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Towards an informative comparison of heterogeneous, synthetic and biological electrocatalysis in energy conversion

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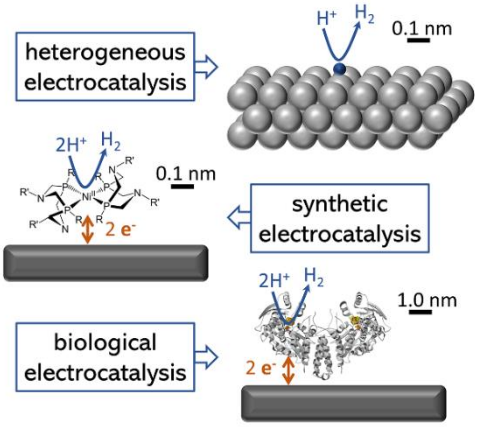
The bigger picture

Challenges and opportunities

- Electrocatalysis will play an important role in society's transition to renewable energy.
- Knowledge exchange between the communities that study heterogeneous, synthetic and biological molecular electrocatalysis is challenging due to divergent nomenclature, analytical approaches and definitions of catalytic activity.
- Harmonizing approaches will facilitate the sharing of best practices and provide new opportunities to improve performance in electrocatalysis.

Summary



An urgently needed transition towards a sustainable and renewable energy landscape compels an increasing role for electrocatalysis. Distinct classes of electrocatalysts have each shown important benefits in energy conversion and activation of small molecules such as CO_2, H_2O, O_2 and H_2: synthetic and biological molecular electrocatalysts, and heterogeneous and reticular material electrocatalysts. This Perspective seeks to foster knowledge exchange between the scientific communities by comparing these different electrocatalytic systems. The different subdisciplines employ divergent nomenclature, analytical approaches and definitions of catalytic activity, even in cases of substantial overlap in chemical principles. We propose a set of conditions that must be met to ensure an unbiased comparison. Through sustained efforts to share best practices and harmonize approaches, we anticipate enhanced collaboration among subdisciplines, thereby facilitating innovative thinking and advancing the field of electrocatalysis towards its full potential in contributing to a sustainable and renewable energy future.

Keywords: reaction mechanisms; Sabatier principle; volcano plot; scaling relationship; reversibility; foot-of-the-wave analysis; turn over frequency; kinetics; second coordination sphere; optimising electrocatalysis

Introduction

A transition to a sustainable and renewable energy economy is urgently required and electrocatalysis is expected to make a key contribution.[1,2] The synthesis of chemicals and fuels using renewable energy and small molecules (i.e. water and carbon dioxide) as primary feedstocks is a recognised key step in addressing the global demand for resources.[3-5] This approach, underpinned by the application of electrocatalysis, offers an innovative path to a sustainable society. In the last decades, several electrocatalytic systems have been developed and studied for small molecule activation.[6-8]

A good catalyst should have high thermodynamic and Faradaic efficiency, have high catalytic rates and be robust (high longevity under operating conditions). To achieve optimal Faradaic efficiency, the catalyst must be fully selective for the desired reaction, while high thermodynamic efficiency requires significant catalytic rates at low overpotential. Four classes of electrocatalysts have been extensively studied, each with their own advantages and disadvantages: synthetic and biological molecular electrocatalysts, and solid-state and reticular material electrocatalysts. Solid-state electrocatalysts are almost always the surface atoms on metals, alloys or metal oxides (either bulk materials or (nano)particulates) and are known as heterogeneous catalyst as they operate in a different phase as the reactants. Some systems blur the boundaries between heterogenous and homogenous catalysis, which here will be referred to as “heterogenized” systems. Synthetic or biological molecular catalysts can be “heterogenized” by immobilisation on electrode surfaces, while hybrid organic/inorganic catalysts or reticular materials such as metal-organic frameworks (MOFs) and covalent-organic frameworks (COFs) also bridge the heterogeneous and homogeneous classes.[9-11]

Historically, research into these four classes of electrocatalyst have adopted different terminologies and methodologies to analyse, interpret and report data. Furthermore, distinct areas of expertise are required for the diverse physical methods used to characterize objects that are as different as a surface, an organic framework, an inorganic compound and an enzyme. Although there is a tantalising prospect that electrocatalysts can be further optimized at the interface of these subdisciplines, different experimental conditions and methodologies have hampered direct comparison. Indeed, the literature on the direct comparison between the electrocatalytic systems is scarce.[12-16]

This Perspective aims to provide the research communities with a discussion on how we might start to compare these catalytic systems and their performance, facilitating the exchange of knowledge. This aim was initiated by discussions held at a Kroese-Duijsters symposium meeting, held in Leiden, the Netherlands, 19-20 June 2023, during which the authors reflected on how their respective research fields approach current challenges. Although a wide variety of electrocatalytic systems could in principle be compared, in this Perspective we have limited the discussion to those that are key in the renewable energy economy: the catalysis of hydrogen evolution reaction (HER), hydrogen oxidation reaction (HOR), oxygen reduction reaction (ORR), oxygen evolution reaction (OER) and carbon dioxide reduction reaction (CO_2RR). This Perspective will begin by providing some examples where different subdisciplines have provided insights into electrocatalysis and end with recommendations on how catalytic performances might be compared in the future.

Optimising catalysis: Reaction mechanisms and intermediates

Analysis of reaction mechanisms and its intermediates is key to an informed approach to optimise performance. The reaction mechanism identifies the different steps in the overall reaction, which key catalytic intermediates are involved, and which step (if any) in the mechanism is rate determining. Based on such knowledge, strategies can be defined to optimize catalysis.

A popular approach towards the optimization of heterogeneous (electro)catalysis is based on the Sabatier principle and the descriptor-based volcano plots that follow from this approach (see Supplementary Information, Box 1). The Sabatier principle states that for a good catalyst, the key catalytic intermediate(s) should neither bind too weakly nor too strongly to the catalyst, creating a flat energy landscape. Plotting the catalytic activity versus the binding energy of the presumed catalytic intermediate then yields a plot that typically shows the highest activity at the optimal binding energy. Often, optimal binding energies can be predicted from a thermodynamic analysis, and actual values of binding energies can be calculated from first-principles density functional theory (DFT)-based quantum-chemical calculations.[17,18] This approach has proved very successful in guiding the formulation of new electrocatalysts and elucidating the principles of electrocatalysis.[1,18] Transformations of the catalysts during reaction conditions or the influence of defect sites might complicate such approach.[19,20] Furthermore, electrocatalytic reactivity often depends on more than one descriptor, and the interaction with local (electrolyte) environment (often not included in the DFT calculations) also plays an important role (see also the section on environmental effects).

Lessons have been learned from these descriptor-based Sabatier analyses. First, if there is only a single catalytic intermediate in the mechanism, which is typically the case for a two-electron transfer reaction, such as HOR or HER, optimization of this catalyst should display reversible catalysis (see Supplementary Information, Box 1). HOR/HER on platinum is a classic case of a reversible catalysis as it is bidirectional and shows significant reaction rates at small perturbations of the equilibrium potential (E_{eq}, see Figure 1). Here, we define E_{eq} as the equilibrium potential at the concentration of the reactants used in the experimental system. Reversibility is defined by having only a single inflection point in the electrocatalytic wave when going through E_{eq} (Figure 1). Correspondingly, irreversibility is defined as a reaction that requires a large over-potential in order to obtain an appreciable rate.[21-23] According to this definition, a reversible electrocatalyst is necessarily bidirectional, whereas an irreversible electrocatalyst can be uni- or bidirectional. We note that irreversible catalysis does not require that different catalytic pathways operate under oxidizing and reducing conditions.[21,24]

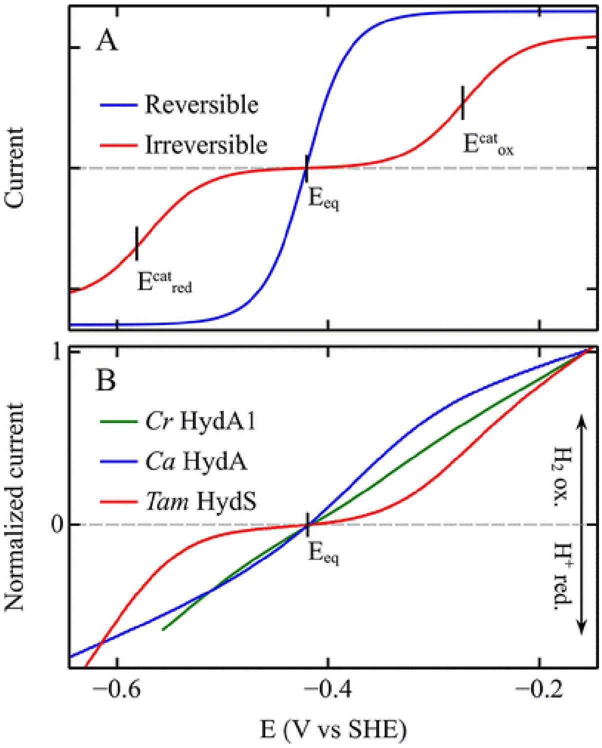


Figure 1: (Top) Illustration of reversible (blue) and irreversible (red) catalysis. (Bottom) examples of steady-state voltammograms of three biological electrocatalysts ([FeFe] hydrogenases) catalysing HER/HOR. The biological electrocatalysts are adsorbed onto a rotating disc electrode spun at a high rate to avoid mass transport limitations. Reprinted with permission from Fasano et al.[24] Copyright 2021 American Chemical Society.

“DuBois” catalysts (mononuclear bis(diphosphine)-nickel complexes with pendant amines) are one of the most thoroughly investigated molecular electrocatalysts for HER and HOR.[23,25] Many structural modifications have been produced of which some illustrate very high rates for the HER (up to 1.5×10^6 s^{-1} per catalyst molecule at an over-potential of 300 mV) and HOR. Whether these Ni-catalysts are capable of catalyzing HOR, HER or show reversible activity depends to which extent the catalyst is biased towards H_2 uptake or H_2 release (see Supplementary Information, Box 2).[23,26] DuBois catalysts for which this equilibrium is biased towards H_2 uptake are good HOR catalysts, while systems that bind H_2 less strongly are more active for the HER. Given that in DuBois catalysts, H_2 is formed by combining a hydride with a proton, $K(H_2)$ can be fully described by the hydricity of the Ni-H and the pKa of the proton donor within the ligand framework. The hydricity of Ni-H and the basicity of N-H can be tuned independently via electron withdrawing and electron donating groups directed towards the metal (hydricity) or the proton donor (basicity).

Kinetic studies of hydrogenases and DuBois complexes have shown that, for these molecular catalysts, reversibility requires the half-reduced state of the active site to be unstable (and the two potentials of the active site “inverted”[27]). Inverted potentials of the two electron transfer steps are indeed required to bring the catalytic oxidation and reduction waves closer to one another on the electrode potential axis.[21,26,28] On first reflection, such a requirement for unstable half-reduced states contrasts with the Sabatier principle and the approach in heterogeneous catalysis to create a flat energy landscape. However, it is important to realize that when a catalytic voltammogram is sigmoidal (S-shaped), as often occurs with molecular catalysts (see Supplementary Information, Box 2), reversibility and catalytic reaction rate are two independent measures of catalytic performance. Reversible catalysis describes the catalytic behavior close to E_{eq} (Figure 1), but it does not directly follow that reversibility leads to higher catalytic reaction rates on the plateaus at high overpotential. A kinetic analysis has suggested that also for HER on platinum, a non-flat energy landscapes accelerates the HER at high over-potential (compared to a flat energy landscape), even though this reduces the catalytic rate close to E_{eq}.[29] We thus advocate that the terms of 'reversibility' and 'catalytic reaction rate' need to be carefully defined when comparing the different sub-disciplines, and in doing so, future approaches might take lessons from both heterogeneous and molecular catalysis.

Optimising catalysis: Scaling relationships

For heterogenous catalysis, a second lesson that has been learned from descriptor-based Sabatier analyses is that if the catalytic mechanism features more than one intermediate (two, three, or more), the binding energies of these intermediates can normally not (easily) be optimized independently, because these different reaction intermediates often bind to the catalyst in the same way (e.g. through the oxygen atom). This is typically the case for redox reactions transferring four or more electrons. The binding energies of the intermediates to the catalyst are related to each other through so-called scaling relations (see Supplementary Information, Box 1). These scaling relations limit the extent to which a catalyst can be optimized in terms of the Sabatier principle, and even the best heterogeneous catalysts operate at an overpotential.[30] Hence, the catalyst is not a reversible catalyst (though it may still be bidirectional). It is believed that this principle is the reason for what appears to an unavoidable overpotential for the four-electron oxygen evolution reaction (OER) and oxygen reduction reaction (ORR). Overcoming or "breaking" scaling relationships has therefore become a very active area of research in heterogeneous electrocatalysis.

One can consider optimisation of molecular electrocatalysts to be equivalent to optimizing or overcoming of the scaling relationship approach in heterogeneous catalysis, noting that the reaction mechanism of molecular electrocatalysts can be tuned using a wider chemical parameter space to modify the reaction energy landscape. For instance, one can envision changes in activity upon introduction of electron withdrawing and/or donating substituents, 2nd coordination sphere modifications, employing redox active ligand, and employing multicompartmental ligands enforcing multiple metal sites in close proximity. Still, volcano approaches have been successfully applied to synthetic molecular catalysts.[31,32] Although such studies suggest that most molecular catalytic systems seem to be limited by the same scaling relations as the heterogeneous systems[33], it has been argued that the success of volcano approaches to molecular catalysis depends on the reaction mechanism and on the (over-)potential at which catalytic performance is compared.[34]

In the development of molecular electrocatalysts, inspiration has been taken from biological electrocatalysts. For instance, synthetic copper complexes structurally resemble biological electrocatalysts such as laccases for ORR, but operate via different reaction pathways.[35] In contrast, breakthroughs are perhaps more likely to occur in mimicking mechanisms and principles rather than in mimicking the structure of biological electrocatalysts. For instance, the DuBois catalysts, which are uniquely active for H_2 oxidation and proton reduction, do not resemble the active sites of hydrogenases, but in terms of chemistry, the reaction pathways share common features and principles, with for instance the pendant amine of the catalyst mimicking the azodithiolate ligand of [FeFe] hydrogenases.[23] Similarly, the biological molecular catalyst for OER is the Mn_4CaO_5-cluster from the oxygen-evolving complex in photosystem II, while the most successful synthetic molecular catalysts that operate in a wide range of pH (acidic, neutral and basic) are based on ruthenium (Ru) and iridium (Ir) complexes.[36-40]

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For biological electrocatalysts, evolution can be considered to have already 'tuned' or optimised reaction pathways and the frontiers of what is chemically possible. We note, however, that biology is limited to using (relatively) abundant metals and hence synthetic catalysts based on rare metals can exploit chemistries that biology does not. Some metalloenzyme active sites are bi- to trinuclear, and thus offer binding sites which can bind distinct intermediates, expanding the way that the scaling relationship can be optimised. Besides the reaction mechanisms at the active site of enzymes, the catalytic cycles of many enzymes involve steps that are not common in synthetic molecular catalysts, such as diffusion of reactants along substrate channels and long-range proton and electron transfers, each with different energy barriers. Homologous enzymes (enzymes with the same active site but different protein environments) can have very distinct catalytic properties, which illustrates the importance of these long-range effects in biological catalysis.[41,42] For instance, Figure 1B illustrates the reversible and irreversible responses that are observed with homologous [FeFe] hydrogenases (a biological molecular catalyst), which contain the same catalytic [FeFe] site, but differ in terms of active site environment and proton transfer chain.[24]

Interaction of the active site with its environment and second coordination sphere

All reactions in energy conversion (HER, HOR, ORR, OER, CO_2RR) involve protons and thus are affected by pH. In the absence of a second coordination sphere, heterogeneous catalysis is not only dependent on pH, but also on the buffer system, ionic strength and type of ions, which can all influence reaction rates and Faradaic efficiency.[43] Synthetic and biological molecular electrocatalyst do have a second coordination sphere, but are differently affected by environmental conditions. When a proton is transferred to the reactant or intermediate in a fast pre-equilibrium, a pre-equilibrium approximation can be employed (see also Supplementary Information, Box 1). Under these conditions the catalytic rate is independent of the concentration and pKa of the buffer, and depends only on the pH of the electrolyte solution.[44] When (de)protonation is not in a fast pre-equilibrium, the catalytic rate becomes dependent on the concentration and pKa of the buffer.[44] Diagnostic tools are a buffer dependence on the reaction rate and a significant kinetic isotope effect that is sensitive on the buffer composition. In enzymes, protons are transferred between the solution and the buried active site along chains of acidic residues, that play the same role as the buffer. Difference in (apparent) pK_a's and (de)protonation rates for residues in proton relays have been found to determine kinetic properties of hydrogenases with otherwise identical catalytic sites.[28]

Synthetic molecular electrocatalysts with a mechanism in which proton transfer is rate limiting often benefit from inclusion of a proton shuttle in the 2nd coordination sphere (Figure 2A). By employing this strategy some of the fastest molecular electrocatalysts in OER[36], ORR[45], CO_2RR[46], HER/HOR[47] have been reported. In contrast, several synthetic molecular electrocatalytic systems have been developed where good catalytic activity is obtained not by introduction of a proton shuttle, but instead by positioning of another metal site in the 2nd coordination sphere (Figure 2B). Here, the key lies with a bimetallic activation or formation of chemical bonds such as for example the O-O bond in oxygen reduction and water oxidation catalysis. Typically, but not always, such bimetallic pathways can be triggered by linkage of two catalytic sites in close proximity to one another (such as ref. [48]). Yet, particularly high catalytic rates in the water oxidation reaction have been obtained in an approach where two catalytic sites are kept in close proximity through weak supramolecular π-stacking interactions, while the catalytic site remains sufficiently flexible to turnover rapidly.[37] By switching between a proton shuttle and a second metallic site in the 2nd coordination sphere, the reaction path can be adjusted between a proton assisted reaction pathway and a bimetallic pathway, respectively. For a given metallic site, typically one of the two reaction strategies is significantly more successful.

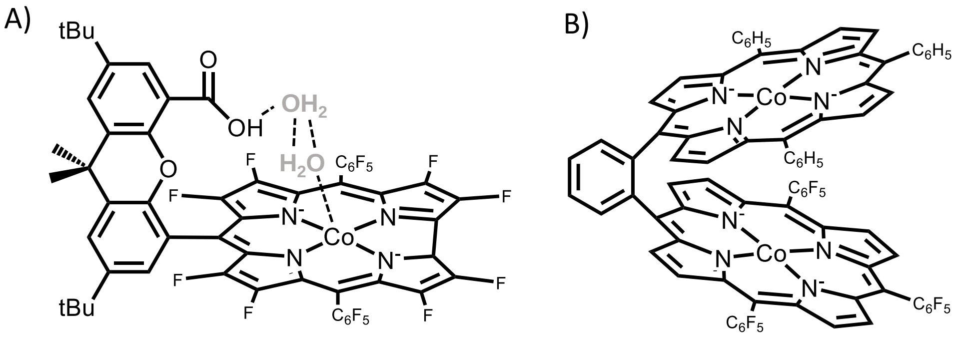

Figure 2: Examples of molecular electrocatalyst in which the catalytic rate is improved by (a) the addition of a proton shuttle in the 2nd coordination sphere (example taken from [49]) or by positioning a second metal site in the 2nd coordination sphere (example taken from [48]).

Comparing catalytic performance

A key performance parameter of electrocatalysts is the current density at a given (over)potential, which is often used as an indicator for electrocatalytic activity. The use of current density to quantify activity, and compare activity between the different subclasses of electrocatalysis, immediately raises several issues. The first is whether the activity should be reported as a current per geometric electrode area, per electrochemically active surface area (ECSA), per catalyst mass or as a turn-over frequency (TOF) per active site. The geometric electrode area is commonly used in all electrochemical subdisciplines and is of direct relevance when applying electrocatalysts in devices such as electrolysers and fuel cells. For molecular electrocatalysis (synthetic or biological), normalisation against the number of catalytic molecules, for instance per active site, to give a TOF, is common. In contrast, in heterogeneous electrocatalysis, activity is more commonly normalised against ECSA due to the fact the catalyst is the electrode's surface. We note, however, that for research and development, we consider TOF per active site the most meaningful parameter because it measures the intrinsic activity.

The activity is dependent on the applied potential, and different subdisciplines approach this potential-dependency differently. A common approach in heterogeneous electrocatalysis is to analyse activity by means of a Tafel plot (see below). In contrast, even when not diffusion limited, molecular electrocatalysts often display a plateau in current at high over-potential (see below), which enables the determination of a TOF_{max}, which is the maximum turn-over rate of the catalyst. In biology, TOF_{max} is also known as k_{cat} if the biological electrocatalyst is saturated with its substrate (substrate concentration >> Michaelis constant (K_M)). In synthetic molecular catalysis, TOF_{max}, k_{max} and k_{obs} are used, typically depending on the analytical method that is applied. Although the term TOF is sometimes used inconsistently in the scientific literature, leading to confusion[50], for simplicity we will only use the terms TOF or TOF_{max} in this Perspective (see also Supplementary Information, Box 2).

For the different electrocatalysts, electrocatalytic performance is reported very differently, while the determination of suitable parameters differs between the subdisciplines. Here, we briefly describe the basic methods used in each subdiscipline, after which we propose guidelines to compare electrocatalytic performance of the different classes of electrocatalysts.

In heterogenous or "heterogenized" electrocatalytic systems, electrical currents often become limited by mass transport of the reactants (substrates and/or products). One common approach is to increase mass transport by using rotating disc electrodes (RDEs), but even at high rotation rates, electrocatalysis may still be limited by mass transport. In the latter case it might still be possible to model catalysis performance and determine TOF_{max} by using the Koutecky-Levich equation. When the catalyst is not part of or attached to the electrode, measuring its TOF_{max} also requires consideration of the diffusion of the catalysts to and from the electrode.

For solid-state material electrocatalysts, the current density as a function of the applied potential is often analyzed by means of a "Tafel plot", in which the log(current)) is plotted against potential. By extrapolation to the equilibrium potential (E_{eq}), the so-called exchange current density (i_0) is extracted, which is taken as a "fundamental" measure of activity. Further, the slope of the linear Tafel plot may inform about the nature of the rate limiting step (see Supplementary Information, Box 1). If extrapolation is not possible (for instance because the overpotential, $\eta = E - E_{eq}$, is so high that extrapolation is not accurate), one often resorts to reporting the overpotential required to reach a certain current density threshold (onset potential): a lower overpotential then signifies a more active catalyst. The activity metric that is used to compare the intrinsic activity of different solid-state material catalysts is the current density per ECSA. The accurate determination of the ECSA varies: for metals, the ECSA is usually based on an electrochemical adsorption reaction, whereas for oxides often the electrochemical capacitance serves as surface area normalization (the accuracy of which is however often debated[51]). If the number of active sites per cm^2 of ECSA would be known, this could allow the determination of the TOF per active site. Note, however, that in such an activity measure, many catalyst atoms do not contribute to the overall activity. Furthermore, formation of gaseous products can create bubbles, which can reduce the electroactive surface area that actively contributes to catalysis.[52] In practice, a mass activity is often used, which measures the current density as normalized by *all* the catalyst atoms, even if they are not involved in the catalysis. For nanostructured electrodes, the determination of ECSA is particularly challenging due to non-homogeneous electrocatalytic activity.[53] In this case, it might be possible to express activity as TOF per nanoparticle.[54]

Tafel plot analysis is useful when the current exponentially increases with potential, which, for instance, occurs when catalysis is rate limited by an electron transfer or redox step (for the range of electrode potential that is considered). However, for "heterogenized" systems with molecular electrocatalysts, the rate limiting step is often not the interfacial electron transfer to the molecular catalyst, but the rate of the chemical transformation that typically involves making or breaking of chemical bonds (see Supplementary Information, Box 2). In this situation, the current as a function of applied potential is sigmoidal (S-shaped), rather than exponential, and a Tafel plot is thus less suitable. When a sigmoidal current dependency is observed (that is not limited by mass diffusion), activity is typically reported as the measured current at the plateau region of the sigmoid, i_{max}. To determine the TOF_{max} from i_{max}, knowledge about the surface coverage of the catalyst is needed, as well as the fraction of immobilized catalysts that remains active upon immobilization.[55] The surface coverage can be obtained from the peak area of the redox catalyst (from the voltammogram measured in the absence of substrate). When a biological electrocatalyst is immobilized on the electrode surface, such as in protein-film electrochemistry[55-60], the number of active catalysts on the surface is often unknown. Using surface analytical techniques like quartz-crystal microbalance, the weight and thus amount of biocatalyst immobilized on an electrode surface can be quantified, but not all adsorbed biocatalysts might be equally active. Furthermore, variations in enzyme orientations on the electrode might lead to a distribution in interfacial electron transfer rate, which may prevent the measurement of i_{max}.[61]

When the molecular electrocatalyst is dissolved in solution (rather than immobilized on the electrode), only a fraction of the molecular catalyst in the bulk is sufficiently close to the electrode to be involved in redox catalysis. Since in this case both the reactants and the catalysts are diffusive, typically stationary techniques are employed to determine catalytic activities. When the current of homogeneous catalysis and stationary electrode is sigmoidal with respect to the potential, the catalytic reaction at i_{max} is solely dependent on a rate-limiting chemical transformation. From such a curve, and on the condition that catalysis is unidirectional[62], the TOF_{max} can be derived by calculating the current enhancement, which is the ratio between i_{max} obtained in the presence of reactant (substrate), and the peak current (i_p) of the reversible redox couple of the catalyst in the absence of substrate.[63,64]

In practice, however, the catalytic wave often peaks, which is due to side phenomena such as substrate depletion or product inhibition. Costentin et al. have introduced the foot-of-the-wave analysis (FOWA) analysis for such systems, in which the plateau current is modelled by extrapolation of the S-shaped curve from the foot of the unidirectional catalytic wave, where the catalytic current is least affected by side phenomena such as mass transport.[65,66] As FOWA extrapolates the data from a part of the voltammogram, there are limitations to this analysis. Modeled TOFs (TOF_{max}) can be larger than the rates determined by other methods and, in case of cascade reactions, only the TOF_{max} of first chemical transition is determined. Although TOF_{max} is an extrapolation of the catalytic current at the foot-of-the-wave to a non-observed plateau current, it does give valuable information on, for example, intrinsic barriers within the catalytic cycle. Of note is that the FOWA equations are derived for one electron processes, but can be extended to multi-electron processes provided that these can be ascribed to a unidirectional EC mechanism. When additional ET steps become potential determining or when the catalysis is reversible, finding TOF_{max} becomes notoriously more difficult and requires increasing complex mathematical analysis.[62,67,68]

For molecular electrocatalysis, TOF or TOF_{max} values are often given without (clearly) reporting the required (over)potential at which the TOF is determined, a practice we do not recommend (see below). In general, there are two methods to compare performance and mechanism of catalysis. The logarithm of the TOF_{max} obtained by FOWA can be plotted versus the applied potential, and is typically referred to as a catalytic Tafel plot.[69] Alternatively, the logarithm of the TOF_{max} can be plotted versus the η_{eff}, which is the difference between the equilibrium potential of the reaction (E_{eq}) and the redox potential of the molecular electrocatalyst under the reaction conditions, typically obtained from the halfwave potential of the catalytic wave.[70,71] The latter plots may result in a linear correlation and is sometimes referred to as a scaling relation between TOF_{max} and the effective overpotential, η_{eff}. This linear scaling is in line with the Bronsted-Evans-Polanyi principle, and different from the binding-energy scaling in case of heterogeneous catalysis mentioned above.

When comparing electrocatalysts, the lifetimes or robustness of the different electrocatalysts is an important parameter to consider. Reasons why electrocatalysts have a limited lifetime are very different between the subdisciplines but are typically either due to loss or dissolution of the catalyst or due to chemical conversion of the catalyst into an inactive form. Heterogeneous catalysts can lose activity due to poisoning by impurities or minor products and intermediates, or by dissolution of the catalyst. Biological electrocatalysts can desorb from the electrode (for heterogenized systems), inactivate due impurities or side reactions or denature. Similarly, synthetic molecular electrocatalysts can lose activity due to unwanted side reactions that change the catalyst, or even gain activity if the decomposition product accumulates on the electrode. When comparing the different electrocatalytic systems, we thus recommend to not only measure activity at the start, but also after a set time, and in case of homogeneous catalysts also in a blank electrolyte solution after catalysis. In cases where this is possible, an activity half-life should be determined.

In summary, as catalytic activity is differently defined between the subdisciplines working with solid-state material electrocatalysts and molecular catalysts (synthetic and biological), comparison between i_0, onset potential or i_{max} is not straightforward. Even if a TOF_{max} can be determined, a straightforward comparison is not always possible. For instance, synthetic molecular electrocatalysts that operate at large over-potentials with respect to E_{eq} can produce very high TOF_{max}, but at the cost of thermodynamic efficiency. This can lead to conflicting conclusions when only comparing TOF_{max}, as a catalyst with a higher TOF_{max} might still be less efficient because a larger over-potential might be needed to reach TOF_{max}. TOFs between systems thus need to be compared at the same overpotential or at an overpotential that is required to obtain maximal activity.

Noting the difficulties in each subdiscipline, we propose the following conditions need to be met to enable an unbiased comparison of electroactivities: (a) the reaction (conditions) should not be mass diffusion limited (or the RDE data should be subjected to Koutecky-Levich analysis), (b) catalytic activities should be normalised to the number of active sites, the ECSA and the geometric area, where possible. (c) For each system, optimised electrolyte conditions can be used, but a meaningful direct comparison would be facilitated if a set of conditions can be agreed upon (pH and buffers, electrolyte, temperature). (d) As the number of active sites is often difficult to determine, we propose a *minimal TOF* should be determined in which it is assumed that all observable active sites (or surface atoms, for a heterogeneous system) are equally active. (e) one should be careful drawing meaningful comparisons from FOWA data if the TOFs are not verified via at least a second method (e.g. from the ratio between i_p and i_{max}). (f) Activity of electrocatalyst should be determined both at the start and after a set time to evaluate robustness under operating conditions. (g) Finally, the applied (over-)potential at which the TOF is determined should be reported and preferably be identical when comparing two systems. For biological or synthetic molecular electrocatalysts immobilised on the surface, we propose that the minimal TOF is determined for the total amount of catalyst immobilised, independent of the fraction that might be electroactive.

Conclusion

In conclusion, we argue that it is possible to directly compare heterogeneous, synthetic and biological molecular electrocatalyst, and suggestions are given on how to conduct and report experimental results to facilitate this. The different fields use different nomenclatures, and we advocate continued efforts to instead align terminology and report performances such that direct comparison is feasible. In some cases, it has proven possible for the different subdisciplines to exchange knowledge, such as ‘breaking’ scaling relationships or understand reversibility. Due to large differences between the fields, this has remained limited, but we are confident that electrocatalysis will benefit by more collaboration between the subdisciplines.

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Declaration of interests

The authors declare no competing interests.

Supplementary Information

Box 1: Analytical approaches in heterogeneous electrocatalysis
Box 2: Analytical approaches in molecular electrocatalysis
Box 3: Lexicon

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Figure Legends

Figure 1: (Top) Illustration of reversible (blue) and irreversible (red) catalysis. (Bottom) examples of steady-state voltammograms of three biological electrocatalysts ([FeFe] hydrogenases) catalysing HER/HOR. The biological electrocatalysts are adsorbed onto a rotating disc electrode spun at a high rate to avoid mass transport limitations. Reprinted with permission from Fasano et al.[24] Copyright 2021 American Chemical Society.

Figure 2: Examples of molecular electrocatalyst in which the catalytic rate is improved by (a) the addition of a proton shuttle in the 2nd coordination sphere (example taken from [49]) or by positioning a second metal site in the 2nd coordination sphere (example taken from [48]).

SUPPLEMENTARY INFORMATION

Towards an informative comparison of heterogeneous, synthetic and biological electrocatalysis in energy conversion

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Content

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Box 1: Analytical approaches in heterogeneous electrocatalysis

A brief background is provided to commonly taken approaches to analyse heterogeneous electrocatalysis. For a more in-depth introduction to heterogeneous electrocatalysis, we refer the reader to the following tutorial review.[1]

In heterogeneous electrocatalysis, the catalysts are the surface atoms of the solid-state electrode, either the metal, alloy or metal oxide layer formed at the solid-liquid interface. As the catalytic atoms are part of the metallic electrode, they do not adopt discrete oxidation states in the absence of reactants (as for a molecular catalyst). Catalytic intermediates are formed with reactants during catalysis. Figure S1 shows this schematically for HER/HOR reactions under acidic conditions.

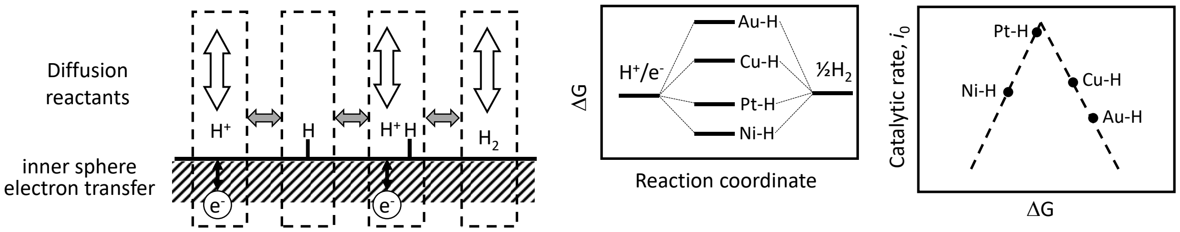

Figure S1: (Left) Schematic representation of the steps that affect the rate of HER and HOR reactions in acidic conditions in heterogeneous electrocatalysis. (Middle) Energy diagram of the reactants and intermediates of the HER and HOR reactions, indicating how the energy of the catalytic intermediate affects the reaction rate.[2] In this particular energy diagram, the applied electrode potential is equal to the equilibrium potential of HER and HOR (the applied potential equals E_{eq}). (Right) Volcano plot in which the catalytic rate of a heterogeneous HER/HOR reaction at E_{eq} is plotted against the energy of the intermediate.

The catalytic performance of a heterogeneous catalyst is often analysed by the use of a Tafel plot (Figure S2). In a Tafel plot, the log of the absolute current ($\log|i|$), ideally from steady-state measurements or a slow linear-sweep voltammogram, is plotted against potential. By extrapolating the cathodic and/or anodic catalytic current to the equilibrium potential of the reaction (E_{eq}), the current at zero over-potential (i_0) is obtained. The Tafel slope of the cathodic and/or anodic current is used to inform on the reaction mechanism, and is typically lower the more electrons are transferred before the rate-determining step.[3,4]

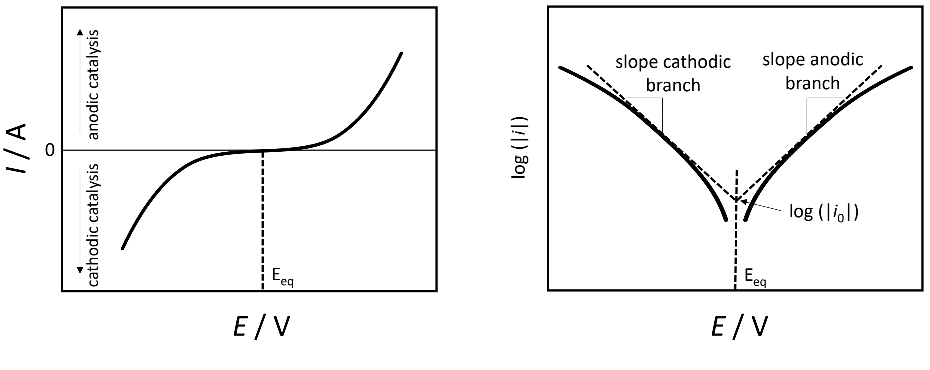

Figure S2: (Left) Current-potential ($I - E$) curve of an irreversible, bidirectional electrocatalysis. **(Right)** A Tafel plot of the current-potential curve on the left, in which the logarithms of the absolute anodic and cathodic currents are plotted against the potential. The equilibrium potential of the reactions, E_{eq}, and the current at zero over-potential (i_0) are indicated, as well as how the slopes of the anodic and cathodic currents are measured.

Optimisation of electrocatalytic performance often follows the **Sabatier principle**, which states that the intermediates neither bind too strong, nor too weak to the electrode catalyst. In other words, the energy of the intermediate is neither much higher nor much lower than that of the reactants, as this would increase the energy barrier of the reaction (see Figure S1, middle).

Moreover, when the energy of the intermediate is much lower, a stable intermediate will form on the electrode, thereby reducing the number of surface atoms that can take part in the reaction. Plotting the energy of the intermediates against the performance in terms of the catalytic rate, i_0, gives a so-called **volcano plot** with the best performing catalyst at the apex of the 'volcano' (see Figure S1, right).

In the representation of the Figure S1 (middle), the electrode potential is set at the equilibrium potential of the reaction (E_{eq}), which is the potential for which i_0 is determined. Thus, ΔG of $2H^+$ and H_2 are identical at this applied potential, and the reaction rates in both directions are, by definition, identical without a net formation of product. When the reaction is performed at a potential other than the equilibrium potential, the energy diagram obviously changes (in the Figure S1 (middle), the energy level of H^+/e^- will go up or down). As mentioned, the best performing catalyst has a 'flat' energy landscape. For such catalyst, small perturbations of the applied potential around E_{eq} will drive the reaction in either direction, and thus the electrocatalyst is reversible (see Figure 1 of the main text).

In the HER/HOR example so far, only one intermediate needs to be considered (-H). For reactions such as OER/ORR, multiple intermediates are formed (for OER/ORR, these are -OH, -O and -OOH). As the each of these intermediate typically bind through the same atom (in this example, oxygen O), the binding energies to these different intermediates to the catalyst follow a so-called **scaling relationship** and can therefore not be optimized independently. This hampers the design of catalyst with a flat energy landscape, leading to inherent irreversibility. Approaches to solve this issue by differentiating the way in which each intermediate is bound to the catalyst, for instance by changing the bond to the catalyst or by changing to a different atom in an alloy, is known as **breaking the scaling relationship** (see for instance, reference[5,6]).

Box 2: Analytical approaches in molecular electrocatalysis

In this box a brief background is provided into commonly taken approaches to analyse molecular electrocatalysis. For a more in-depth introduction into molecular electrocatalysis, we refer the reader to the following tutorial reviews.[7,8]

In molecular electrocatalysis, the catalyst is an entity separate from the electrode. The electrode reduces or oxidises the molecular electrocatalyst, which can thus adopt discrete oxidation states. As schematically shown in Figure S3 for HER and HOR reactions, even in this relatively simple scenario, many properties contribute to electrocatalysis: (a) the redox potential(s) of the catalyst, (b) electron transfer rates between the electrode and the catalyst, (c) binding of the reactants to and release of the products from the molecular catalyst, (d) diffusion of the reactants and catalysts to and from the electrode and (e) the catalytic conversion rate by the catalyst.

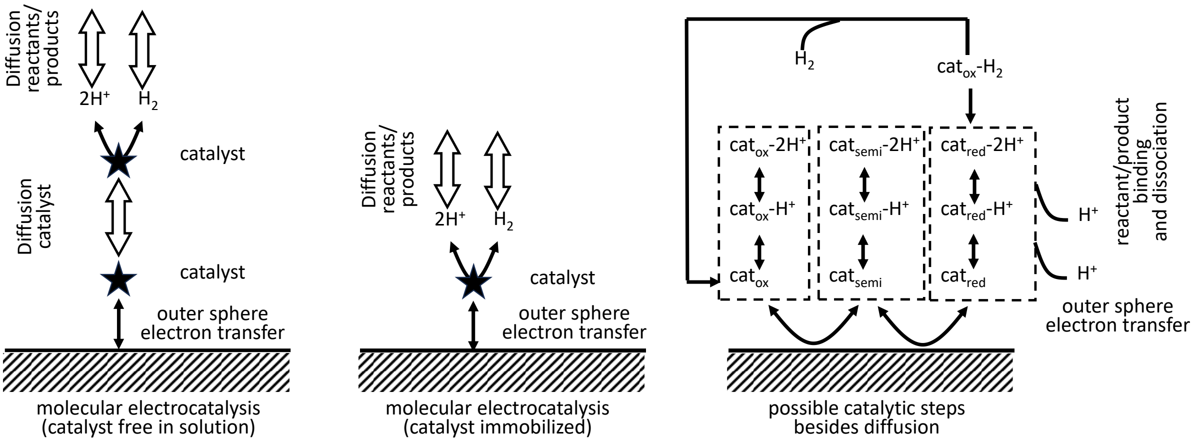

Figure S3: (Left and middle) Schematic representation of the steps that affect the rate of the HER and HOR reactions in molecular electrocatalysis when (left) the catalyst is free in solution and (middle) immobilized on the electrode surface in a heterogenized system. (Right) The binding and release steps, together with the two-electron oxidation and reduction steps in molecular electrocatalysis of HER and HOR.

A common approach for the quantitative analysis of heterogenized systems is to determine the current at high overpotential, using RDEs at sufficiently high rotation rates to ensure that diffusion of the reactants is not rate limiting. Under these conditions, sigmoidal waves can be observed in voltammetry (see Figure 1 in the main text). In this situation, the plateau current at high overpotential (i_{max}) is limited only by the amount of catalyst immobilized on the surface (Γ), the catalytic conversion rate and/or the rate of reactant binding/dissociation. By dividing the current by the amount of catalyst, TOF_{max} is obtained ($= i_{max}/nF\Gamma$, in which F is the Faraday constant and n the number of electrons exchanged in the redox reaction that is catalysed).

For example, under steady state at sufficiently large (reductive) overpotential, all catalyst molecules immobilized on the electrode will be in their reduced forms (cat_{red} , cat_{red}-H^+ and cat_{red}-$2H^+$ in Figure S3, right). TOF_{max} is then determined by the rate of the protonation steps, the catalytic conversion rate of the catalyst (from cat_{red}-$2H^+$ to cat_{ox} in Figure S3, right) and release of H_2. It follows that TOF_{max} can only be improved by optimising the electrocatalyst as the interfacial electron transfer kinetics do not influence TOF_{max}. It also follows that the reduction potential of the catalyst in the semi-reduced state (cat_{semi}), which influences the stability of one of the intermediates, does **not** directly influence i_{max} or $TOF_{max,}$ even though it will affect the catalytic behaviour closer to the reduction potential of the catalyst.

Simulations are sometimes performed to model the voltammetry, for instance by modelling the outer sphere electron transfer kinetics with Butler-Volmer equations, diffusion of reactants or catalyst by Fick's law, binding and release of reactants by binding constants and (first order) rate constants and, finally, catalytic turn over by a rate constant. In each of these parameters, non-ideal behaviour might require the application of more complex models. Although the latter gives rise to valuable insight into the reaction mechanism of electrocatalysis, it also increases the mathematical complexity of the simulations.

When the catalyst is not immobilized on the surface, a sigmoidal wave is still obtained when the diffusion is much faster than TOF$_{max.}$ This applies for catalysts with low TOF$_{max}$. For faster catalysis, diffusion becomes limiting and without a RDE, a peak-shaped CV is obtained. In this situation, or when other side phenomena such as product inhibition prevent the formation of a plateau current, a foot-of-the-wave analysis (FOWA) can be used to predict TOF$_{max}$ (Figure S4). In this analysis, the shape of the voltammogram at the onset of catalysis, for which diffusion or electron transfer kinetics is not yet limiting, is extrapolated to obtain a sigmoidal curve. The plateau of the simulated curve gives i_{max} from which TOF$_{max}$ can be determined by dividing by the peak current in a CV of the catalyst in the absence of substrate (i_p^0). We note that in Figure S4, the current is already divided by i_p^0 and hence the rate is given in i/i_p^0. In Figure S4a', b' and c' (right hand side), the x-axis is transformed, resulting in plots from which the slope gives access to the TOF$_{max}$ (see reference [9] for further details).

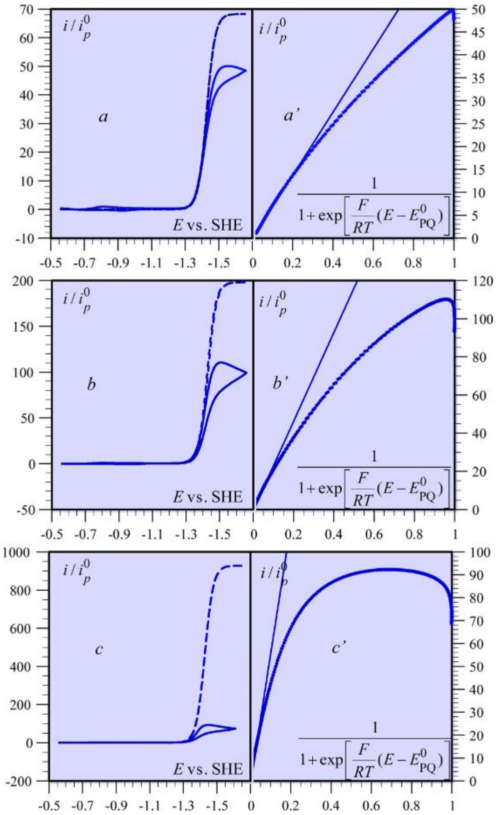

Figure S4: Example of a FOWA. (a, b, c) Cyclic voltammograms (CVs) in which the currents (*i*) are normalised against the peak current in a CV of the catalyst in the absence of substrate (i_p^0). The lines are experimental data at increasing substrate concentration (from a to c). The dashed lines are simulated using FOWA. (a', b', c') The potential at the x-axis is replotted using the formula given (E^0_{PQ} = reduction potential of the catalyst in the absence of substrate; *F*, *R* and *T* have their usual meaning). The experimental data is given by squares. In this representation, FOWA shows that the slope at high over potential (the slope is represented by the thin lines) become linearly related to the product of TOF$_{max}$ and the bulk substate concentration. We refer to [9] for experimental details. Reprinted with permission from Costentin et al. [9] Copyright 2012 American Chemical Society.

Box 3: Lexicon

Bidirectional electrocatalysis: An electrocatalytic system that can catalyze both directions of a redox reaction at applied potentials both positive and negative of the equilibrium potential (E_{eq})

Catalytic Tafel plot: An approach in synthetic molecular electrocatalysis in which the logarithm of the FOWA derived TOF, with TOF_{max} being the maximum plateau current, is plotted versus the applied potential during a potential sweep.

ECSA: The ElectroChemically active Surface Area, often determined for heterogeneous electrocatalyst. For metals and alloys, the ECSA is usually based on an electrochemical adsorption reaction, whereas for metal oxides it is often based on the electrochemical capacitance.

Foot-of-the-wave analysis (FOWA): An analysis used in molecular electrocatalysis to determine TOF_{max} at stationary electrodes. In FOWA, diffusion limitations are mathematically removed by extrapolating the onset of catalysis in a voltammogram to determine TOF_{max} at high over-potential.

I_{max}: A parameter used in molecular electrocatalysis, which signifies the maximum catalytic current obtained at a sufficiently high overpotential. At this overpotential, the voltammetry displays a plateau in catalytic current (see Figure 1 of main text).

Irreversible electrocatalysis: The opposite of reversible electrocatalysis. In these systems, electrocatalysis is only observed at a significant overpotential (with respect to the equilibrium potential of the reaction).

Koutecky-Levich analysis: When a RDE is used to analyze electrocatalysis and it is observed that even at the highest rotation rate catalysis is still limited by diffusion, a Koutecky-Levich analysis can be performed. In this analysis, the reciprocal current at a chosen potential is plotted against the reciprocal of the square-root of the rotation rate (in rad/s) for several different rotation rates. A Koutecky-Levich plot is obtained in which the data points form a straight line. The intercept of this line with the y-axis (at infinite rotation rate) then gives the reciprocal current in the absence of diffusion limitations.

Reversible electrocatalysis: A catalyst in which a small perturbation around the equilibrium potential of the reaction (E_{eq}) leads to a significant catalytic rate. In a linear voltammogram, this results in a single inflection point around E_{eq} (see Figure 1 of main text).

Rotating disc electrode (RDE): An electrode that rotates with the purpose of inducing convection of reactants to and from the electrode. When an RDE rotates sufficiently fast (with respect of the TOF of the electrocatalysts), the electrocatalytic reaction is not limited by diffusion. This can be combined with a Koutecky-Levich analysis.

Sabatier principle: The principle that a good catalyst should neither bind its intermediates too strongly, nor too weakly (see Box 1). Used most frequently in heterogeneous (electro)catalysis.

Stationary electrode: An electrochemical system in which the working electrode is stationary. For electrocatalysis with stationary electrodes and homogeneous electrocatalysts, a foot-of-the-wave analysis (FOWA) can be performed.

Tafel plot: A plot commonly used in heterogenous electrocatalysis in which the logarithm of the electrocatalytic current (density) is plotted against potential (see Box 1).

TOF_{max}: (Maximum turn-over frequency) A parameter used in molecular electrocatalysis, which signifies the maximum turn-over rate obtained a sufficiently high overpotential. At this overpotential, the voltammetry displays a plateau in catalytic current (see Figure 1 of main text). To obtain TOF_{max}, the maximum current at this plateau needs to be normalized by the number of catalysts (see Box 1). In biological electrocatalysis, TOF_{max} is equal to k_{cat} when the substrate concentration is >> K_M. In synthetic molecular electrocatalysis, TOF_{max} is also known as k_{max} or $k_{obs.}$

Volcano plots: A plot in which the electrocatalytic reaction rate of a catalyst is plotted against the binding energy of the key catalytic intermediate (see Box 1), or any other (thermodynamic) descriptor of the catalytic rate.

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