https://doi.org/10.1038/s41929-025-01461-z

The overlooked role of adsorption isotherms in electrocatalysis

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Electrocatalysts enable the efficient interconversion of electrical and chemical energy for the sustainable production of fuels and chemicals. Here we highlight the importance of developing electrochemical adsorption isotherms to demystify complex reaction mechanisms and rationalize catalytic activity.

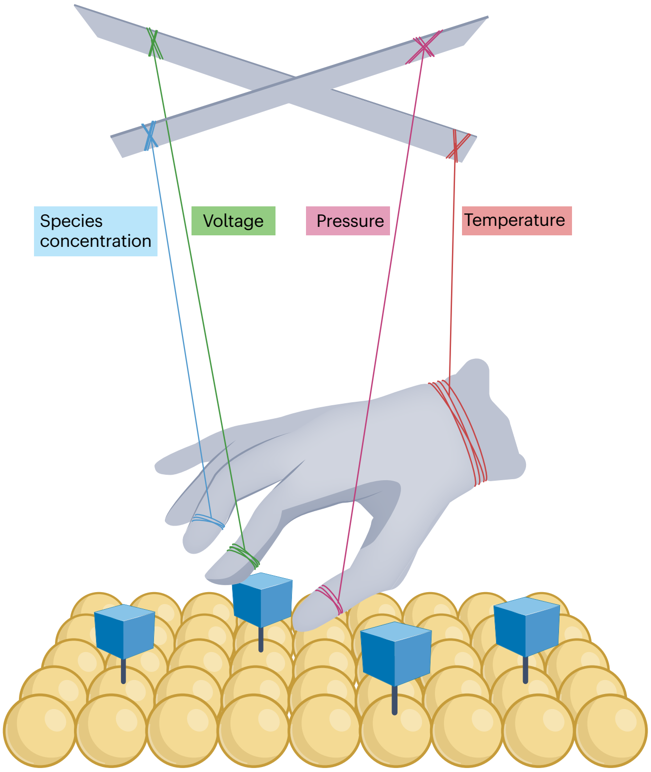

Fig. 1 | Thermodynamic parameters influencing surface coverage during electrocatalysis. Species concentration, applied electrochemical potential (voltage), pressure and temperature all influence the population of adsorbed reactive species at solid–electrolyte interfaces.

The development of heterogeneous catalysts has been essential to modern society, enabling the mass production of chemicals underpinning energy, infrastructure and human health. A central research focus in heterogeneous catalysis is to develop predictive mechanistic models, informed by investigations of reaction kinetics at solid–liquid and solid–gas interfaces. Mechanistic understanding of surface-catalysed reactions relies on an understanding of how the surface coverage of adsorbates (the proportion of occupied active sites) changes with system variables such as pressure, species concentrations, temperature and applied potential (Fig. 1).

When probed under constant temperature, these models are specifically referred to as adsorption isotherms, although we use the term to describe the dependence of surface coverage on any thermodynamic parameter. The first pioneering isotherm models were described by Irving Langmuir in the early twentieth century to predict coverage-dependent reaction kinetics. For example, consider the reaction of reactant A going to product B, transiting through a surface-bound intermediate *A, and where the second step is rate-determining (Fig. 2a). Under the assumptions of the idealized Langmuir isotherm model, all binding sites and species *A are chemically identical across the catalyst surface and are non-interacting with each other (leading to coverage-independent adsorption free energies).

For this sequence, the Langmuir isotherm predicts a sigmoidal relationship between the surface coverage, θ_A (where θ represents the fraction of occupied sites), and the logarithm of the pressure or concentration of the reactant, A (Fig. 2b). Under Langmuirian assumptions[1,2], the surface coverage of *A influences the overall reaction order. For example, in the limit of low surface coverage ($\theta_A \approx 0$), the reaction is first-order in A, yet in the limit of saturated surface coverage ($\theta_A \approx 1$), the reaction is zeroth-order in A. In the latter scenario, an increase in the concentration of A would not increase the surface concentration of *A, nor the overall rate of conversion to B. Owing to this tight relationship between adsorbate coverage and reaction rates, isotherm quantification and analysis has greatly facilitated the rational optimization of heterogeneous catalysts, in particular for well defined reaction systems occurring at solid–gas interfaces (such as CO oxidation in catalytic converters)[2]. Indeed, isotherms can be used to predict or rationalize complex phenomena such as fractional reaction orders and rate maxima across varying driving forces[3,4].

Within the broader field of heterogeneous catalysis, surface electrocatalysis has been championed for its potential to decarbonize the production of value-added fuels, commodities and fine chemicals with renewable electricity input. A predictive understanding of reaction rates in electrocatalytic systems is essential to improve their development, necessitating knowledge of surface coverage and applicable isotherm models. Historically, the physical electrochemistry community has pioneered the development of adsorption isotherm models for electrochemical systems, recognizing that models pertinent to solid–electrolyte interfaces can be more complex than those developed for the solid–gas interfaces usually found in thermal heterogeneous catalysis. Despite this, adsorption isotherms are seldom invoked in contemporary research in electrocatalytic mechanisms, where they could play a critical part in understanding trends in rates or selectivity.

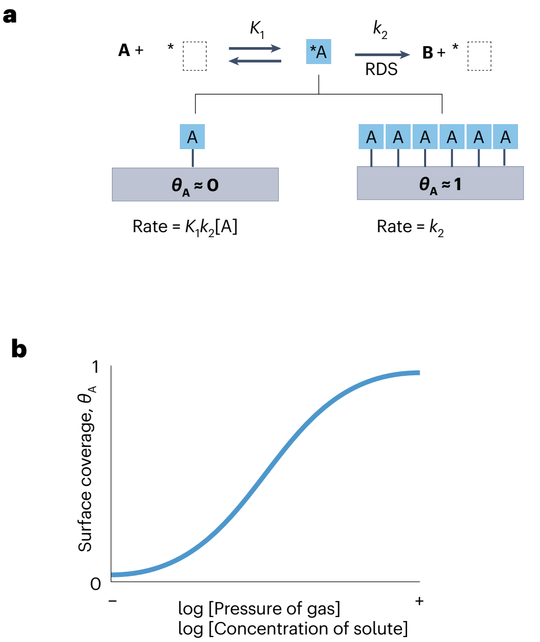

Fig. 2 | Characteristics of a surface-catalysed reaction operating within the Langmuirian limit. a, Rate dependence of a generic reaction of A to B, with formation of surface-bound intermediate *A. The second step is the rate-determining step (RDS). A single asterisk denotes an empty surface site. **b**, An idealized Langmuirian isotherm describing the surface coverage of *A.

In this Comment, we describe the importance and nuances of adsorption isotherm models in electrocatalytic systems as well as challenges to their investigation. We also suggest research opportunities to reveal the key features of isotherms using experimental and computational tools that, if pursued, should ultimately enhance our understanding of reaction rates at electrified interfaces.

Isotherm nonidealities underpin electrocatalytic function

Compared to the idealized behaviour predicted by the Langmuir adsorption model, the behaviour of real catalytic systems is substantially different (Fig. 3). For instance, commonly studied catalyst materials can exhibit active site heterogeneity, resulting in non-uniform adsorption energies (Fig. 3a). Adsorbates can also assume multiple binding modes, leading to a population of adsorbates that prefer coordination to multiple sites rather than only one (Fig. 3b). In these scenarios, the observed or measured isotherm is best viewed as the aggregate of individual isotherms describing each chemically distinct surface site. The standard adsorption energy for each site may be substantially distinct or similar, leading to well separated or overlapping sigmoids (Fig. 3c), respectively.

Within such an aggregate, it is possible that only a fraction of the surface sites in the overall isotherm is kinetically relevant to catalytic turnover. Additional non-idealities may accrue from lateral interactions between adsorbates at common or distinct binding sites (Fig. 3d). These interactions can be attractive, leading to compressed isotherms, or repulsive, leading to stretched isotherms (Fig. 3f). These complexities are further compounded in multistep reactions, where there may be many possible surface-bound intermediates, each with their own site preference and coverage (Fig. 3g). The balance of the formation and consumption rates of these intermediates can lead to apparent, non-sigmoidal isotherms that peak and decline (Fig. 3i).

We note that the relative rates of formation and consumption of intermediate species may change as a function of the driving force. Hence, adsorption processes that are assumed to be in thermodynamic quasi-equilibrium during catalytic turnover may, in some regimes, instead become kinetically controlled. Regardless, under the quasi-equilibrated limit, advanced isotherm models have been developed to account for some of these non-idealities. For example, the Frumkin and Temkin isotherm models account for the presence of co-lateral interactions and site heterogeneity by treating the free energy of adsorption to be linearly dependent on surface coverage[1]. Freundlich isotherms account for the multilayer adsorption of species to an interface and site heterogeneity using empirical constants[1].

These non-idealities apply to catalysis at both solid–gas and solid–electrolyte interfaces, but the latter requires additional consideration. Unlike in classical chemisorption processes of non-polar substrates in the gas phase, the free energy change in an electrosorption process – particularly of an ion – is strongly dependent on the electrochemical potential, E, of the surface. The electrosorption valency, which describes the fractional electron flow that compensates adsorbate binding, determines the dependence of the adsorption free energy on E. In the limit of unity electrosorption valency (for example, one electron compensates for each adsorbed proton), and the absence of all other non-idealities noted above, the potential dependence of the coverage will be Langmuirian.

However, electrosorption valencies are known to be fractional in many cases and can lead to a stretched isotherm (Fig. 3e). The electrosorption valency is dependent in part on the fraction of the electrostatic potential drop traversed by the adsorbing ion; thus, electrosorption valencies are expected to depend on the electrolyte concentration and speciation. The presence of the electrolyte itself introduces additional complexities. For example, competing adsorption of solvent and ions (Fig. 3h) – and their interaction with reaction intermediates – can contribute to isotherm non-idealities such as adsorption maxima (Fig. 3i). Some models have been developed to consider these factors, such as the Bockris, Devanathan and Muller (BDM) isotherm model, as well as various models proposed by Gileadi[1,5]. These models have been applied to account for the maximum in the adsorption of neutral species when the surface has zero net charge[4], as well as to describe competitive electrolyte adsorption, the size-dependent adsorption kinetics of solution-phase molecules, and their impact on measured Tafel slopes[5].

As this discussion highlights, electrocatalysis on electrolyte interfaces can introduce isotherm non-idealities that are not present in thermal catalysis at solid–gas interfaces. The aggregate influence of all these non-idealities is a complex relationship between system variables and observable adsorbate populations. On top of that, there is also a complex relationship between the total observed adsorbate population, and the specific identification of the most kinetically relevant adsorbates that participate in subsequent reactions. The influence of either or both factors can substantially complicate mechanistic analysis. We note also that many thermochemical reaction sequences have recently been shown to proceed via electrochemical mechanisms or are sensitive to electrochemical driving forces[6]; these adsorbate effects may therefore need to be considered more generally in thermochemical catalysis as well.

Examples of isotherm studies in electrocatalysis

Despite the complexities of nonideal isotherms, attempts to incorporate analysis of adsorption isotherms in the interpretation of

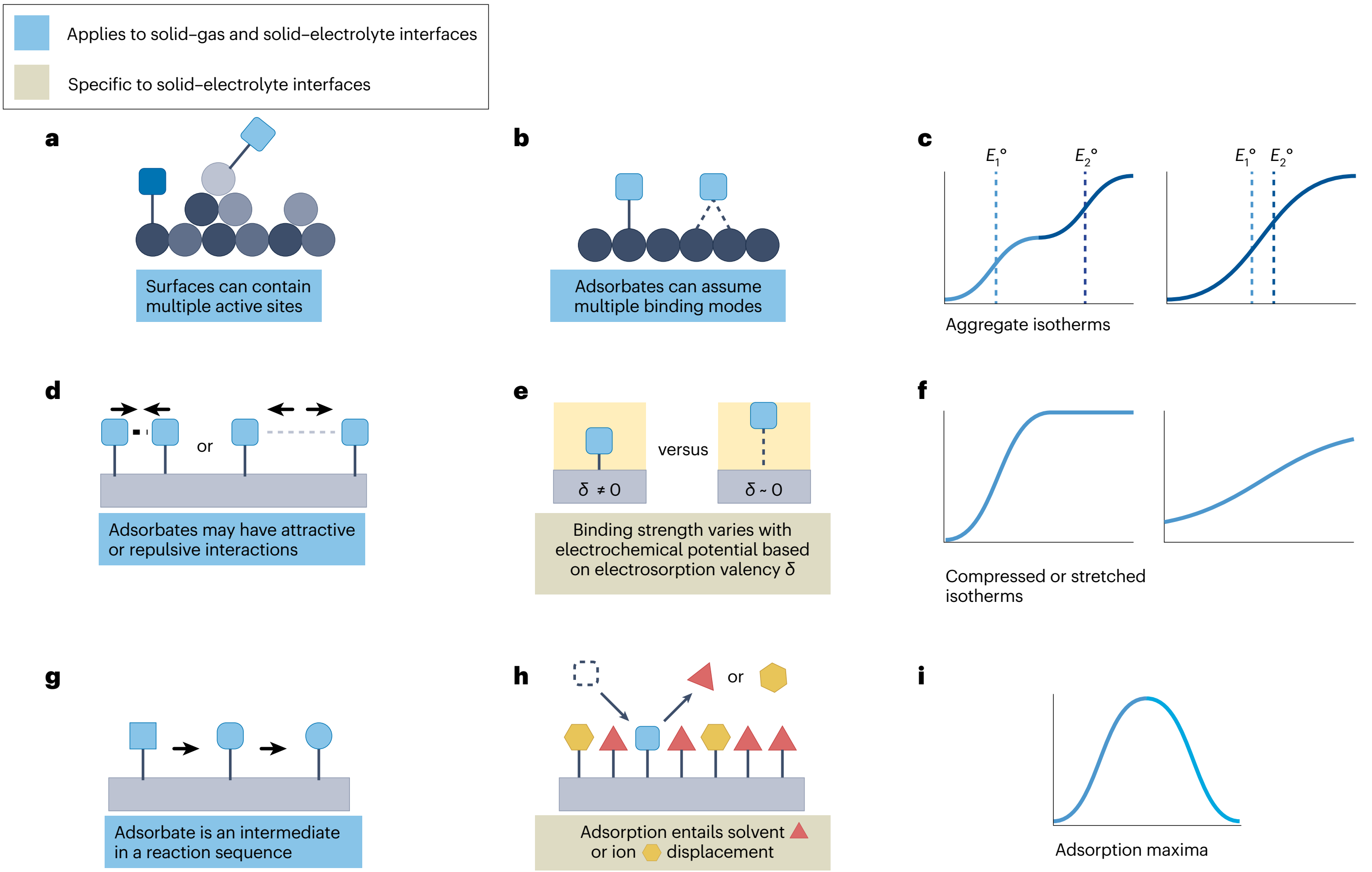

Fig. 3 | Examples of non-idealities that can result in complex isotherm profiles. **a**–**c**, Surfaces can contain multiple active sites (**a**), and adsorbates (blue squares, **b**) can assume multiple binding modes, leading to aggregate isotherms (**c**) comprised of multiple individual isotherms on a per-site/per-adsorbate basis. *E*, standard potential of the adsorbate. **d**–**f**, The free energy of adsorbates (**d**) can be affected by adsorbate–adsorbate interactions, as well as field-dependent electrosorption valencies *δ* (**e**), leading to compressed or stretched isotherm profiles (**f**). **g**–**i**, When adsorbates are formed and consumed as intermediates (**g**) or when reactive adsorbates compete for sites with adsorbed solvent molecules (pink triangles) or ions (yellow hexagons) (**h**), non-sigmoidal adsorption profiles (**i**), such as adsorption maxima, can be observed. Non-idealities highlighted in blue apply to heterogeneous catalysis at both solid–gas and solid–electrolyte interfaces; those highlighted in yellow are specific to solid–electrolyte interfaces.

experimental data are worthwhile, in the hope of uncovering electrocatalytic reaction mechanisms. For example, a recent study investigated the hydrogen evolution reaction on Pt and Au surfaces over a wide pH range[3]. Microkinetic models were fitted to experimentally measured kinetic data to understand the (pH-dependent) reaction mechanism for the hydrogen evolution reaction. The authors concluded that mechanisms accounting for intermediate *H coverage as predicted by Frumkin-type isotherms are needed to rationalize the observed pH dependence, fractional reaction orders and Tafel slopes. These results highlight the shortcomings of assuming a limiting coverage in catalysis, as described by Langmuir isotherm models, and imply that operation at intermediate *H coverage may be characteristic of highly active catalysts for the hydrogen evolution reaction, such as Pt.

Similar conclusions can be drawn from recent studies on the oxygen evolution reaction. Recent work employed optical spectroscopy to characterize electrochemical adsorption isotherms during the oxygen evolution reaction on Co-based electrocatalysts[7]. The authors found *O isotherms to be well described by Frumkin-type models, and the adsorbate–adsorbate interactions to be dependent on the electrode material. A different study also reported the adsorbate–adsorbate interactions of *O isotherms for RuO_2 to depend on the electrolyte pH[8]. Consequently, the Tafel-slope values are dependent on these non-idealities, and ignoring their influence can lead to incorrect conclusions about the identity of the rate-limiting step.

In a subsequent study, a similar optical spectroscopy technique was used to estimate *O isotherms on amorphous and rutile Ir oxide surfaces[9]. The intrinsic activity for the oxygen evolution reaction as measured by the per-site turnover frequency was found to increase with *O coverage, highlighting the mutual influence of lateral interactions and intrinsic binding energies on electrocatalytic activity. These observations also imply that volcano-activity plots should consider the potentially large range of coverage-dependent adsorption energies (as opposed to singular adsorption energies at a fixed coverage) to be the relevant activity descriptors of electrocatalysts[10].

For the electrochemical CO_2 reduction reaction, several studies have highlighted the importance of understanding *CO isotherms in order to determine the activity towards multi-carbon products on Cu. Recent studies using chemical transient kinetics and microkinetic modelling highlighted the presence of multiple site types on Cu surfaces, such as reservoir and defect sites with varying *CO binding strengths and reactivities[11]. These observations emphasize the fact that aggregate ensemble *CO isotherms of these active sites may not, in many cases, reflect the portion of the isotherm that is kinetically relevant to catalysis.

Another study used operando Raman spectroscopy to track the dynamics of *CO coverage on Cu, leading to the hypothesis that the ratio of the atop- versus bridge-bonded *CO is dependent on surface coverage, which in turn affects the activation energy for the key CO–CO coupling step[12]. Contrary to the intuition that *CO coverage on Cu is relatively high under the conditions of the CO_2 reduction reaction, low *CO coverage (~0.05 monolayer) has been reported, using surface enhanced infrared adsorption spectroscopy (SEIRAS) measurements[13]. The authors attribute the low *CO coverage under electrochemical environments to the competitive adsorption of electrolyte species (such as water). Taken together, these examples demonstrate the value of understanding and probing electrochemical isotherms to aid mechanistic interpretations and rate predictions of electrocatalytic processes.

Deepening our understanding of electrochemical isotherms

The examples discussed above highlight the value of characterizing electrochemical isotherms, but there remain numerous outstanding challenges that must be overcome before their treatment becomes mature (Fig. 4). This requires advances in experimental characterization techniques and computational modelling approaches, in order to better understand what isotherms are at play and how.

When it comes to the experimental characterization of adsorbates, not all species are equally observable. For instance, species are easiest to electrochemically detect and quantify when their adsorption involves substantial charge transfer (that is, their adsorption carries a non-zero electrosorption valency) and when they can be adsorbed in the absence of follow-up reactions. When these criteria are met, isotherms can often be resolved and quantified using electrochemical techniques (Fig. 4a, d). Indeed, numerous studies have used voltammetric analysis to quantify the isotherms for hydrogen adsorbed at potentials positive of the H^+/H_2 equilibrium potential (that is, the underpotential deposited hydrogen, H-upd) and halide adsorption, both of which involve substantial charge transfer and are single-step adsorption processes[14]. Because these studies provide direct access to electrochemical isotherms, they can be used to derive parameters to develop advanced isotherm models and help to validate first-principles-based predictions of the parameters.

On the other hand, electrochemically characterizing and quantifying adsorbates with low electrosorption valency is more challenging. For example, CO adsorption often carries a very low electrosorption valency, eliciting negligible electrochemical current flow. Likewise, it is challenging to electrochemically characterize isotherms for highly reactive intermediates that are consumed in follow-up reactions. For example, hydrogen adsorbed negative of the H^+/H_2 equilibrium potential (that is, the overpotential deposited hydrogen, H-opd) is difficult to detect electrochemically owing to the convoluting current flow towards H_2 evolution catalysis.

In both situations, spectroscopic techniques may be of value. For example, CO isotherms have been probed by SEIRAS during CO reduction catalysis and H-opd has been putatively identified using SEIRAS and surface-enhanced Raman spectroscopy (SERS) with binding site assignments (atop, bridge, hollow and so on) based on stretch frequencies and comparison to density functional theory calculations[12,14].

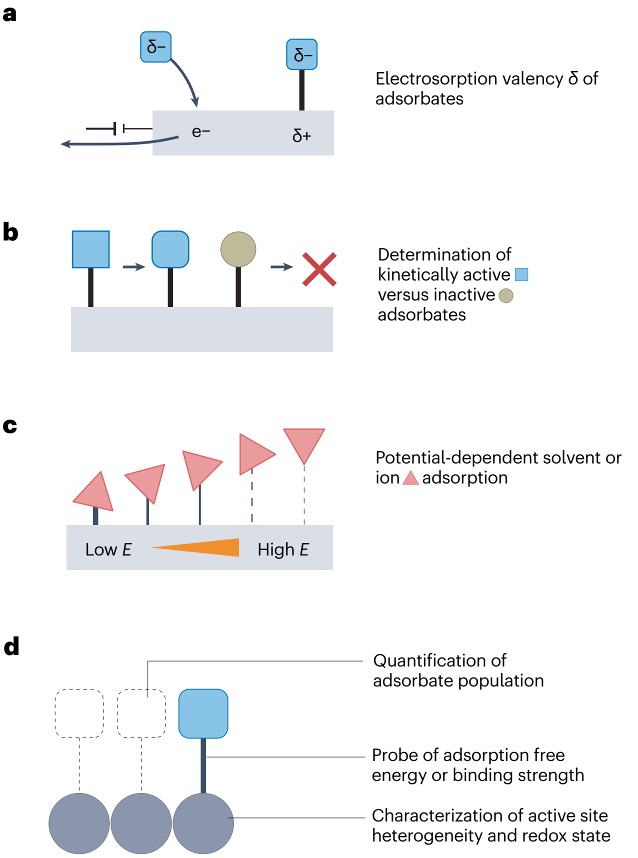

Fig. 4 | Knowledge gaps towards developing electrochemical adsorption isotherm models. a–**c**, Characteristics of adsorbates which, once determined, could contribute to a better understanding of adsorption isotherms on electrochemical interfaces: **a**, the electrosorption valency *δ* of adsorbates; **b**, discrimination between kinetically active adsorbates (blue squares) versus kinetically inactive species (beige circle); and **c**, the potential dependence of solvent and ion (pink triangle) adsorption. **d**, Structural descriptors of adsorption that would be useful to characterize, including adsorbate populations, characterization of active sites and their heterogeneity, and the adsorption free energies or binding strength of reactive species.

These spectroscopic methods are highly sensitive and can detect a wide range of adsorbates in the sub-monolayer coverage regime. However, quantifying adsorbate coverage from spectroscopic data is rarely straightforward because the extinction coefficients for surface species can depend strongly on many complicating factors including dynamic dipole coupling, co-adsorbate effects and surface reconstruction. Another way to quantify surface coverage is to track the redox state of the surface sites and their transitions using spectro-electrochemistry (Fig. 4d), which is how recent studies were able to obtain hydrogen and oxygen adsorption isotherms on NiO and CoOOH respectively[7,14], although this approach has yet to be demonstrated using other materials.

Techniques that probe the steady-state surface population, whether electrochemical or spectroscopic, often cannot clearly distinguish between kinetically active and inactive species (Fig. 4b), with the former being inherently difficult to characterize owing to their short lifetimes. There exists therefore a rich opportunity to utilize time-resolved techniques to distinguish the lifetimes and kinetic relevance of adsorbates. For example, in electrochemical mass spectrometry (ECMS), an electrode is positioned close to a mass spectrometer inlet to enable detection of volatile, adsorbate-derived reaction products with millisecond time resolution[4].

Such capabilities can then be coupled to transient kinetic measurements. One example is steady-state isotopic transient kinetic analysis (SSITKA), in which the isotope of an input reactant gas is swapped during catalysis, and the resulting product stream is tracked by mass-sensitive analytical methods[15]. The time-dependent change in product masses yields information on adsorbate populations and lifetimes. Additionally, isotopic scrambling can be used to diagnose the reversibility of adsorption steps during turnover. Thus, SSITKA studies provide insight into the kinetics of forming adsorbed species and their relevance within a catalytic cycle.

In addition, alternating-current techniques can be utilized to study the adsorption and desorption of intermediates by perturbing them away from steady-state conditions. One example is Fourier-transformed alternating current voltammetry, which superimposes a fast alternating-current perturbation onto a slow potential sweep to resolve the kinetic relevance of active sites and surface-confined (adsorbed) species[16]. We note that temperature-based techniques could be used to study adsorption isotherms, but advances are required to systematically deconvolute the simultaneous impact of temperature on activation barriers, transfer coefficients and other kinetic parameters. We also stress that the experimental techniques mentioned here are by no means exhaustive and invite the community to creatively apply and develop other methods to probe the population and distribution of kinetically relevant adsorbates during catalysis.

From a computational modelling standpoint, there exists a rich opportunity in developing advanced isotherm models that can account for the complexities present in surface electrocatalysis (Fig. 3). Atomistic simulations based on density functional theory and molecular dynamics can be used to estimate binding energies, to account for lateral interactions between the adsorbates and the electrolyte species, and to estimate the reaction energetics of the elementary steps in the mechanism as a function of the applied potential and electrolyte pH (Fig. 4c, d). Mean-field microkinetic or kinetic Monte Carlo models based on reaction energetics derived from density functional theory can then be used to predict the adsorption isotherms and surface coverage of the various reaction intermediates and the overall rate of electrocatalytic reactions[17,18].

Although using first-principles-based approaches to derive isotherm models is highly desirable, there exist several challenges in routinely incorporating de novo approaches owing to the inherent errors in density functional theory calculations, in the computational expense of accounting for multiple site types, in sampling the various (coverage-dependent) adsorbate configurations, in the complexity of modelling the electrolyte environment, and in existing debates on the various approaches to estimating reaction energetics. Although there are few examples of such detailed simulations on electrocatalytic systems, they have provided valuable insights into the identity of active sites, adsorption isotherms and reaction mechanisms[17,18].

Going forwards, experimental characterization of isotherms is essential to inform the computational development of isotherm models that are consistent with measured reaction kinetics. Even for relatively simple reactions such as the two-electron hydrogen evolution reaction, which can be reasonably well described with Frumkin isotherms[3], there could be multiple binding modes, active sites and intermolecular interactions that contribute to the observed shape of the isotherm[14]. To begin, we recommend benchmarking studies that compare isotherms obtained from computational methods with easy-to-measure isotherms derived from experiments. This will serve as a good starting point, before gaining confidence in modelling isotherms involving more complex reaction networks and under operando conditions.

Given that only a portion of the ensemble isotherm may be catalytically active, it is important to assess mismatches between independently measured adsorption profiles and measured catalytic rates. We expect that a suite of kinetic data (reaction orders, Tafel behaviour, degree of rate control and reversibility analysis, and so on) will be needed to understand when and how kinetic incongruence is relevant for a given reaction and material system. Studies that inventory the diversity of active sites of a given electrocatalytic material should be useful for studying potential modes of adsorption. However, accurate modelling of such systems should be complemented by studies of surface diffusion or dynamic restructuring: both effects can blur accurate assignments of per-site contributions to overall reaction kinetics. Eventually, a combination of various experimental and computational approaches will be needed to fully resolve electrochemical isotherms and advance mechanistic understanding, thereby leading us closer to predictive models of reaction rates in electrocatalysis.

Concluding remarks

The development of adsorption isotherm models has been instrumental in the understanding of heterogeneous catalysis at gas–solid interfaces, but a similar level of understanding and application in surface electrocatalysis is far from mature. In this Comment, we have summarized existing knowledge gaps in the development of electrochemical isotherms and suggest some (but by no means a comprehensive list of) approaches to characterize and model them. By raising awareness of the potential impact of isotherms on mechanistic studies and electrocatalyst design, we anticipate that the translation of their understanding into utilitarian models will advance electrochemical technologies for energy and chemical conversion.

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Acknowledgements

This work was performed under the auspices of the United States Department of Energy by Lawrence Livermore National Laboratory (LLNL) under contract DE-AC52-07NA27344. N.G. acknowledges support from a startup grant at NTU (award number 024462-00001). C.H. acknowledges support as part of the Center for Closing the Carbon Cycle, an Energy Frontier Research Center funded by the United States Department of Energy, Office of Science, Basic Energy Sciences under award number DE-SC0023427. Y.S. acknowledges the United States Department of Energy, Basic Energy Sciences award number DE-SC0020973. The authors thank J. Cataldo from Lawrence Livermore National Laboratory's Program Development Support Office for assistance with graphic design. The authors also thank N. Razdan for his comments on the manuscript. Manuscript released as LLNL-JRNL-2003233.

Author contributions

N.G. and A.T.C. contributed equally to this work. N.G., A.T.C. and Y.S. conceived the idea and wrote the manuscript with input from C.H.

Competing interests

The authors declare no competing interests.

Additional information

Peer review information *Nature Catalysis* thanks Jason Bates and the other, anonymous, reviewer(s) for their contribution to the peer review of this work.