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Enhancing the connection between computation and experiments in electrocatalysis

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Combining computational and experimental methods is a powerful approach to understand the variables that govern catalyst performance and ultimately design improved materials. However, the effectiveness of this approach rests on the strength of the relationships between calculated parameters and experimental measurements. These relationships are complicated by the intricacy and dynamic behaviour of catalytic active sites, and by the non-trivial relationship between calculated reaction energetics and observed rates. In this Perspective, we highlight opportunities to enhance the connection between computation and experiment in electrocatalysis. These include measuring the intrinsic kinetic behaviour of catalysts, creating precise models for the active site and its environment, and forming clear relationships between calculated reaction energetics and observed rates. As experimental and computational methods continue to become more powerful, clear connections between the two will maximize their utility to guide the design of efficient and selective electrocatalysts.

Catalysis is central to today's society. It is the key to producing fertilizers that support nearly half of the world's population, converting oil into gasoline that fuels our cars and cleaning pollutants from the air we breathe[1]. Looking forward, catalysis will also be critical in the transition to a more environmentally sustainable world while seeking or maintaining a high standard of living[2]. More efficient catalysts that make use of renewable resources to produce carbon-neutral fuels, chemical building blocks and harmless products in waste streams are needed. To develop effective catalysts for these applications an understanding of the way that they carry out reactions and the variables that govern their performance is needed[3].

Computational studies, particularly those that employ density functional theory (DFT), are invaluable in developing our understanding of heterogeneous catalysis[4]. These studies have demonstrated that, although catalytic rates depend on the reaction and transition state energies of a number of elementary steps, the energetics of each elementary step are not independent[5,6]. Therefore, complex rate expressions can be simplified to the point that one or two variables, termed descriptors, can describe the rate of reaction[7]. Understanding the variation of descriptor values between catalysts allows us to build intuition about which catalysts are most effective for a given reaction and why the design of new catalysts that surpass their activity is challenging. Computational studies also describe the relationships between catalyst descriptor values and their electronic structure, which offers a physical explanation of why catalysts behave the way they do[8].

Given this success, DFT has become increasingly common in studies of heterogeneous catalysis. Although DFT is employed in many ways, perhaps the most common is as a tool to explain the experimentally measured performance of a new catalyst formulation. However, the connections between the insights extracted from DFT calculations and experimental rates are often tenuous.

Here we survey the ways in which computational and experimental studies are combined in catalysis and suggest opportunities to strengthen the connections between the two. We focus on electrocatalysis as this field is less mature than thermochemical catalysis, and because reactions in electrochemical environments pose unique challenges for DFT calculations. We suggest that these connections may be improved through experiments that measure the intrinsic kinetic behaviour of the catalyst and provide clear insights into the structure and composition of active sites. Computational studies that accurately treat the active site and its environment should be used to calculate parameters that have straightforward relationships with measured rates. We expect that enhancing the way that DFT calculations and experimental measurements are used in concert could maximize the insights derived from both tools and advance our understanding of heterogeneous catalysis (Fig. 1).

Considerations for measuring catalytic rates

DFT allows us to calculate the energies of adsorbates on a catalyst surface and the energies of transition states that connect these adsorbed species. It can therefore describe the energetics of elementary steps that control the rate of catalytic reactions. This ability has led to the widespread application of DFT calculations in electrocatalysis to attempt to explain the activity of a new catalyst formulation.

As DFT does not simply output a rate, decisions need to be made about what parameters to calculate and what connection these parameters have with measured experimental rates. However, before discussing how DFT calculated parameters can be more intimately connected with experimental data, several criteria must be fulfilled for any relationship to exist between the calculations and experiments.

To compare with DFT calculations, catalytic rates must be measured under experimental conditions in which reaction kinetics, rather than mass transport, control the performance[9]. Furthermore, catalytic rates must be normalized by the number of active sites. DFT calculations only provide information about the intrinsic kinetic behaviour of catalytic sites[10].

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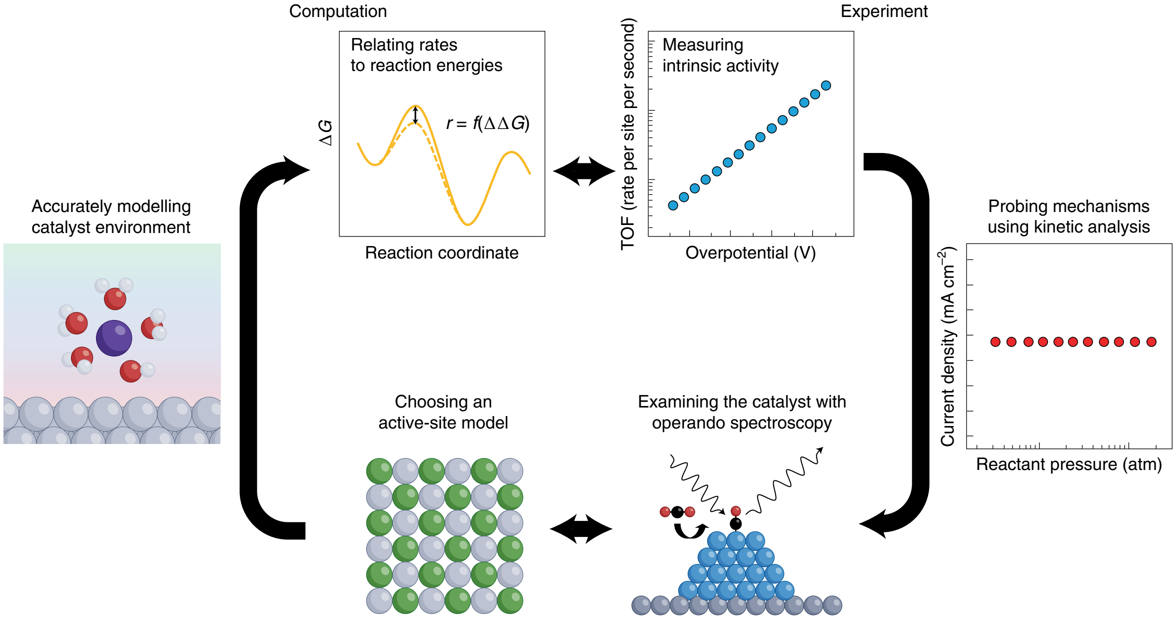

Fig. 1 | Enhancing the connection between computation and experiments in electrocatalysis. Connections between computation and experiments in electrocatalysis can be enhanced by measuring the intrinsic kinetic behaviour of catalysts, creating accurate models for the active site and its environment, and forming clear relationships between the calculated reaction energetics and observed rates.

These points have caused considerable misunderstanding in electrocatalysis about the behaviour of catalytic materials. For example, extensive research has been done to develop Earth-abundant catalysts to replace platinum for the hydrogen evolution reaction (HER)[11,12]. Based on activity metrics that do not account for the number of catalytic sites, for example, the overpotential required to reach a geometric current density of 10 mA cm^{-2}, many researchers concluded that these catalysts are similarly active to Pt. However, the intrinsic activity of these catalysts, defined by the catalytic rate per active site, or turnover frequency (TOF), still lags 3–4 orders of magnitude behind that of Pt (Fig. 2a)[13,14]. Furthermore, recent studies demonstrated that even these values probably underestimate the intrinsic activity of Pt, based on the ubiquity of mass transport limitations for this highly active catalyst[13]. This implies meaningful progress remains to be made in the development of active and inexpensive HER catalysts.

In the development of catalysts for the electrochemical reduction of carbon dioxide (CO_2R), intensive research has been done to modify copper catalysts to improve their ability to produce multicarbon hydrocarbons and alcohols[15]. However, analysis of these catalysts shows that, on normalization by their active surface area or number of sites, none significantly outperform the standard Cu catalysts (Fig. 2b)[15–17]. This conclusion is valid whether the comparison is based on total CO_2 reduction rates or on rates of multicarbon product formation[17,18]. Although extensive research efforts have aimed to evaluate the role of particular active sites in nanostructured Cu catalysts (for example, subsurface oxygen atoms and grain boundary defects), the analysis shown here suggests that, if present, these sites do not have an exceptional activity[19]. As we showed previously, it is likely that high Faradaic efficiencies to multicarbon products over these catalysts are related to low surface-area normalized rates of hydrogen evolution, rather than to high intrinsic rates of multicarbon product formation[17].

Although transport limitations may be present in a practical device, to include these in studies aimed to understand the behaviour of a catalyst confuses interpretation. Under transport limitations, the conditions under which the catalyst operates (reactant and product concentrations, temperature and pH) differ significantly from their well-defined values in the bulk of the electrolyte. The magnitude of these deviations depends both on the rate of reaction at the catalyst surface and on the reactor hydrodynamics. Recent studies quantified these effects using multiphysics simulations[20,21]. Testing catalysts under these non-standard and ill-defined conditions prevents an accurate comparison with other catalysts.

Similarly, although increasing catalyst loading without improving the per-site activity could be an effective strategy to improve the performance of a practical device, care must be taken in catalyst discovery studies to not conflate this with an enhanced intrinsic activity. Therefore, in studies that aim to understand or discover new catalytic materials, and combine experimental insights with computational studies, activity measurements that are not influenced by transport phenomena and account for the number of catalytic sites are critical.

Choosing a model for the active site

An important decision that we must make when performing a DFT calculation is how to model the catalytic active site and its environment. The utility of the information DFT provides is determined by how closely this model reflects reality[22]. Although other sources of error exist in DFT, these errors can be quantified and are more important for calculating absolute rates than for comparing differences in rate from one catalyst to the next[23,24]. Conversely, the errors introduced by an active site model that does not reflect the real system are difficult or impossible to quantify and can vary between catalysts.

To develop an accurate model for a catalytic active site is nontrivial. Even simple metal surfaces have a diversity of possible active sites, and although a given atomic configuration may be the most stable or abundant, this does not guarantee that it is the catalytically relevant site[25,26]. The number of possible active sites grows rapidly when considering metal alloy or compound catalytic materials (oxides, nitrides, phosphides and carbides)[27].

Even if we accurately describe the structure of the catalyst in its resting state, additional complexities may still exist. The structure and composition of the active site may change under reaction conditions and the environment that surrounds the active site may

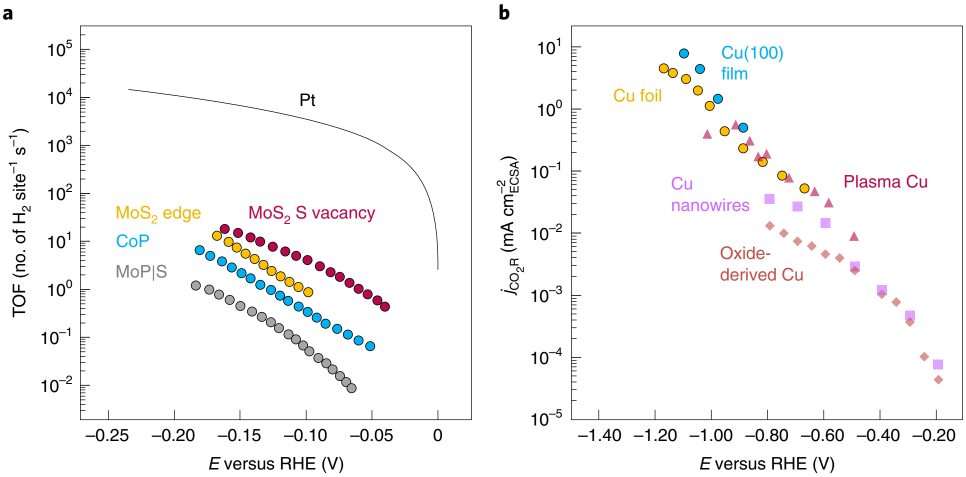

Fig. 2 | Intrinsic activity measurements of electrocatalysts. a, Comparison of hydrogen evolution activity for Pt catalysts and that of high performing Earth-abundant catalysts. The activity is normalized to the number of sites to obtain a TOF[13,81–83]. **b**, Comparison of the CO_2R activity between various nanostructured Cu electrocatalysts and polycrystalline Cu. The CO_2R partial current density is normalized to the electrochemical surface area (ECSA). More complete comparisons can be found in refs. [15–17]. Panel **b** adapted with permission from ref. [15], American Chemical Society.

have an important influence on reactivity. For instance, a reactive metal exposed to oxygen-containing species may oxidize. The newly formed oxide surface may have a different reactivity to that of the parent metal surface. These surface composition changes were observed for catalysts that form metal oxides, hydrides, (oxy)nitrides and (oxy)carbides under reaction conditions[28]. Furthermore, high coverages of the reaction intermediates may also lead to reconstruction of the catalyst as it attempts to minimize the surface energies in the presence of the adsorbates[29]. The influence of adsorbate coverage on reaction energetics should also be considered, as the binding of adsorbates to a populated catalyst surface is often significantly weakened relative to that of a clean surface[30,31].

In electrocatalysis, perhaps the most important consideration when selecting an active site model is how to treat the electrochemical environment that surrounds the catalyst and how to accurately include the electrode potential. The computational hydrogen electrode provides a simple method to calculate electrochemical reaction energetics without an explicit treatment of electrons and ions in solution[32]. Instead, the chemical potential of the proton–electron pair is dictated by its equilibrium with molecular hydrogen. This model has therefore been very successful in assessing the reaction thermodynamics for chemistries that involve proton-coupled electron-transfer steps, and in predicting new materials based on these thermodynamics[3]. However, evaluating the reaction kinetics or chemistries in which these proton and electron transfer steps are decoupled complicates modelling[33]. In the computational hydrogen electrode, simulations are conducted at a constant number of electrons. This results in a change in the potential of the electrode surface along the reaction path. Conversely, in experiments, the electrode potential sets the chemical potential of electrons, and the number of electrons adjusts continuously in response. The change in interfacial charge density, and therefore the associated errors, can be mitigated using cell extrapolation schemes[34–37]. Alternatively, grand canonical DFT calculations mimic the experimental condition, with the chemical potential of electrons being fixed, rather than their number[38]. In addition to accurately modelling the electrode potential, a complete description of the reaction kinetics requires inclusion of the reaction environment in the computational model. The presence of a liquid solvent, electrolyte ions and interfacial fields have all been experimentally shown to have a direct impact on the surface chemistry[39–45]. For instance, the choice of electrolyte cation markedly impacts the performance of catalysts in the electrochemical reduction of CO_2 and O_2, whereas hydrogen evolution activity varies by orders of magnitude as the electrolyte pH is changed[39,40,44,45]. Physical models have been proposed to explain these behaviours—we suggested, for example, that cation effects are the result of an electric field stabilization of polarizable intermediates—but generalizable explanations are still lacking[40,41]. Thus, it is important to consider what elements of the electrochemical environment are treated computationally, and what effect model simplifications may have on the computational results. Although a full discussion of these effects is beyond the scope of the current work, several discussions on the topic were recently published[46–48].

The complex and dynamic nature of electrocatalytic interfaces highlights the usefulness of experimental studies on well-defined catalytic materials[49]. Single-crystal surfaces reduce the complexity in computationally describing the active site, which facilitates comparisons with the calculated parameters. Using single crystals to validate computational models can enhance our confidence in subsequent calculations over more complicated catalytic materials. In situ or operando measurements that describe the structure and composition of dynamic catalytic materials under the working conditions are also valuable for forming accurate computational models. Together, these experiments can reduce the risk of confirmation bias. As the number of choices available in simply selecting a model for the active site expands, the likelihood that one model will align with a given conclusion also increases. Thus, we must always be cautious against bias towards an analysis that fits our preconceptions and seek experimental evidence to guide our decisions[50].

Calculated parameters and their connection to measured rates

Once we have selected an appropriate model for the active site and its surroundings, we must decide which parameters to calculate and what connection these parameters have with the measured experimental rates. One of the simplest parameters of potential value in describing rate differences in one catalyst with respect to another is the adsorption energy of a chosen molecule. In some cases, a detailed analysis was conducted that linked the adsorption energy of a descriptor molecule to the overall reaction rates using a Sabatier analysis or complete microkinetic model[7]. Generally, however, the relationship between the adsorption energy and the rate of reaction is non-trivial. A degree of rate-control analysis can describe the relationship between changes in adsorption energy of the intermediates

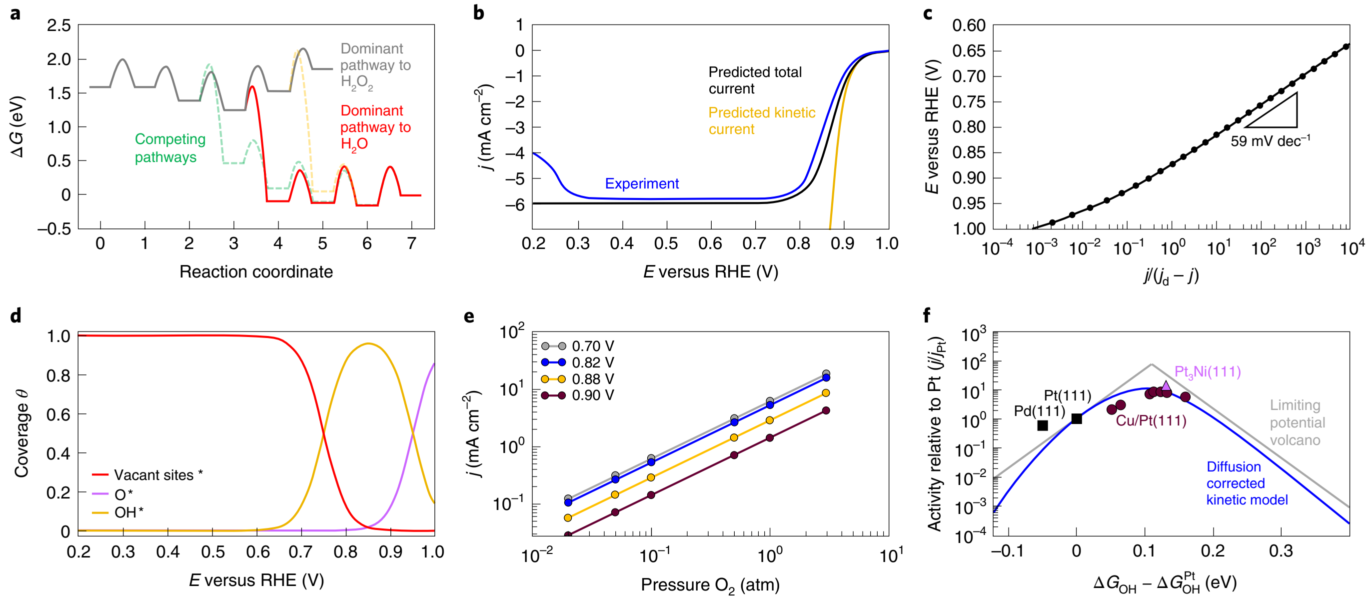

Fig. 3 | Microkinetic modelling of oxygen reduction. a, Free energy diagrams for the oxygen reduction reaction via various mechanisms on Pt(111) at 0.9 V versus RHE. **b**, Comparison between predicted and experimental polarization curves and kinetic current density on Pt(111) at a rotation speed of 1,600 revolutions per minute. **c**, Predicted Tafel plot with a 59 mV dec^{-1} slope indicated. j_d is the diffusion-limited current. **d**, Simulated coverages of the most abundant adsorbates on Pt(111) as a function of electrode potential. **e**, Current density as a function of O_2 pressure at different potentials. The reaction is seen to be first order in O_2. **f**, Simulated kinetic volcano at 0.9 V versus RHE compared with the potential limiting volcano and experiments on (111) facets. Experiments labelled Cu/Pt(111) are Pt overlayers on CuPt near-surface alloys[76]. For details on computational methods refer to ref. [73]. Panels **a**,**b**, adapted with permission from ref. [73], American Chemical Society. Panels **c**–**f** reproduced with permission from ref. [73], American Chemical Society.

and the rates, but this analysis is rare in electrocatalysis[51,52]. Therefore, in most cases, the computational results only agree in direction: a new catalyst should outperform a standard catalyst because the adsorption energy increases or decreases. However, the magnitude of the predicted changes in rates and the experimentally measured ones may have discrepancies of several orders of magnitude. In less favourable situations, there is no explicit connection between the adsorption energies and measured rates. For instance, a study may find that a novel Cu-based CO_2 reduction catalyst has an enhanced ethanol selectivity relative to that of polycrystalline Cu, but a straightforward relationship between the intrinsic rate of ethanol production (and not that of other multicarbon products) and the adsorption energy of an intermediate is lacking[53]. Adsorption energies may also reflect catalytically irrelevant spectator species or poisons, as they are based on the most stable adsorption site. Adsorbates in less stable sites may have a lower coverage but dominate measured rates[54]. Finally, in electrocatalysis research, calculated adsorption energies are rarely directly verified by experimental methods, such as temperature-programmed desorption, adsorption calorimetry or kinetic analysis that extracts equilibrium constants. Adsorption energies extracted from gas-phase techniques could yield useful insights for electrocatalytic systems, but care must be taken to understand the influence of the solvent on measured values[55].

A second potential parameter that is often calculated is the activation energy for some reaction elementary step. To form a clear relationship between an activation energy and measured rates, some assumption of the kinetic relevance of the elementary step chosen is required. In some well-studied reactions, a rate-limiting step for the formation of a certain product may be known. In these circumstances, it is common for studies to compare a standard and novel catalyst on the basis of the activation barrier for this elementary step, and conclude that the lower barrier on the novel catalyst supports the higher experimental rates observed. Again, however, it is rare that a quantitative comparison is shown. If a sole rate-limiting step is present (that is, a certain elementary step has a kinetic degree of rate control equal to one), the change in rate of reaction with a change in activation energy is given by:

$$\partial \ln r = \partial \left(\frac{-\Delta G_i^{\mathrm{TS}}}{RT} \right)_{\Delta G_{j \neq i}^{\mathrm{TS}}, \Delta G_n} \quad (1)$$

where r is the reaction rate, ΔG_i^{TS} is the free energy of activation of the elementary step of interest, R is the gas constant, T is the temperature in K and $\Delta G_{j \neq i}^{\mathrm{TS}}$, ΔG_n are the activation and reaction energies of all the other elementary steps[52].

As discussed previously, calculating activation barriers with DFT in electrochemistry presents considerable computational challenges. In favourable cases, DFT can calculate the activation energies for electrochemical reactions with an intrinsic error of ~0.2 eV. For this change in barrier, a three-orders-of-magnitude change in rate is predicted for an electrochemical reaction conducted at room temperature[18,52]. Therefore, researchers should be cautious when asserting agreement between computational and experimental work if the magnitude of the observed rate enhancements are not commensurate with these predictions. As with adsorption energies, it is also rare that activation energies are measured experimentally for comparison with calculated values[56,57]. We note that measurements of activation barriers may be corrupted by mass-transport limitations, and thus care should be taken to ensure the measurements are done under kinetic control.

DFT calculations provide information on the enthalpy of adsorption or activation, but simple approximations to the adsorption potential are generally used to account for entropic terms. For instance, under the harmonic approximation, a molecule can lose a large fraction of its translational degree of freedom upon adsorption. For some systems these approximations provide sufficient accuracy. However, entropic effects can often have considerable impacts on catalytic rates, which introduces additional sources

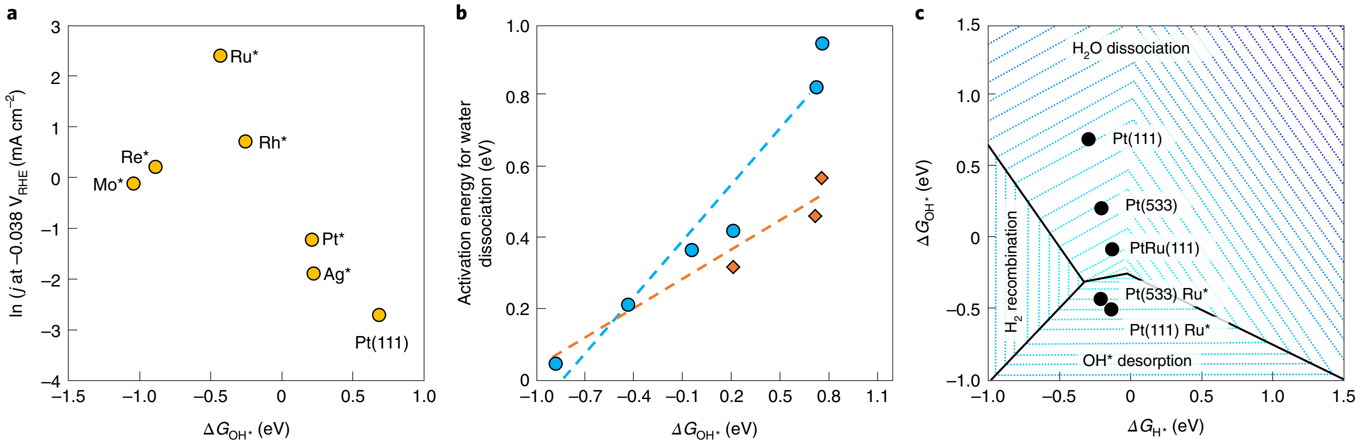

Fig. 4 | Understanding hydrogen evolution in alkaline media using computation and experiments. **a**, Experimental HER rates on Pt(553) with Mo*, Re*, Ru*, Rh* and Ag* adsorbed at the step edge plotted against the calculated hydroxide adsorption free energy. **b**, DFT-calculated activation energies for water dissociation on the same surfaces plotted against the adsorption energy of the hydroxide. Calculations are done both with OH* as a product (blue circles) and with OH^- as a product (orange diamonds), **c**, Logarithm of the rate of hydrogen evolution (contours) as a function of hydrogen binding energy and hydroxide binding energy. The most active catalysts bind hydrogen at an intermediate strength. Catalysts with weak hydrogen binding and weak hydroxide binding (top right) yield the lowest rates (purple). Panels **a**,**c** reproduced with permission from ref. [45], Springer Nature Ltd. Panel **b** adapted with permission from ref. [45], Springer Nature Ltd.

of uncertainty. Compensation effects between the entropy and enthalpy of activation are common, in which a decrease in barrier is accompanied by a decrease in entropy of the transition state[58,59]. As rates depend exponentially on both terms, overcompensation could result in qualitatively inaccurate predictions about the relationship between rates and barrier heights. More detailed estimates of pre-exponential factors can be calculated using statistical mechanics, with assumptions derived from the results of DFT calculations[60].

Phenomenological descriptions of electrochemical rates

Classic electrochemical kinetics are also often applied in an attempt to understand the activity of electrocatalytic materials. The Butler–Volmer equation is a phenomenological description of the rate of an electrochemical reaction, in which rates increase exponentially as a function of potential away from the equilibrium potential. For some arbitrary electrode reaction:

$$\mathrm{A} \leftrightarrows \mathrm{B} + \mathrm{e}^- \quad (2)$$

It can be written as

$$j = k_\mathrm{a}^0 \exp\left[\frac{\alpha_\mathrm{a} F\left(E-E^0\right)}{RT}\right][\mathrm{A}] - k_\mathrm{c}^0 \exp\left[\frac{-\alpha_\mathrm{c} F\left(E-E^0\right)}{RT}\right][\mathrm{B}] \quad (3)$$

where j is the current density, k_a^0 and k_c^0 are the standard anodic and cathodic rate constants, α_a and α_c are the anodic and cathodic transfer coefficients, E^0 is the equilibrium potential, E is the potential of the working electrode, [A] and [B] are the species bulk concentrations, and F is Faraday's constant. The current is related to the current density as $I = jA$, where A is the electrode area.

Tafel analysis, used in the regime in which one redox reaction dominates, entails plotting $\ln|I|$ versus E to extract the slope, which is related to the transfer coefficient. Often, so-called Tafel slopes are defined with units of mV per decade of current as:

$$\text{Tafel slope} = 2.3\frac{RT}{\alpha_\mathrm{a} F} \quad (4)$$

Cardinal values of the Tafel slope were calculated for several important electrocatalytic reactions[61]. Different kinetically relevant steps give rise to different values of the Tafel slope, so many studies compare experimental measurements with cardinal values to attempt to extract mechanistic insight. However, this analysis can be muddied by several factors. To obtain cardinal values, analysis typically assumes limiting coverage values (nearly empty surface or full adsorbate coverage). Changes in coverage with potential give rise to non-linear Tafel behaviour, even for reactions with a single rate-limiting step and non-interacting adsorbates[62]. The presence of mass transport limitations, multiple kinetically relevant steps or non-Langmuirian adsorption behaviour adds further ambiguity to this analysis[63,64]. As recently mentioned, even the determination of an appropriate potential region for Tafel analysis is non-trivial, and can bias analysis towards the expected values[65].

Enhancing the connection between computation and experiments

With these limitations in mind, we now consider what opportunities exist to more effectively use computational methods to understand the performance of new electrocatalysts. We have noted that calculations of simple parameters, such as adsorption energies or activation energies, do not always have straightforward relationships to measured rates. Similarly, it is difficult to extract insights about reaction mechanisms using a phenomenological Tafel analysis in even the simplest cases[66].

By performing a more complete set of calculations, however, more direct comparisons can be made between predicted and measured rates. The development of a microkinetic model involves proposing a sequence of elementary steps, and writing an expression that is consistent with this mechanism and relates rates to the energetics of reaction intermediates and transition states[67–69]. The energies of all the intermediates and transition states can then be calculated using DFT. Pre-exponential factors can be estimated using statistical mechanics. Prior knowledge of a rate-limiting elementary step is not required, although it is unlikely that all the steps are kinetically relevant. This procedure can also be employed to assess various potential mechanisms against one another. Microkinetic models can provide computationally predicted rate versus potential information that can be directly compared to experimental measurements.

But a microkinetic model can provide additional useful information that can be compared with experiments besides rates[67–69]. A solved microkinetic model provides the coverages of adsorbed species and can identify those that are most abundant. It is worth noting that these coverages can differ from those used in the initial calculation, so an iterative approach in which energetics are recalculated at predicted coverages is most accurate[68]. DFT-informed microkinetic models can also assess how adsorbate coverages change as a function of applied potential. In situ spectroscopic probes, such as infrared or Raman spectroscopy, can be compared with these predictions. Further, the identification of adsorbed species through a comparison of calculated and experimental vibrational frequencies can be useful in assessing reaction mechanisms and active-site models[70].

The rate expressions derived from microkinetic models also predict values that are testable through kinetic analysis. Reaction orders, or the sensitivity of reaction rate to reactant or product feeds, are predictable using a microkinetic model. Experimental measurements of reaction orders can help discriminate between competing mechanisms. Kinetic tests that use isotopically labelled molecules can also be used to assess the validity of the hypothesized mechanism. Measurements of isotope exchange rates can assess the reversibility of a chemical step, and measurements of the kinetic isotope effect (the ratio of rates using one isotopically labelled molecule versus another) can assess the kinetic relevance of a particular reaction step[71]. Experimental studies that feed reaction intermediates can also be used to glean information about the reaction mechanism and validate the proposed microkinetic model[72].

Microkinetic models that use reaction and transition-state energies derived from DFT have been used to understand electrocatalytic reactions, such as the oxygen reduction reaction, the oxygen evolution reaction, the reduction of carbon dioxide and the borohydride oxidation reaction[62,69,73–75]. They have also been applied widely in thermochemical catalysis[67,68]. Below, to illustrate their utility, we examine example studies on the oxygen reduction and HER[45,73].

Microkinetic models for oxygen reduction

The oxygen reduction reaction over Pt(111) has been the subject of extensive computational and experimental study. In the work of Hansen et al. a DFT-based microkinetic model was developed[73]. The following sequence of elementary steps was considered:

$$\mathrm{O_2} + * \rightarrow \mathrm{O_2^*} \tag{5}$$

$$\mathrm{O_2^*} + \mathrm{H^+} + \mathrm{e^-} \rightarrow \mathrm{OOH^*} \tag{6}$$

$$\mathrm{OOH^*} + \mathrm{H^+} + \mathrm{e^-} \rightarrow \mathrm{O^*} + \mathrm{H_2O} \tag{7}$$

$$\mathrm{O^*} + \mathrm{H^+} + \mathrm{e^-} \rightarrow \mathrm{OH^*} \tag{8}$$

$$\mathrm{OH^*} + \mathrm{H^+} + \mathrm{e^-} \rightarrow \mathrm{H_2O} + * \tag{9}$$

The reaction was proposed to follow a series of proton-coupled electron–transfer steps that sequentially reduce O_2 to OOH* (where OOH* denotes an adsorbed OOH species), O*, OH* and finally liberate water as a product. No assumption of the rate-limiting step is needed a priori. The study also considered alternative pathways: the chemical dissociation of O_2 to form two O*, and the chemical dissociation of OOH* to OH* and O*. Figure 3a shows the free energy diagrams for these various pathways in which the energies are derived from DFT calculations. For Pt(111), the reduction of OH* to form water is the rate-limiting step. The model also accounts for selectivity between the four-electron reduction of oxygen to give water, and the two-electron pathway to give hydrogen peroxide. We note that the inaccuracies associated with calculating activation barriers lead to challenges in predicting selectivity from microkinetic analysis[18]. This is an important consideration for reactions in which selectivity is an issue or there are many possible products, such as in the reduction of CO_2 (refs. [15,16]). Figure 3b,c shows that the microkinetic model can be used to directly predict rate versus potential information and Tafel slopes. As mentioned above, however, outputs such as adsorbate coverages and reaction orders (Fig. 3d,e) can also be obtained from the solved microkinetic model and can fortify the link between experimental and computational measurements. Having developed this robust connection between a computational model and experimental measurements, the performance of a new catalyst formulation can be understood. Figure 3f shows that the enhanced performance of Pt overlays on CuPt near-surface alloys (denoted Cu/Pt(111)) can be understood using the microkinetic model[76]. This overlayer structure reduces the adsorption energy of OH* to the Pt active site, which results in a more facile reduction of the OH* to form water.

Combining computation and experiments for hydrogen evolution

In acidic media, the HER can occur via two main mechanisms. In both, the first step, termed the Volmer step, involves the adsorption of a proton from solution coupled with an electron transfer to form adsorbed hydrogen:

$$\mathrm{H^+} + \mathrm{e^-} + * \rightarrow \mathrm{H^*} \tag{10}$$

Here the * denotes a surface site and H* is an adsorbed hydrogen atom. The two mechanisms differ in how hydrogen is formed after this step. In the Tafel step, molecular hydrogen is produced by a surface reaction of two adsorbed hydrogen atoms. This Langmuir–Hinshelwood type of mechanism is termed the Volmer–Tafel mechanism:

$$\mathrm{H^*} + \mathrm{H^*} \rightarrow \mathrm{H_2} + 2* \tag{11}$$

Alternatively, molecular hydrogen can be formed by a direct attack on the adsorbed hydrogen by a proton from the solution, coupled with an electron transfer. This Eley–Rideal type of reaction is termed the Volmer–Heyrovsky mechanism:

$$\mathrm{H^*} + \mathrm{H^+} + \mathrm{e^-} \rightarrow \mathrm{H_2} + * \tag{12}$$

In alkaline media, in which the proton (or hydronium) concentration is low, water becomes the source of protons for HER. The Volmer step can therefore be written as:

$$\mathrm{H_2O} + \mathrm{e^-} + * \rightarrow \mathrm{H^*} + \mathrm{OH^-} \tag{13}$$

The difficulty of this step relative to the Volmer step in acidic media has been posited as the reason why HER rates are roughly two orders of magnitude lower for Pt catalysts in alkaline media than they are in acidic media. Consistent with this, studies have demonstrated that decorating Pt catalysts with clusters of oxophilic metals, such as Ni, Rh or Ru, can enhance the HER rates, presumably by lowering the barrier for water dissociation[77,78]. The differences in HER rates in acid and base have also been explained by changes in interfacial electric fields, water reorganization energies or hydrogen binding energies with pH[44,79,80].

To understand these effects, recent work used a combination of experimental measurements and DFT calculations to examine stepped Pt single crystals decorated by metals of varying oxophilicity (Mo, Re, Ru, Rh and Ag)[45]. In this system, hydrogen binding energies are fixed as it is assumed that hydrogen adsorbs only on Pt terraces and is unaffected by the presence of the transition metals at the steps. This study found that decorating the Pt steps with these metals enhanced the HER rates in alkaline media, with the trends in activity described by the adsorption energy of hydroxide on the transition metal adatom (Fig. 4). This correlation does not imply, however, that adsorbed hydroxide is an intermediate of the reaction that directly influences the reactivity for all these catalysts. Instead, DFT calculations demonstrated that the activation energy for water dissociation, which is kinetically relevant, is linearly correlated with the hydroxide adsorption energy whether the final state involves adsorbed hydroxide (OH^*)) or solvated hydroxide (OH^-) as a product (Fig. 4). This trend can be understood as a Brønsted–Evans–Polanyi relationship in which stabilization of the final state linearly reduces the transition state energy. Hydroxide is only directly involved as an intermediate on oxophilic metals (for example, Pt–Ru alloys), for which its desorption can be kinetically relevant. The combination of DFT studies with experimental work on well-defined catalytic materials has allowed the description of the reactivity of catalysts for alkaline HERs and provided new guidance for rational catalyst design. Namely, these studies show that both hydrogen and hydroxide binding strengths must be optimized for optimal catalyst performance.

Outlook

DFT calculations have played an important role in developing our understanding of heterogeneous catalysis. This role is likely to only increase as computational techniques become more powerful. However, to maximize the utility of these techniques, strong connections between experimental measurements and computed parameters are needed. These connections can be enhanced by experimentally measuring electrocatalytic rates that reflect the intrinsic activity of catalytic active sites, and by providing detailed information about the nature of these sites. In this sense, well-defined single-crystal materials can provide simplified and unambiguous information to help understand more complex catalysts. However, understanding the active site in its resting state is not always sufficient to rationalize catalytic performance. The surrounding medium can have a profound effect on reactivity, either by directly participating in the reaction or by influencing the structure and composition of the catalyst. Including these complexities into computational models is an ongoing challenge. Once models that accurately represent the active site are determined, discernment must be used to ensure that links exist between what is calculated and what is measured experimentally. We hope that this Perspective highlights opportunities as to how these connections can be made effectively.

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J.R. wrote the article and all the authors contributed to the discussion, reviewing and editing of the manuscript.

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The authors declare no competing interests.

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