surprisingly low intrinsic electrocatalytic activity.<sup>2,4,5,15,17–19</sup>

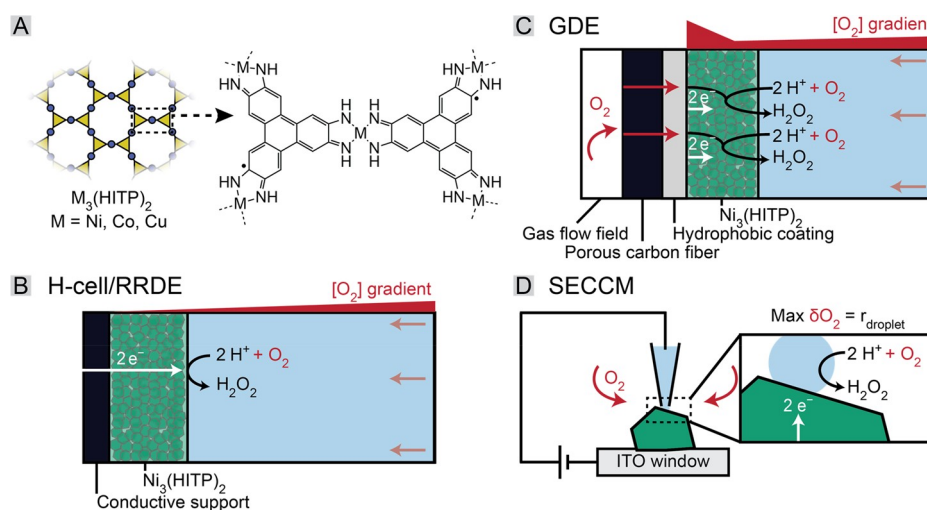
The performance of ORR electrocatalysts is most commonly measured using rotating ring disk electrodes (RRDEs) immersed in an electrolyte within two-compartment “H-cells”.<sup>4,20,21</sup> During ORR catalysis in an H-cell, a region of depleted O<sub>2</sub> concentration (the concentration boundary, or diffusion layer) is formed adjacent to the catalyst layer (Figure 1B), because O<sub>2</sub> is reduced to H<sub>2</sub>O<sub>2</sub> or H<sub>2</sub>O at the electrode/electrolyte interface. In combination with the low saturation concentration of O<sub>2</sub> in water ( $\sim 1 \text{ mM}$  at 1 bar of O<sub>2</sub> and 298 K), O<sub>2</sub> must diffuse over distances of ca.  $100 \mu\text{m}$  from the bulk electrolyte in order to reach the electrode/electrolyte interface.<sup>22</sup> Concentration gradients are further exacerbated in porous electrodes, where diffusion within the porous layer can be severely restricted;<sup>23,24</sup> the resulting transport resistance depresses the mass activity of the electrocatalyst and leads to underutilization of the active sites.

Under these circumstances, it is unclear whether the  $-1 \text{ mA cm}^{-2}$  limit arises from mass transport limitations or in fact reflects intrinsically slow ORR kinetics with molecular materials. To probe the fundamental limitations of ORR catalysis with

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**Figure 1.** Controlling mass transport during ORR electrocatalysis with conductive MOFs: (A) atomic structure and connectivity of  $M_3(\text{HITP})_2$ ; (B) schematic of transport gradients during ORR catalysis in a conventional electrochemical H-cell using RRDEs; (C) schematic of transport dynamics in a GDE combined with flow fields; (D) mass transport of  $\text{O}_2$  across a nanodroplet in SECCM.

MOFs and potentially unlock a much higher intrinsic activity, we pursued a campaign to lift mass transport limitations by integrating  $\text{Ni}_3(\text{HITP})_2$  with gas diffusion electrodes (GDEs) and by leveraging the rapid transport environment afforded by scanning electrochemical cell microscopy (SECCM).

Here, we show that conductive MOFs enable geometric ORR current densities greater than  $-150 \text{ mA cm}^{-2}$  if the mass transport of  $\text{O}_2$  is carefully controlled. When it is supported on a GDE (Figure 1C),  $\text{Ni}_3(\text{HITP})_2$  exhibits ORR activity and  $\text{H}_2\text{O}_2$  electrosynthesis rates  $>100$ -fold higher and  $>740$ -fold higher, respectively, than in an H-cell. At low mass loadings in a GDE, the gravimetric rates of  $\text{H}_2\text{O}_2$  electrosynthesis using  $\text{Ni}_3(\text{HITP})_2$  rival those of the highest rates reported for state of the art heterogeneous electrocatalysts. Together with efficient  $\text{O}_2$  mass transport, metal ion substitution revealed that the intrinsic porosity and conductivity of  $M_3(\text{HITP})_2$  are the major drivers of activity during ORR catalysis. By enforcing the fastest accessible mass transport rates using SECCM (Figure 1D), we find that  $\text{Ni}_3(\text{HITP})_2$  is capable of at least another 130-fold higher mass activity than has been observed in GDEs. Our results directly implicate precise control over mass transport to achieve high-current-density electrocatalysis in molecularly defined, conductive MOFs.

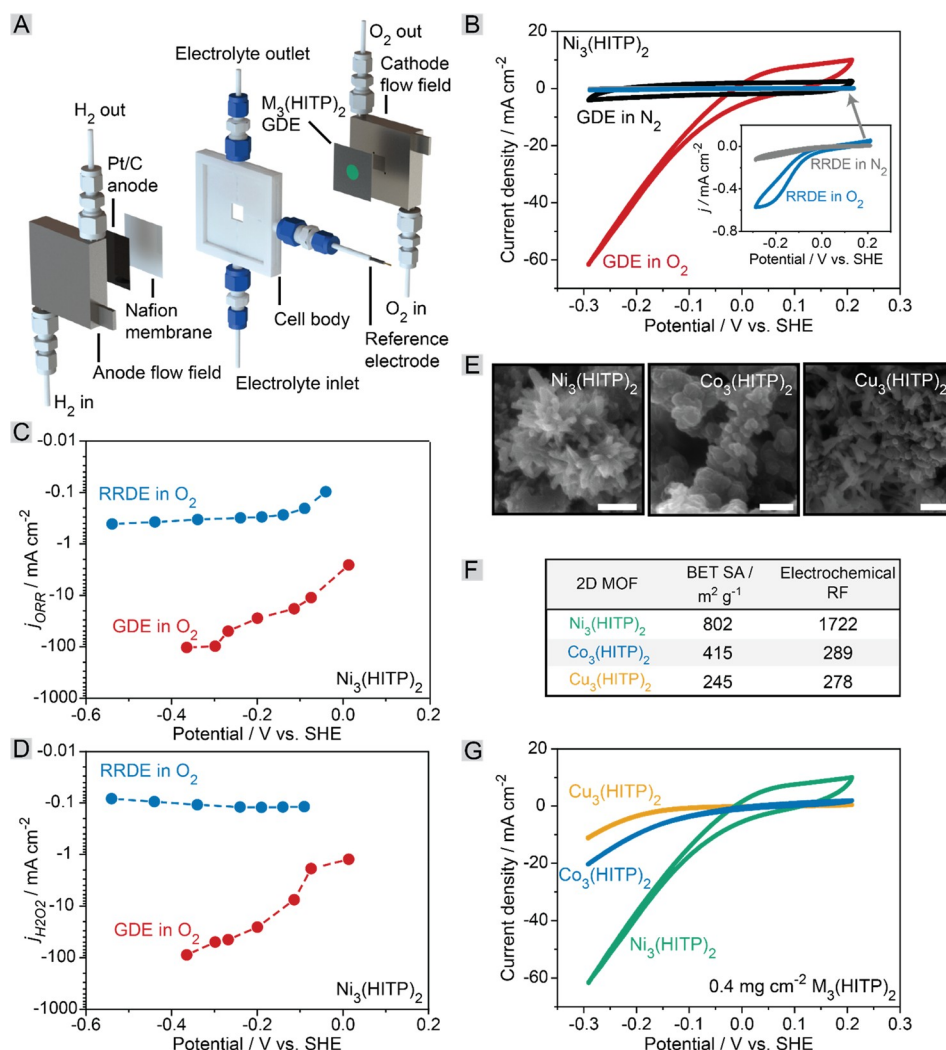
## RESULTS AND DISCUSSION

Due to its high conductivity, intrinsic porosity, and established activity for the ORR, we prepared  $\text{Ni}_3(\text{HITP})_2$ , an archetypal 2D conductive MOF, to understand mass transport effects on ORR catalysis.<sup>19</sup> Powder X-ray diffraction (PXRD) patterns (Figure S1) and X-ray photoelectron spectra (XPS; Figure S2) were consistent with literature precedent and indicated the formation of a monophasic and highly crystalline 2D framework.<sup>19,25</sup>  $\text{N}_2$  adsorption measurements of  $\text{Ni}_3(\text{HITP})_2$  (Figure S3) at 77 K after activation at 373 K under dynamic vacuum revealed a high Brunauer–Emmett–Teller (BET) surface area of  $802 \pm 0.8 \text{ m}^2 \text{ g}^{-1}$ . SEM imaging (Figure S4) indicated that the  $\text{Ni}_3(\text{HITP})_2$  powders were composed of crystallites measuring 50–200 nm agglomerated into  $1 \mu\text{m}$  wide clusters.

We drop-cast a suspension of as-synthesized  $\text{Ni}_3(\text{HITP})_2$  particles sonicated with Nafion (to act as a binder; see the Supporting Information and Figure S5) onto glassy-carbon

electrodes (GCEs) for a total mass loading of  $0.4 \text{ mg cm}^{-2}$  of  $\text{Ni}_3(\text{HITP})_2$ . We then evaluated the performance of the  $\text{Ni}_3(\text{HITP})_2$ -loaded GCEs for the ORR in a two-compartment H-cell combined with a RRDE setup (Figure 2B). We measured cyclic voltammograms (CVs) in  $\text{O}_2$  and  $\text{N}_2$ , using 1.0 M sodium chloride electrolyte buffered with 0.3 M sodium phosphate ( $\text{NaPi}$ ) at pH 7. Polarization from +0.21 to  $-0.29 \text{ V}$  versus the standard hydrogen electrode (SHE, to which all potentials are referenced), indicated that  $\text{Ni}_3(\text{HITP})_2$  exhibited less than  $-1 \text{ mA cm}^{-2}$   $\text{O}_2$  electroreduction activity. The onset of catalytic activity was observed at  $-0.05 \text{ V}$ , and a plateau in the CV (around  $-0.6 \text{ mA cm}^{-2}$ ) was observed beginning at  $-0.2 \text{ V}$  (Figure 2B, inset). Polarization to more negative potentials or an increase in the rotation rate did not significantly increase the current density for  $\text{O}_2$  reduction ( $j_{\text{ORR}}$ ; Figure S6A,B). We quantified the partial current density for  $\text{H}_2\text{O}_2$  synthesis ( $j_{\text{H}_2\text{O}_2}$ ) under potentiostatic conditions while applying an oxidizing potential of 0.91 V at the Pt ring to simultaneously detect  $\text{H}_2\text{O}_2$ .<sup>15</sup> (Figure 2C,D). The Faradaic efficiency (FE) for  $\text{H}_2\text{O}_2$  peaked at 60% ( $-0.121 \text{ mA cm}^{-2}$ ) at 0.09 V and decreased upon application of more cathodic potentials, dropping to 21% ( $-0.085 \text{ mA cm}^{-2}$ ) at  $-0.54 \text{ V}$  (Figure S6C). The small limiting current values ( $j_{\text{ORR}} = -0.4 \text{ mA cm}^{-2}$ ) are less than expected from the Koutecky–Levich equation ( $j_d \approx -2.5 \text{ mA cm}^{-2}$  at 1500 rpm for the  $2e^-$  process), indicative of slow  $\text{O}_2$  mass transport not only from the bulk solution to the  $\text{Ni}_3(\text{HITP})_2$  catalyst layer but also within the immersed  $\text{Ni}_3(\text{HITP})_2$ /Nafion catalyst layer.<sup>20</sup>

To investigate whether the ORR activity of  $\text{Ni}_3(\text{HITP})_2$  would improve under a rapid bulk mass transport regime, we drop-casted  $\text{Ni}_3(\text{HITP})_2$  particles onto GDEs, at the same mass loading of  $0.4 \text{ mg cm}^{-2}$  (SEM imaging in Figure S7 and S8). Composed of a carbon fiber support and a hydrophobic microporous conductive coating, GDEs enhance gas mass transport by providing a gas flow pathway unimpeded by electrolyte through the back of the electrode (Figure 1C).  $\text{Ni}_3(\text{HITP})_2$  GDEs were interfaced into a custom-built gas diffusion flow electrolyzer (Figure 2A, detailed in the Supporting Information)<sup>26–29</sup> with a microfluidic pocket that limits the contact area ( $\sim 0.8 \text{ cm}^2$ ) between the MOF-loaded GDE and electrolyte (Figure 2A). The  $\text{Ni}_3(\text{HITP})_2$  GDE was compressed



**Figure 2.** Polarization of  $\text{M}_3(\text{HITP})_2$  in an H-cell and using a GDE flow electrolyzer. All current densities reported are normalized to the geometric surface area. (A) Schematic of the gas diffusion flow electrolysis cell used in this study. (B) Cyclic voltammograms of  $0.4 \text{ mg cm}^{-2}$   $\text{Ni}_3(\text{HITP})_2$  GDEs in 1 M NaCl, 0.3 M sodium phosphate ( $\text{NaP}_i$ ) electrolyte at pH 7. Inset CVs show RRDE data at the same  $0.4 \text{ mg cm}^{-2}$  mass loading, but where the current scale is much smaller. Scan rate:  $50 \text{ mV s}^{-1}$ . The RRDE was rotated at 1000 rpm. Potentials vs SHE reported in (B) are not corrected for the system  $iR$  drop. (C) Geometric current densities for  $\text{O}_2$  reduction during potentiostatic polarization for both the RRDE and GDE electrolyses. The RRDE was rotated at 1500 rpm. (D) Partial current densities for  $\text{H}_2\text{O}_2$  synthesis during potentiostatic polarization for both the RRDE and GDE electrolyses. The RRDE was rotated at 1500 rpm. (E) SEM images of  $\text{M}_3(\text{HITP})_2$ . Scale bar: 200 nm. (F) BET surface area derived from  $\text{N}_2$  adsorption measurements and electrochemical roughness factors (RF) represented as multiples of geometric surface area, calculated from CVs obtained in  $\text{N}_2$ . (G) CVs of the three isorecticular  $\text{M}_3(\text{HITP})_2$  GDEs in  $\text{O}_2$ . Scan rate:  $50 \text{ mV s}^{-1}$ .

against a conductive, interdigitated flow field that rapidly transports  $\text{O}_2$  to the  $\text{Ni}_3(\text{HITP})_2/\text{electrolyte}$  interface. Electrolyte flowed through the cell and into a collection vial, enabling quantification of electrogenerated  $\text{H}_2\text{O}_2$ . Enhancing  $\text{O}_2$  transport to the  $\text{Ni}_3(\text{HITP})_2/\text{electrolyte}$  interface led to orders of magnitude higher ORR current densities using  $\text{Ni}_3(\text{HITP})_2$  GDEs. Across the same potential range as was used with RRDEs, CVs of a  $\text{Ni}_3(\text{HITP})_2$  GDE indicated that the geometric  $j_{\text{ORR}}$  was ca. 1–2 orders of magnitude larger with the GDE relative to the RRDE (Figure 2B). At  $-0.29 \text{ V}$ , whereas  $\text{Ni}_3(\text{HITP})_2$  exhibited a  $j_{\text{ORR}}$  value of only  $-0.6 \text{ mA cm}^{-2}$  on the RRDE, its activity on the GDE was  $-62 \text{ mA cm}^{-2}$ . Control experiments of both the GDE support under an  $\text{O}_2$  atmosphere (Figure S9) and the  $\text{Ni}_3(\text{HITP})_2$  GDE under an  $\text{N}_2$  atmosphere (Figure 2B) indicated that essentially all of the observed current could be attributed to ORR catalysis (i.e., no  $\text{H}_2$  evolution) occurring at the  $\text{Ni}_3(\text{HITP})_2$  sites. These data indicate that  $\text{Ni}_3(\text{HITP})_2$  was

starved of  $\text{O}_2$  during polarization in the H-cell, which led to a vast underestimation of its intrinsic electrocatalytic performance.

We evaluated the ORR performance of the  $\text{Ni}_3(\text{HITP})_2$  GDEs by measuring the current during step-potential polarization (Figure 2C). Unlike the case in the H-cell, the geometric  $j_{\text{ORR}}$  value using the GDE increased monotonically with the applied potential in a broader range, reaching a maximum current density of  $-103 \text{ mA cm}^{-2}$  at  $-0.36 \text{ V}$ , an approximately 310-fold improvement in  $j_{\text{ORR}}$  relative to those measured in the RRDE/H-cell. Similarly, the  $j_{\text{H}_2\text{O}_2}$  value using the  $\text{Ni}_3(\text{HITP})_2$  GDE increased as a function of applied potential from  $-1.2 \text{ mA cm}^{-2}$  at  $0.01 \text{ V}$  to a maximum current density of  $-88.5 \text{ mA cm}^{-2}$  (or 85% FE for  $\text{H}_2\text{O}_2$ ) at  $-0.36 \text{ V}$ , a 740-fold improvement over the maximum  $j_{\text{H}_2\text{O}_2}$  value measured using the RRDE/H-cell at the same mass loading (Figure 2D). With  $0.2 \text{ mL min}^{-1}$  of electrolyte flowing through the cell, we measured a 108 mM

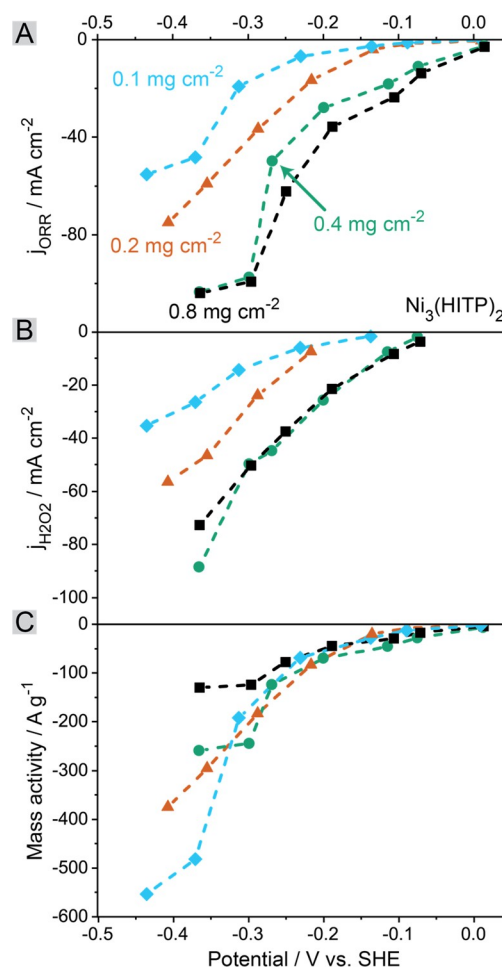


(~3270 ppm)  $\text{H}_2\text{O}_2$  product stream at  $-0.36$  V. These high ORR current densities corresponded to a mass activity of  $259 \text{ A g}^{-1}$  at  $-0.36$  V, which is competitive with state of the art,  $\text{H}_2\text{O}_2$ -producing heterogeneous electrocatalysts in a neutral electrolyte.<sup>30</sup> PXRD patterns and XPS spectra obtained immediately after polarization indicated that  $\text{Ni}_3(\text{HITP})_2$  retained its crystallinity, and we found no evidence for the formation of metallic Ni from reduction of framework  $\text{Ni}^{2+}$  (Figures S10 and S11). As  $\text{H}_2\text{O}_2$  concentrations were likely even higher within the  $\text{Ni}_3(\text{HITP})_2$  pores, these data indicate that  $\text{Ni}_3(\text{HITP})_2$  is stable to high local concentrations of electrogenerated  $\text{H}_2\text{O}_2$ .

Supporting conductive MOFs on GDEs is a general strategy that allowed us to probe the effect of metal ion substitution in  $\text{M}_3(\text{HITP})_2$  under a high  $\text{O}_2$  flux. We integrated two additional, isostructural HITP-based frameworks, namely  $\text{Cu}_3(\text{HITP})_2$  and  $\text{Co}_3(\text{HITP})_2$  with GDEs (Figure 2E–G; characterization in Text 1 in the Supporting Information and Figures S12–S17), to evaluate their ORR activity under high-mass-transport conditions.<sup>25</sup> Polarization in  $\text{O}_2$  revealed that the total  $j_{\text{ORR}}$  and  $j_{\text{H}_2\text{O}_2}$  values both depend on the identity of the MOF and vary in the order  $\text{Ni} > \text{Co} > \text{Cu}$  (Figure 2G). This reflected the trend in electrochemical surface area (ECSA, a composite value of intrinsic surface area and conductivity) among the three MOFs ( $\text{Ni} > \text{Co} > \text{Cu}$ ; Figure 2F and Figure S18).  $\text{Ni}_3(\text{HITP})_2$  exhibits more than 6-fold higher ECSAs in comparison to the Cu or Co analogues, characteristic of its high conductivity and porosity. On a mass activity basis,  $\text{Ni}_3(\text{HITP})_2$  exhibits the highest activity at the lowest driving forces (Figure S17A). These data provided a simple model to rationalize the observed  $j_{\text{ORR}}$  value:  $\text{Ni}_3(\text{HITP})_2$  is the most active of the three  $\text{M}_3(\text{HITP})_2$  because it possesses an intrinsically higher ECSA and therefore a higher density of active sites. Given that crystallinity generally engenders high conductivity and surface area in conductive MOFs, and noting that as-synthesized  $\text{Ni}_3(\text{HITP})_2$  is intrinsically more crystalline than either  $\text{Co}_3(\text{HITP})_2$  or  $\text{Cu}_3(\text{HITP})_2$  (cf. Figures S1 and S12), these results suggest that high conductivity, porosity, and crystallinity are the keys to unlocking high rates of ORR catalysis in MOFs.<sup>2</sup>

Motivated by the apparent dependence of  $j_{\text{ORR}}$  on  $\text{M}_3(\text{HITP})_2$  ECSA in the GDE and because maximizing  $j_{\text{ORR}}$  is technologically desirable, we sought to understand how much of the ECSA in  $\text{Ni}_3(\text{HITP})_2$  could be productively recruited for catalysis. To this end, we varied the  $\text{Ni}_3(\text{HITP})_2$  mass loading from  $0.1$  to  $0.8 \text{ mg cm}^{-2}$  (Figure 3; chronoamperograms are given in Figure S20). The geometric  $j_{\text{ORR}}$  value generally increased with higher catalyst loading (Figure 3A). For instance, at  $-0.36$  V, the geometric  $j_{\text{ORR}}$  value at  $0.4 \text{ mg cm}^{-2}$  was ~2-fold higher than that at  $0.1 \text{ mg cm}^{-2}$ . CVs in  $\text{N}_2$  showed that the ECSA also increased with increased mass loading (Figure S21 and Table S1). These mass-dependent increases in ECSA correlate with the increase in  $j_{\text{ORR}}$  and indicate a larger number of active sites available for ORR catalysis. Additionally, higher values of  $j_{\text{H}_2\text{O}_2}$  are correlated with higher mass loadings of up to  $0.4 \text{ mg cm}^{-2}$  (Figure 3B). At  $-0.36$  V,  $j_{\text{H}_2\text{O}_2}$  increased ~3.3-fold as the mass loading increased from  $0.1$  to  $0.4 \text{ mg cm}^{-2}$ . We did not observe a systematic correlation between mass loading and FE (Figure S22A), suggesting that  $2\text{e}^-$  reduction of  $\text{H}_2\text{O}_2$  to  $\text{H}_2\text{O}$ , or framework-catalyzed decomposition of  $\text{H}_2\text{O}_2$  to  $\text{O}_2$ , does not accelerate with higher mass loadings under the conditions employed here.

At a high overpotential, the mass activity decreases as the catalyst loading increases (Figure 3C and Figure S22B), with the



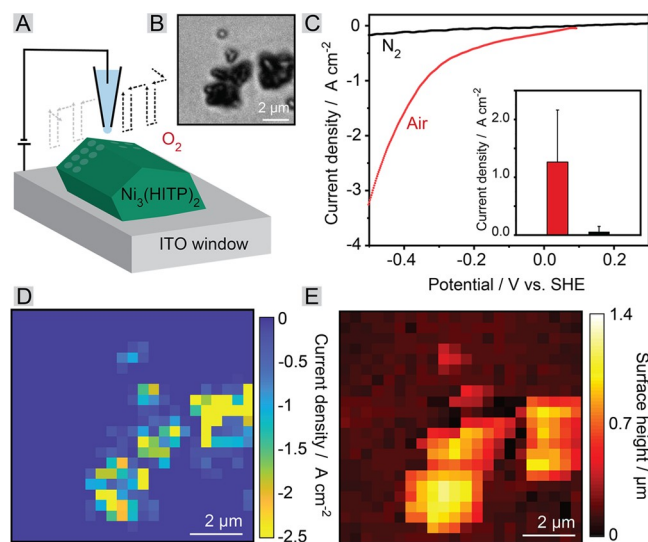
**Figure 3.** ORR activity limits in  $\text{Ni}_3(\text{HITP})_2$  GDEs. (A) Geometric current densities for the ORR during potentiostatic polarization with different catalyst mass loadings: (◆)  $0.1 \text{ mg cm}^{-2}$ ; (▲)  $0.2 \text{ mg cm}^{-2}$ ; (●)  $0.4 \text{ mg cm}^{-2}$ ; (■)  $0.8 \text{ mg cm}^{-2}$ . (B) Partial current densities for  $\text{H}_2\text{O}_2$  synthesis during potentiostatic polarization. (C) Comparison of total ORR mass activities of the four different mass loadings.

lowest mass loading of  $0.1 \text{ mg cm}^{-2}$  being responsible for the highest mass activity of  $553 \text{ A g}^{-1}$  at the most cathodic applied potential. At the highest applied potentials, the rate of  $\text{H}_2\text{O}_2$  production using the  $0.1 \text{ mg cm}^{-2}$  electrode is equivalent to a gravimetric rate of  $6570 \text{ mol H}_2\text{O}_2 \text{ kg}_{\text{MOF}}^{-1} \text{ h}^{-1}$ , better than or competitive with the highest activities reported among state of the art  $\text{H}_2\text{O}_2$ -evolving electrocatalysts.<sup>30–32</sup>

Although low  $\text{Ni}_3(\text{HITP})_2$  mass loadings yield the highest mass activities (Figure 3C), they also exhibit the lowest geometric  $j_{\text{ORR}}$  and  $j_{\text{H}_2\text{O}_2}$  values (Figure 3A,B). This is an important dilemma to address, because it implies that much of the ECSA in  $\text{Ni}_3(\text{HITP})_2$  GDEs remained underutilized at high mass loading. Indeed, an apparent plateau in the geometric  $j_{\text{ORR}}$  value (ca.  $-110 \text{ mA cm}^{-2}$ ) is observed for GDEs with  $0.4$  and  $0.8 \text{ mg cm}^{-2}$  of  $\text{Ni}_3(\text{HITP})_2$  at a high driving force. The contrast between the  $0.8$  and  $0.4 \text{ mg cm}^{-2}$  electrodes is small: doubling the mass loading provides only marginal improvements at low overpotentials and essentially identical activity at high overpotentials. Moreover, the  $j_{\text{H}_2\text{O}_2}$  value for the  $0.8 \text{ mg cm}^{-2}$  electrode is only ~80% of that for the  $0.4 \text{ mg cm}^{-2}$  electrode (Figure 3B). If the mass activity of the  $0.8 \text{ mg cm}^{-2}$  electrode were identical with that of the  $0.1 \text{ mg cm}^{-2}$  electrode ( $481 \text{ A g}^{-1}$

at  $-0.36$  V), the measured  $j_{\text{ORR}}$  value for the  $0.8 \text{ mg cm}^{-2}$  electrode should be  $>380 \text{ mA cm}^{-2}$ , almost  $4\times$  larger than what we observe. In fact, mass activities across the four different mass loadings were relatively uniform at low overpotentials and diverged prominently only at high overpotentials (Figure S22B). This activity plateau limited the single-pass  $\text{O}_2$  conversion rate to just 30% (Figure S22C).

High-resolution scanning electrochemical cell microscopy (SECCM; Figure 4A)<sup>33–35</sup> lent critical insight into the origin of



**Figure 4.** SECCM mapping of ORR activity on  $\text{Ni}_3(\text{HITP})_2$ . (A) Schematic of the experimental geometry in SECCM using a single-barrel nanopipet. (B) Optical image of the  $\text{Ni}_3(\text{HITP})_2$  particles scanned using SECCM under air. (C) Single-pixel LSVs of  $\text{Ni}_3(\text{HITP})_2$  obtained under  $\text{N}_2$  and air. Inset: average current densities at  $-0.36$  V for  $\text{Ni}_3(\text{HITP})_2$  under  $\text{N}_2$  and air. SECCM scans corresponding to those in  $\text{N}_2$  are shown in Figure S24. (D) SECCM map of geometric current densities (defined as the current divided by the tip droplet area) measured on  $\text{Ni}_3(\text{HITP})_2$  at  $-0.36$  V. (E) Corresponding topographic map of  $\text{Ni}_3(\text{HITP})_2$  derived from SECCM mapping.

the plateau in activity observed in our GDE studies (Figure S23 and the Supporting Information for experimental details). By confinement of the entirety of the electrode contact area to the footprint of a droplet at the end of a nanopipet, SECCM offers the fastest gas mass transport rates experimentally accessible for electrocatalysis:  $\text{N}_2$  or  $\text{O}_2$  can rapidly traverse the nanoscale droplet electrolyte and the porous  $\text{Ni}_3(\text{HITP})_2$  particles, with the maximum diffusion length of gaseous species to the catalyst surface being set by the droplet radius.<sup>28,36</sup> For example, a hemispherical droplet with a radius  $r_d = 25 \text{ nm}$  has a sub-microsecond diffusion time, about 6 orders of magnitude higher than that in the RRDE studies. By confining electrocatalytic studies to a nanoscale droplet, SECCM provides a unique platform to measure the intrinsic electrochemical mass activity in the absence of extrinsic transport limitations.

Using a  $50 \text{ nm}$  diameter nanopipet filled with a solution of  $30 \text{ mM NaP}_i$  (pH 7) and  $100 \text{ mM NaCl}$ , we directly mapped the electrochemical activity of  $\text{Ni}_3(\text{HITP})_2$  particles under cathodic polarization under both  $\text{N}_2$  and air ( $P_{\text{O}_2} = 0.2 \text{ bar}$ ) (Figure S24 and Figure 4, respectively).<sup>37</sup> The average current under  $\text{N}_2$  at  $-0.36 \text{ V}$  was negligible at ca.  $-1 \text{ pA}$ , close to the noise limit of the conditions we employ here (Figure S24, Movie S1, histograms in Figure S29). Comparison of individual linear

sweep voltammograms (LSVs) in  $\text{N}_2$  versus those in air indicated that essentially all of the measured current in air arose from the ORR (Figure 4C). Importantly, control experiments probing the nanodroplet while it was in contact with  $\text{Ni}_3(\text{HITP})_2$  revealed that the droplet was stable while it was in contact with the MOF. Furthermore, the droplet contact areas were similar on both  $\text{Ni}_3(\text{HITP})_2$  and ITO, allowing us to estimate the maximum ECSA of  $\text{Ni}_3(\text{HITP})_2$  contacted during SECCM measurements. (Text 2 in the Supporting Information and Figures S26–S29).

In contrast, SECCM scans of  $\text{Ni}_3(\text{HITP})_2$  under air indicated high ORR activity across the MOF particle surface, with an average current of  $-25 \text{ pA}$  at  $-0.36 \text{ V}$  vs SHE (Figure 4B,C, Movie S2, and histograms in Figure S29B). Given a droplet radius of  $25 \text{ nm}$ , this current translates to a geometric  $j_{\text{ORR}}$  value of  $-1273 \text{ mA cm}^{-2}$ , 38-fold greater than the highest current densities observed under air using the GDE (Figure S25). The larger current densities observed in SECCM versus the GDE or RRDE configurations are consistent with the short diffusion pathways enforced by the nanoscopic dimensions of SECCM.<sup>28,35,38–51</sup>

Using the SECCM and topography maps obtained under air, we calculated a lower-bound estimate of the intrinsic mass activity of  $\text{Ni}_3(\text{HITP})_2$ , making a conservative assumption that all of the cylindrical mass of  $\text{Ni}_3(\text{HITP})_2$  under the droplet's  $50 \text{ nm}$  footprint is recruited for catalysis (Figure S30). Strikingly, these estimates yielded a lower-bound average mass activity of  $11250 \text{ A g}^{-1}$  at  $-0.36 \text{ V}$  vs SHE, 136-fold higher than the highest mass activities measured with GDEs in air.

The rapid transport environment of SECCM revealed that  $\text{Ni}_3(\text{HITP})_2$  is even more active intrinsically than has been observed in the GDE, suggesting that even at low mass loadings some  $\text{O}_2$  mass transport resistance persists in the agglomerated  $\text{Ni}_3(\text{HITP})_2$  GDE catalyst layer. At high  $\text{Ni}_3(\text{HITP})_2$  GDE mass loadings, much of the active material is immersed in a thick aqueous electrolyte layer through which  $\text{O}_2$  mass transport is sluggish (Figure S31), with maximum diffusion lengths likely exceeding the thickness of the flooded GDE pores and  $\text{Ni}_3(\text{HITP})_2$  catalyst layer ( $>10 \mu\text{m}$ ; see Figure S8).

Crucially, the high mass activities observed in SECCM mean that the activity plateau observed in the GDE was extrinsic to  $\text{Ni}_3(\text{HITP})_2$ . Identifying slow micrometer-scale  $\text{O}_2$  mass transport, rather than low intrinsic catalyst activity, as the origin of current density limitations observed in the GDE provides an impetus to improve the mass transport properties of the  $\text{Ni}_3(\text{HITP})_2$  GDE. As a simple proof of principle, we reformulated the catalyst ink to include 10 wt % of hydrophobic polytetrafluoroethylene (PTFE) powder that was intimately mixed with the  $\text{Ni}_3(\text{HITP})_2$  nanoparticles, reducing  $\text{Ni}_3(\text{HITP})_2$  particle agglomeration and providing continuous, hydrophobic channels through which  $\text{O}_2$  could diffuse rapidly (Figures S31–S34 and Text 3 in the Supporting Information).<sup>26,29</sup>

The facility of  $\text{O}_2$  transport across the hydrophobic PTFE domains led to substantial increases in ORR activity: a  $0.8 \text{ mg cm}^{-2}$   $\text{Ni}_3(\text{HITP})_2$  GDE with 10 wt % added PTFE passed a total current density of  $-170 \text{ mA cm}^{-2}$  at just  $-0.27 \text{ V}$  (Figure S34A). By comparison, the previous best-performing PTFE-free  $0.4 \text{ mg cm}^{-2}$   $\text{Ni}_3(\text{HITP})_2$  electrode reached a peak  $j_{\text{ORR}}$  value of  $-103 \text{ mA cm}^{-2}$  while also requiring a  $90 \text{ mV}$  higher driving force of  $-0.36 \text{ V}$ . This activity translated to a 60% higher total single-pass  $\text{O}_2$  conversion rate of 48% at an  $\text{O}_2$  flow rate of  $1.5 \text{ mL min}^{-1}$  (Figure S34F). With the addition of 10 wt % PTFE, the  $0.8 \text{ mg}$

$\text{cm}^{-2}$  electrode exhibits 70% greater mass activity than its PTFE-free analogue: 212 vs  $\sim 124 \text{ A g}^{-1}$  (Figure S34C). Incorporating PTFE into the catalyst ink increased the apparent mass-transport-limited current from  $-110$  to  $-180 \text{ mA cm}^{-2}$ , an increase of  $\sim 60\%$ . These large differences in activity demonstrate that enhancing  $\text{O}_2$  mass transport in the  $\text{Ni}_3(\text{HITP})_2$  catalyst layer allows more of the  $\text{Ni}_3(\text{HITP})_2$ 's ECSA to be recruited for productive catalysis. However, the mass activity of the 10% PTFE electrode with  $0.8 \text{ mg cm}^{-2}$   $\text{Ni}_3(\text{HITP})_2$  remains more than a factor of 2 below the mass activity of the PTFE-free electrode with only  $0.1 \text{ mg cm}^{-2}$   $\text{Ni}_3(\text{HITP})_2$  and  $>50$ -fold below those recorded in SECCM. Further improvements in the geometric  $j_{\text{ORR}}$  value in practical devices are gated not by the intrinsic activity of  $\text{Ni}_3(\text{HITP})_2$  but by the facility of  $\text{O}_2$  mass transport. Identifying the multiscale transport bottlenecks that prevent MOFs from delivering high current densities motivates the broader exploration and deployment of these designer materials for a variety of electrocatalytic processes.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at (PDF). The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscentsci.2c00509>.

Experimental details, materials and electrochemical characterization, Texts 1–3, SECCM control experiments, mass activity estimation, and movie captions (PDF)

Spatially resolved electrochemical video of  $\text{Ni}_3(\text{HITP})_2$  under an  $\text{N}_2$  atmosphere (AVI)

Spatially resolved electrochemical video of  $\text{Ni}_3(\text{HITP})_2$  under an air atmosphere (AVI)

## ■ AUTHOR INFORMATION

### Corresponding Authors

Patrick R. Unwin – Department of Chemistry, University of Warwick, Coventry CV4 7AL, U.K.; [orcid.org/0000-0003-3106-2178](https://orcid.org/0000-0003-3106-2178); Email: [p.r.unwin@warwick.ac.uk](mailto:p.r.unwin@warwick.ac.uk)

Mircea Dincă – Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States; [orcid.org/0000-0002-1262-1264](https://orcid.org/0000-0002-1262-1264); Email: [mdinca@mit.edu](mailto:mdinca@mit.edu)

### Authors

Ruperto G. Mariano – Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

Oluwasegun J. Wahab – Department of Chemistry, University of Warwick, Coventry CV4 7AL, U.K.; [orcid.org/0000-0003-4280-9089](https://orcid.org/0000-0003-4280-9089)

Joshua A. Rabinowitz – Department of Chemistry, Stanford University, Stanford, California 94305, United States

Julius Oppenheim – Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

Tianyang Chen – Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States; [orcid.org/0000-0003-3142-8176](https://orcid.org/0000-0003-3142-8176)

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acscentsci.2c00509>

## Author Contributions

Conceptualization: R.G.M., P.R.U., M.D. Methodology: R.G.M., O.J.W., J.A.R., P.R.U., M.D. Investigation: R.G.M., J.A.R., O.J.W., J.O., T.C. Visualization: R.G.M., J.O., O.J.W. Funding acquisition: R.G.M., P.R.U., M.D. Project administration: R.G.M., P.R.U., M.D. Supervision: P.R.U., M.D. Writing—original draft: R.G.M. Writing—review and editing: R.G.M., O.J.W., J.A.R., J.O., T.C., P.R.U., M.D.

## Author Contributions

<sup>||</sup>O.J.W. and J.A.R. contributed equally.

## Notes

The authors declare no competing financial interest.

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