How to Decipher Electrocatalytic Reactions with

Theory and Computation

Xinwei Zhu,^{a,b} Jun Huang,^{a,c,*} Michael Eikerling,^{a,b,*}

^a Theory and Computation of Energy Materials (IEK-13), Institute of Energy and Climate Research, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

^b Chair of Theory and Computation of Energy Materials, Faculty of Georesources and Materials Engineering, RWTH Aachen University, 52062 Aachen, Germany

^c Theory of Electrocatalytic Interfaces, Faculty of Georesources and Materials Engineering, RWTH Aachen University, 52062 Aachen, Germany

* Corresponding authors, email:

Jun Huang: ju.huang@fz-juelich.de

Michael Eikerling: m.eikerling@fz-juelich.de

ORCID:

Xinwei Zhu: 0000-0002-4636-8893

Jun Huang: 0000-0002-1668-5361

Michael Eikerling: 0000-0002-0764-8948

CONSPECTUS

Electrocatalytic reactions, such as oxygen reduction/evolution reaction and CO₂ reduction reaction that are pivotal for the energy transition, are multi-step processes occurring in a nanoscale electric double layer (EDL) at solid-liquid interfaces. Conventional analyses based on the Sabatier principle, using binding energies or effective electronic structure properties of the d-band center as descriptors, are able to grasp overall trends in catalytic activity in groups of catalysts. However, thermodynamic approaches fail to account for a plethora of electrolyte effects that arise in the EDL, including pH effects, cation effects, and anion effects. These effects have been observed to strongly influence electrocatalytic reactions. There is a growing consensus that the local reaction environment (LRE) prevailing in the EDL is the key to deciphering these complex and hitherto perplexing electrolyte effects. Equal attention is thus paid to designing appropriate electrolytes, positioning the LRE at center stage. Achieving this is essential for designing electrocatalysts with specifically tailored properties, which could enable much needed breakthroughs in electrochemical energy science.

Theory and modeling are becoming increasingly important and powerful in addressing this multifaceted problem that involves physical phenomena at different scales interacting in a multidimensional parametric space. Theoretical models developed for this purpose should treat intrinsic multistep kinetics of electrocatalytic reactions, EDL effects from sub-nm scale to the scale of 10 nm, and mass transport phenomena bridging scales from < 0.1 to 100 μ m. Given the diverse physical phenomena and scales involved, it is evident that the challenge at hand surpasses the capabilities of any single theoretical or computational approach.

In this Account, we present a hierarchical theoretical framework to address the above challenge. It seamlessly integrates several modules: (i) a comprehensive microkinetic model accounting for various reaction pathways; (ii) an LRE model that describes the interfacial region extending from the nanometric EDL continuously to the solution bulk; (iii) first-principles calculations that provide parameters, *e.g.*, adsorption energies, activation barriers and EDL parameters. The microkinetic model considers all elementary steps without designating an a *priori* ratedetermining step. The kinetics of these elementary steps are expressed in terms of local concentrations, potential and electric field that are co-determined by EDL charging and mass transport in the LRE model. New insights on electrode kinetic phenomena, *i.e.*, potentialdependent Tafel slopes, cation effects, and pH effects, obtained from this hierarchical framework is presented, in view of recent developments in first-principles based simulation of electrocatalysis, observations of dynamic reconstruction of catalysts, and machine-learning assisted computational simulations.

KEY REFERENCES

- Huang, J.; Zhu, X.; Eikerling, M. The Rate-Determining Term of Electrocatalytic Reactions with First-Order Kinetics. *Electrochim. Acta* **2021**, *393*, 139019.¹ *Analytical expressions of the activity of multi-step reactions with first-order kinetics, including oxygen evolution reaction and electrochemical carbon dioxide reduction as examples, were derived under steady-state conditions. Expression for inverse net rates allows rate-determining term (RDT) to be identified, a concept that is insightful in analyzing potential-dependent Tafel slopes and volcano plots.*
- Huang, J.; Li, M.; Eslamibidgoli, M. J.; Eikerling, M.; Groß, A. Cation Overcrowding Effect on the Oxygen Evolution Reaction. *JACS Au* **2021**, *1*, 1752–1765.² *Application of the hierarchical framework to the oxygen evolution reaction with a focus on cation effects. The observed decrease in activity with increasing effective size of electrolyte cations was interpreted as a consequence of cation overcrowding near the negatively charged electrode surface.*
- Zhu, X.; Huang, J.; Eikerling, M. Electrochemical CO₂ Reduction at Silver from a Local Perspective. ACS Catal. 2021, 11, 14521–14532.³ Application of the hierarchical framework to understand kinetic phenomena observed in electrochemical CO₂ reduction at silver, such as potential-dependent Tafel slopes, cation effects, and bicarbonate effects, from the perspective of the local reaction environment.
- Zhu, X.; Huang, J.; Eikerling, M. pH Effects in a Model Electrocatalytic Reaction Disentangled. JACS Au **2023**, *3*, 1052–1064.⁴ Systematic comparison of the hierarchical framework and its simplified variants allows us to disentangle various interwoven factors influencing pH effects in formic acid oxidation. Long-debated activity-pH relations, specifically the bell-shaped

activity-pH relation in phosphate solution and the trapezoidal-shaped activity-pH relation in perchlorate solution, are explained.

INTRODUCTION

Electrocatalysis stands as the cornerstone discipline to deliver breakthroughs in electrochemical energy conversion technologies, including fuel cells, carbon dioxide reduction, nitrate reduction and water splitting electrolysers.^{5,6} Nevertheless, crucial electrocatalytic reactions grapple with sluggish kinetics and inadequate selectivity.^{5,7} A fundamental understanding of reaction mechanisms and factors that limit activity and selectivity towards targeted products is imperative in order to prompt progress in electrocatalyst design and development.^{5,8} However, these endeavors are complicated and hindered by the intricate multistep mechanisms and concurrent interrelated factors on multiple scales. Figure 1 depicts four essential components of a comprehensive understanding of electrocatalytic reactions:

- Multi-step thermodynamics. The thermodynamics of an elementary step are determined by binding energies of adsorbed intermediates involved in this step. Past approaches have correlated the overall activity and selectivity of a specific reaction with the binding energies of key intermediates, which are readily calculated using first-principles based methods.^{9–13} This line of research leads to the development of efficient tools for screening catalysts, including the d-band model,^{9,10} the generalized coordinate number.^{12,13}
- Multi-step kinetics. Beyond thermodynamics, kinetic parameters, including but not limited to activation barriers, transfer coefficients and preexponential factors, are important for a quantitative understanding of electrocatalysis.^{14,15} In a few recent reports, these kinetic factors can even change the qualitative trend of activity and selectivity.^{16–19} For instance, in a microkinetic analysis accounting for various relevant activation barriers

and transfer coefficients for elementary steps, the peak of the volcano plot on the binding energy axis changes with electrode potential.^{16–18} In the quest to simplify the microkinetic analysis, it has become a customary practice to identify a single step that governs the overall rate of the reaction, termed the rate-determining step (RDS).^{20–22} The transition of the RDS from one step to another is often regarded as the cause of potential-dependent Tafel slopes.^{20,21}

- Electric double layer effects. Electrocatalytic reactions take place in the electric double layer (EDL) at the catalyst-electrolyte interface.^{23–27} There exist many EDL effects, including the famous Frumkin corrections (*i.e.*, the effects on potential and reactant concentration at the most probable reaction plane)²³, field-dependent adsorption energies of intermediates,^{26,27} and dependency of the solvent reorganization energy on the surface charge density.^{28,29} In addition to these equilibrium EDL effects, nonequilibrium EDL effects, firstly proposed by Levich *et al.* in the 1950s,³⁰ are surfacing again in recent studies.^{31,32}
- Mass transport. The consumption (production) of reactants (products) significantly influences local reactant/product concentrations and pH in the near-surface region.^{4,33}
 Recent progress has enabled direct probes of changes in the ion concentration and pH with a spatial resolution down to a few hundreds of nanometers.^{34–37}



Figure 1. Four crucial components, *i.e.*, thermodynamics of elementary steps, multi-step kinetics, mass transport, and electric double layer, constitute a proper understanding of the activity and selectivity of electrocatalytic reactions. Existing theoretical methodologies for electrocatalytic reactions are categorized into four levels based on the components treated. Models on level 1 (L1) consider only thermodynamics, while those on level 2 (L2) incorporate both thermodynamics and kinetics of multiple steps into a microkinetic model. Level 3 (L3) improves over L1 and L2 further by integrating the macroscopic mass transport in the electrolyte solution into the microkinetic model. Finally, level 4 (L4) completes the circle by adding electric double layer effects.

We categorize existing theoretical methodologies for modeling electrocatalytic reactions into four levels, as summarized in Figure 1. Level 1 (L1) considers only thermodynamics. Specifically,

L1 models focus on the potential energy profiles of electrocatalytic reactions with the binding energies of intermediates that can be readily calculated from density functional theory (DFT)based first-principles simulations.^{5,11} Despite the simplicity, L1 models can explain, surprisingly well, overall trends of activity and selectivity within groups of catalysts with simulating electronic structures. The success of these models is evidenced by effective and easy-to-implement tools for screening catalyst materials, encompassing the d-band model,^{9,10} the generalized coordinate number,^{12,13} and the volcano plots.^{38,39} In view of the simplicity of L1 models, it is unsurprising that counterexamples have been reported in the literature.^{19,40} For instance, the volcano plot predicts a sequence Pt(111) > Pt(100) > Pt(110) > Pt(211) for the oxygen reduction reaction (ORR), yet experiments show Pt(211) > Pt(110) > Pt(111) > Pt(100).¹⁹ Additionally, concerns have been raised that the thermodynamics-centered method may yield inaccurate results near the volcano apex, due to the neglect of kinetic factors.^{17,18}

As an obvious step, kinetic factors are incorporated into L1 models on level 2 (L2). L2 models treat kinetics on two sublevels. The first sublevel relies on the RDS concept, and only the kinetics of the RDS is considered.^{20,21} Practically, the RDS is often identified based on Tafel slope analysis that is, however, problematic. The values of the Tafel slope vary to a great extent among different measurements, leading to disparate reaction mechanisms reported in different studies.^{20,21,41–44} Furthermore, the Tafel slope exhibits a high sensitivity to adsorbate coverages.^{1,21,45} Therefore, the RDS typically changes with electrode potential. These inconsistencies necessitate a full microkinetic model that treats the thermodynamics and kinetics of all elementary steps without singling out an RDS, constituting the second sublevel on the L2. These models have been utilized to rationalize potential-dependent Tafel slopes and volcano plots for various reactions.^{1,17,46}

Recent years have witnessed growing awareness of the significance of electrolyte composition. Various electrolyte effects, including cation,^{47–50} anion,^{25,51} and pH effects,^{51–54} have been observed for many reactions. Notably, most models on L1 and L2 fall short in interpreting electrolyte effects, as they often ignored the role of the electrolyte. Consensus is growing that these electrolyte effects originate from the change of the local reaction environment (LRE) at the catalyst-electrolyte interface, which is shaped by the interplay of macroscopic mass transport and microscopic EDL charging. Therefore, resolving the LRE and its influence on the multi-step kinetics has transpired as the focal point for further improvement, as emphasized in a recent Account,

"The interplay of intrinsic microkinetics, homogeneous reactions, and mass transport limitations in determining the overall activity needs to be investigated in coupled transport–kinetic models."²⁵

Following the classical works on modeling catalyst layer in fuel cells,^{33,55–57} refined models on level 3 (L3) incorporating mass transport into L2 models have recently been applied to the CO₂ reduction reaction (CO₂RR),⁵⁸ hydrogen evolution/oxidation reaction (HER/HOR),⁵⁹ and oxygen evolution reaction (OER).⁶⁰ L3 models are able to calculate the local pH and reactant concentration in the diffusion layer (0.1-100 μ m), on which scale models meet experimental measurements.^{34–37} For instance, Monteiro *et al.* measured the local pH during CO₂RR at a distance of 80 μ m from catalyst surface, which is consistent with numerical simulations.³⁵

While L3 models often claim they can calculate a local concentration, it should be emphasized that the term "local" is defined from a macroscopic perspective. This is still a long way from the microscopic reacting zone that is located in the EDL. The EDL is not resolved in L3 models, while

recent experimental evidences point to the central role of the EDL in understanding electrolyte effects.^{61–64} Incorporating EDL effects into L3 models to accomplish a unified treatment of all components on the level 4 (L4) has been attempted in recent works.^{2–4,26,32,65,66} In this Account, we introduce our approach to this L4 integration challenge. In the next section, we outline the framework of our approach, highlighting important know-hows of handling the coupling between different module components. Afterwards, the framework is employed to understand the potential-dependent Tafel slopes, cation effects, and pH effects that are hot topics of current discussion. Applications will cover the range from ORR, CO₂RR, OER, formic acid oxidation reaction (FAOR), to hydrogen peroxide reduction reaction (HPRR). In the end, we share our perspective on how to further improve integration of theory and computation in L4 models.

SETTING THE FRAMEWORK

The framework comprises two essential submodels, as illustrated in Figure 2. The first one is a microkinetic model that integrates the thermodynamics and kinetics of all elementary steps. The second one processes the LRE, encompassing microscopic EDL effects and mass transport in solution. The two submodels are coupled via boundary conditions at the most probable reaction plane (RP) that is located in close proximity to the surface of the electrocatalyst.⁶⁷



Figure 2. Hierarchical framework for modeling electrocatalytic reactions. The framework consists of two interrelated submodels, including a microkinetic model that accounts for the thermodynamics and kinetics of all elementary steps, and a submodel for the LRE that accounts for microscopic EDL effects and mass transport effects. These two submodels are connected through boundary conditions and are solved in a self-consistent manner, *e.g.*, using COMSOL Multiphysics[®]. The model inputs include the experimental conditions, the reaction mechanism derived from first-principles based calculations, spectroscopic experiments and analytical tools, the energy parameters for reaction paths, *e.g.*, adsorption energies and activation barriers, obtained from DFT calculations, and the EDL parameters extracted from AIMD simulations. The model outputs include activity, selectivity, adsorbate coverages, and local reaction conditions, including surface charging relation, reactant distribution, pH distribution, potential distribution, and electric field.

The microkinetic model requires *a priori* knowledge of the reaction mechanism that is usually inferred by combining key intermediates identified from spectroscopic experiments and first-principles based calculations. A specific reaction mechanism is expressed as a series of elementary steps,

$$R + * + n_1 e \leftrightarrow I_1,$$

$$I_1 + n_2 e \leftrightarrow I_2,$$

$$...$$

$$I_{i-1} + n_i e \leftrightarrow I_i,$$

$$...$$

$$I_{N-1} + n_N e \leftrightarrow P + *,$$
(1)

where *R* and *P* denote the reactant and product, * denotes free sites on the catalyst surface for adsorption, I_i is adsorbed intermediate with coverage θ_i , n_i is number of electrons transferred in *i*th step with n_i being 0 for chemical steps and ± 1 for electron transfer steps.

The net rates of elementary steps are given by,

$$r_i = k_{+i}\theta_{i-1} - k_{-i}\theta_i, i = 1, 2 \dots, N,$$
(2)

where $\theta_0 = \theta_N$ denotes the coverage of free sites. Rate constants, k_{+i} and k_{-i} , are calculated based on transition state theory,

$$k_{\pm i} = \frac{k_{\rm B}T}{h} c_{\pm i} \exp\left(-\frac{G_{a,\pm i}}{k_{\rm B}T}\right). \tag{3}$$

Here $c_{\pm i}$ represents an assembled concentration factor for all other species involved in the forward and backward reactions other than the vacancies, adsorbates, and electrons.

The activation barriers, $G_{a,\pm i}$, can be written using the Brønsted–Evans–Polanyi (BEP) relation,^{46,68}

$$G_{a,+i} = G_{a,i}^0 + \beta_i \Delta G_i,$$

$$G_{a,-i} = G_{a,i}^0 - (1 - \beta_i) \Delta G_i,$$
(4)

where $G_{a,i}^{0}$ is the activation energy of step *i* under standard conditions (298 K, 1 bar pressure, pH = 0) for chemical steps, and at equilibrium potential under the standard state for electrochemical steps, β_i the symmetry factor, and ΔG_i the reaction Gibbs free energy. For the electrochemical steps, ΔG_i shifts with potential in the following way,

$$\Delta G_i = -n_i e \left(E_{\rm M} - \phi_{\rm RP} - E_i^{\rm eq} \right) + \Delta \Delta G_i, \tag{5}$$

with $E_{\rm M}$ being the applied potential relative to the standard hydrogen electrode (SHE), and $\phi_{\rm RP}$ the potential at the most probable reaction plane. $E_i^{\rm eq}$ is the equilibrium potential of step *i* and is calculated using the Nernst equation,

$$E_i^{\rm eq} = -\Delta G_i^0 / n_i e, \tag{6}$$

with ΔG_i^0 being the reaction free energy of step *i* under the standard conditions, which can be determined by first-principles based calculations. Additionally, recent studies have underscored the significance of lateral interactions,⁶⁹ electric field,⁷⁰ or electrode surface charge in influencing the Gibbs free energies of adsorbates.²⁷ These effects can be incorporated into this framework

by introducing the term $\Delta\Delta G_i$, which may be a function of coverages, surface charge density or electric field.

Under steady-state conditions, we have

$$\frac{d\theta_i}{dt} = r_i - r_{i+1} = 0, i = 1, 2 \dots, N - 1.$$
(7)

Combined with the conservation of adsorption sites, *i.e.*, $\sum_{i=1}^{N} \theta_i = 1$, eq (7) can be solved to obtain θ_i and r_i . It is worth noting that an analytical solution can be derived for reactions with first-order kinetics. Further manipulation of the analytical solution leads to the concept of rate-determining-term (RDT).¹ The steady-state current density is written as

$$j = e\rho \sum_{i=1}^{N} n_i r_i, \tag{8}$$

with ρ being the number density of active sites at the electrode surface.

Several variables of the microkinetic model, including $c_{\pm i}$, $\phi_{\rm RP}$, surface charge density and electric field, need to be determined with the LRE model. The modified Nernst-Planck equation, which takes into account steric effects, can be employed to model the mass transport of species,⁷¹

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot J_i + R_i,$$

$$J_i = -D_i \left(\left(1 - \sum_{j \neq i} N_A a_j^3 c_j \right) \frac{\partial c_i}{\partial x} + c_i \sum_{j \neq i} N_A a_j^3 \frac{\partial c_j}{\partial x} + \frac{z_i F}{RT} c_i \left(1 - \sum_j N_A a_j^3 c_j \right) \frac{\partial \phi}{\partial x} \right),$$
(9)

where R_i is the source term due to homogeneous reactions (*e.g.*, conversion between CO₂ and HCO₃⁻ in CO₂RR), J_i the flux of species *i*, D_i the diffusion coefficient, a_j the effective diameter, z_i the charge number, and ϕ the electric potential. The Nernst-Planck equation is complemented by the Poisson equation,

$$-\nabla \cdot (\varepsilon_s \nabla \phi) = F \sum_i z_i c_i, \tag{10}$$

with ε_s being the permittivity of electrolyte.

As shown in Figure 2, the solving domain of the model spans between the reaction plane and the solution bulk, with the diffusion layer thickness determined according to experimental conditions.^{72,73} To solve the Poisson-Nernst-Planck (PNP) equations, appropriate boundary conditions are needed. The right boundary is situated in the solution bulk, where concentrations match the bulk concentrations, and the electric potential is taken as the reference potential, namely, $\phi = 0$. The left boundary is located at the RP, and the fluxes at this side correlate with the current densities obtained from the microkinetic model,

$$J_i = \frac{j}{F} \frac{v_i}{n_{\text{total}}},\tag{11}$$

where v_i is the respective stoichiometric number of species i, with v_i being negative for reactants and positive for products, and n_{total} is the total number of electrons involved in the reaction.

The EDL structure is incorporated into the boundary condition for the electric potential,

$$\sigma_{\rm M} = -\varepsilon_s \frac{\partial \phi}{\partial x}\Big|_{x=0} = \frac{\varepsilon_{\rm ad}}{\delta_{\rm ad}} \Big(E_{\rm M} - E_{\rm pzc} - \frac{\mu_{\rm chem}}{\varepsilon_{\rm ad}} - \phi|_{x=0} \Big), \tag{12}$$

with $\sigma_{\rm M}$ being the free surface charge density, $E_{\rm pzc}$ the potential of zero charge (pzc), $\varepsilon_{\rm ad}$ the permittivity of the adlayer, and $\delta_{\rm ad}$ the thickness of the adlayer. It has been pointed out by Johnson *et al.* that the surface charge boundary conditions are often misused in L4 models, leading to incorrect conclusions regarding EDL effects.⁷⁴ The inconsistencies arise from the adoption of inaccurate permittivity for the adlayer or the artificial imposition of an electric

potential at the RP. In our works, we estimate the key parameters, *i.e.*, ε_{ad} and δ_{ad} , based on ab initio molecular dynamics (AIMD) simulations. In addition, to the best of our knowledge, our approach is unique in that it considers the surface dipole moment induced by partially charged chemisorbates, μ_{chem} . It has been shown that μ_{chem} markedly modifies the surface charging relation and the LRE.^{75,76} Furthermore, it is worth noting that a more detailed EDL structure that accounts for the water layer can also be integrated into eq 12.⁷⁵

The overall model parameters can be categorized into three groups. The first group of parameters describe reaction properties, including the adsorption energies, activation barriers, transfer coefficients and lateral interaction coefficients between adsorbates. These parameters are derived primarily from DFT calculations. The second group characterizes the EDL structure, encompassing the permittivity and thickness of adlayer, effective diameters of solvated ions, and dipole moments of adsorbates. These parameters can be obtained with the aid of DFT and AIMD. The third group defines the mass transport characteristics, incorporating diffusion coefficients, bulk concentrations, diffusion layer thickness. These parameters relate to experimental conditions. For instance, the diffusion layer thickness depends on the rotation speed for the rotating disk electrode (RDE) systems.

With the provided inputs, the overall model can be solved self-consistently, *e.g.*, using COMSOL Multiphysics[®]. The comprehensive array of model outputs includes partial current densities, selectivity, adsorbate coverages, surface charging relation, potential distribution, concentration and pH profiles, and more.

INSIGHTS INTO ELECTRODE KINETICS

The hierarchical framework has been applied to several electrocatalytic reactions, *e.g.*, ORR, CO₂RR, OER, FAOR and HPRR in recent years. In the following sections, we illustrate how our approach helps understand various kinetic phenomena, including potential-dependent Tafel slopes, cation effects and pH effects.

POTENTIAL-DEPENDENT TAFEL SLOPES

Potential-dependent Tafel slopes are prevalent across many reactions,^{21,41} constituting a topic of unattenuated discussions in electrocatalysis. The conventional view relates the potential-dependent Tafel slopes to transitions of the RDS. For a sequence of consecutive elementary steps, the Tafel slope *b* is related to the "overall transfer coefficient" α ,⁷⁷

$$b = \frac{(\ln 10)RT}{F\alpha} = \frac{59}{\alpha} \,\mathrm{mV}\,\mathrm{dec}^{-1} \tag{13}$$

at room temperature. Here, $\alpha = n_f + \beta_r n_r$, with n_f being the number of electrons released before the RDS, n_r the number of electrons involved in the RDS, and β_r the symmetry factor of the RDS.

Provided with *a priori* reaction mechanism, eq 13 allows identifying the RDS from the Tafel slope. For instance, a Tafel slope of ~118 mV/dec is usually taken as evidence for the first electron transfer as the RDS, a Tafel slope of ~59 mV/dec the second chemical step following an electrochemical step as the RDS, and a Tafel slope of ~39 mV/dec the second electron transfer step as the RDS. It is important to note that this designation assumes $\beta_r = 0.5$, which has no fundamental reason; furthermore, the Marcus theory of electron transfer shows that β_r changes with overpotential.⁷⁸ Additionally, the above view relies on two assumptions. Firstly, it presupposes a slow step that controls the overall net rate of the reaction, and all the other steps are in quasi-equilibrium. Secondly, the coverage of adsorbates on the catalyst surface is assumed to be negligible.^{20–22,42} In some cases, the second assumption is alleviated by determining the adsorbate coverages under quasi-equilibrium conditions.²¹ However, the quasi-equilibrium conditions implied in both assumptions contradict with the fact that the reaction has a net rate, and that all elementary steps proceed with the same net rate.⁴⁵ To overcome these problematic assumptions, the development of a microkinetic model, which considers the thermodynamics and kinetics of all the elementary steps, becomes compelling.^{15,45}

The presented hierarchical framework has been demonstrated to be a useful tool in deciphering the potential-dependent Tafel slopes of the OER (Figure 3A), ORR (Figure 3C) and CO₂RR (Figure 3D). A common trend that the Tafel slope increases with overpotential is observed. This can be understood through the RDT analysis of intrinsic multistep kinetics.¹

For the specific example of the OER, the inverse reaction rate, *i.e.*, the reaction resistance, is given by,

$$R = \frac{4e\rho}{j} = \frac{\Theta_1}{k_1} + \frac{\Theta_2}{k_2} + \frac{\Theta_3}{k_3} + \frac{\Theta_4}{k_4},$$
 (14)

with the thermodynamic factors

$$\begin{aligned}
\Theta_{1} &= \frac{1 + K_{2} + K_{2}K_{3} + K_{2}K_{3}K_{4}}{K_{2}K_{3}K_{4}}, \\
\Theta_{2} &= \frac{1 + K_{3} + K_{3}K_{4} + K_{3}K_{4}K_{1}}{K_{1}K_{3}K_{4}}, \\
\Theta_{3} &= \frac{1 + K_{4} + K_{4}K_{1} + K_{4}K_{1}K_{2}}{K_{1}K_{2}K_{4}}, \\
\Theta_{4} &= \frac{1 + K_{1} + K_{1}K_{2} + K_{1}K_{2}K_{3}}{K_{1}K_{2}K_{3}}.
\end{aligned}$$
(15)

Here, $K_i = k_i/k_{-i}$ are equilibrium constants. Equation 14 decomposes the overall reaction resistance into four resistive terms. These terms usually differ by several orders of magnitude, with the largest term determining the overall reaction resistance and thus the net rate. This term is defined as the RDT. The RDT of the OER is shown to be potential-dependent (Figure 3B), which is the fundamental origin of the potential-dependent Tafel slope.¹ Specifically, in the low overpotential region (1.23 ~1.50 V), $\frac{\theta_3}{k_3}$ is the RDT, and the dominant term in the numerator of θ_3 is K_4K_1 . This simplifies $\frac{\theta_3}{k_3}$ to $\frac{1}{k_2k_3}$, which results in $\alpha = 1.5$ and b = 39 mV dec⁻¹. In the high overpotential region (above 1.50 V), $\frac{\theta_2}{k_2}$ becomes the RDT, with the dominant term in the numerator of θ_2 being $K_3K_4K_1$. This simplifies $\frac{\theta_2}{k_2}$ to $\frac{1}{k_2}$, resulting in $\alpha = 0.5$ and b =118 mV dec⁻¹.



Figure 3. (A) Tafel slopes of the OER. The three lines represent intrinsic Tafel slopes derived from the microkinetic model with different kinetic parameters. The symbols denote experimental data measured on NiOOH and NiFeOOH catalysts. (B) The resistance terms, $\frac{\theta_i}{k_i}$, of the OER. (C) Tafel slopes of the ORR. The dotted line represents intrinsic Tafel slopes. The solid line represents apparent Tafel slopes with the EDL effects. The dots are experiment data measured on Pt(111). (D) Comparison of simulations (solid lines) and experiments (symbols) in terms of CO partial current density of CO₂RR at Ag. The intrinsic Tafel slope is 39 mV/dec at low overpotentials and 118 mV/dec at high overpotentials. The Tafel slopes with the LRE effects at different potential ranges are annotated. Panels (A) and (B) are adapted with permission from ref⁻¹. Copyright 2021 Elsevier. Panel (C) is reproduced with permission from ref⁻³. Copyright 2018 Royal Society of Chemistry. Panel (D) is adapted with permission from ref⁻³. Copyright 2021 American Chemical Society.

In addition to the intrinsic multistep kinetics, also the LRE impacts the measured Tafel slopes. Moreover, the influence of the LRE is unavoidable due to the presence of the EDL. We depict the LRE effects on the Tafel slopes of ORR in Figure 3C and CO₂RR in Figure 3D. The mass transport effects tend to increase the Tafel slope with increasing current density, especially for reactions with low reactant concentration in bulk solution (*e.g.*, CO₂RR), due to the decrease of reactant concentration at surface. At low overpotentials, the EDL effects are usually predominant. For instance, the intrinsic Tafel slopes are 39 mV/dec for ORR at 0.9 V and CO₂RR at -0.3 V, while the apparent Tafel slopes are close to 59 mV/dec due to the EDL effects. However, 39 mV/dec and 59 mV/dec imply different RDSs in the conventional analysis. Furthermore, lateral interactions from competitive adsorbates^{3,69} and surface charge effects on adsorption energies^{26,62} are demonstrated to significantly impact Tafel slopes.

Combined, we conclude that the apparent Tafel slope is a composite reaction parameter and may be a poor activity metric as it is influenced by several interacting factors, including the thermodynamics and kinetics of multiple elementary steps, and LRE effects. The proposed

framework aids in revealing the mechanisms behind the apparent potential-dependent Tafel slopes, remedying an oversimplified analysis of the RDS from the Tafel slope.

CATION OVERCROWDING EFFECT

The effects of cation identity and concentration have been extensively explored across various electrocatalytic reactions.^{48–50,79–81} To elucidate the observed cation effects, several mechanisms have been proposed. For instance, Singh *et al.* attributed cation effects in the CO₂RR to cation hydrolysis. Specifically, cations with a smaller hydrated size can buffer the interfacial pH near cathode more effectively.⁴⁹ Using the modified Poisson-Boltzmann model, Ringe *et al.* illustrated that the electrode surface charge density is more negative for Cs⁺ than Li⁺, which, in turn, enhances the stability of intermediates, *e.g.*, *CO₂ and *COOH, in CO₂RR.²⁷ Similar surface charge effects can also explain the cation effects in the HER,⁴⁸ ORR⁷⁹ and OER.⁸⁰ Huang *et al.* rationalized cation-dependent kinetics of HER/HOR by considering the influence of cations on the interfacial water structure and H-bonding network.⁶¹ Furthermore, Qin *et al.* proposed that the CO₂RR proceeds through an inner-sphere electron transfer pathway in presence of alkali cations, and in contrast, through an outer-sphere electron transfer pathway without cations.⁸¹

Most of the above mechanisms assume that the binding energies of adsorbed intermediates are affected by the electric field which is then influenced by the cations. Following this line of thermodynamic binding-energy approach, we would expect opposite sequences of cation size effects for metals on the left and right legs of the volcano plot. Xue *et al.* observed opposite trends of cation size effects on the HER at Pt or Au, which adsorb hydrogen too strongly or too weakly, respectively.⁴⁸ However, opposite trends have been missing for the CO₂RR. In particular, for CO₂RR to HCOOH, Sn locates at the peak of the volcano plot.⁸² Therefore, enhancing the

adsorption of the key intermediate, *OCHO, would decrease the activity. In contrast, since Ag lies at the right leg of the volcano plot, enhancing the adsorption of *OCHO would increase its activity. However, experiments have shown that the CO₂RR to HCOOH follows the sequence of Li⁺ < Na⁺ < K⁺< Cs⁺ at both Sn and Ag.⁴⁷ This discrepancy has motivated us to look beyond the bindingenergy approach and introduce an electrostatic factor, *i.e.*, the cation overcrowding effect, into consideration. This mechanism was previously acknowledged by Frumkin *et al.* in the study of peroxydisulfate anion reduction when the surface charge is very negative.⁶³ We demonstrated that the cation overcrowding effect offers an alternative, or at least, complementary explanation to the previously observed cation effects.

The overcrowding effect describes how cations accumulating exceedingly near the negatively charged surface diminish the space for reactants and influence the local electrostatic potential and electric field.² Theory and simulations accounting for the cation size have shown that this effect is more pronounced for cations with a larger hydrated size,² as depicted in Figure 4A. Consequently, the concentration of reactant, *e.g.*, CO_2 for CO_2RR and OH^- for OER, at the surface follows the order, *i.e.*, $Li^+ < Na^+ < K^+$ (Figure 4B), which results in the same order of activity. Despite its simplicity, this rationale was shown to be relevant in explaining the cation effects in the CO_2RR at Ag (Figure 4C),³ and the OER at Ni-based catalysts.²



Figure 4. (A) Schematic of the cation overcrowding effect on electrocatalysis. Cations accumulated near the negatively charged surface diminish the space for reactants, resulting in a decrease in the reactant concentration. Moreover, this effect is more pronounced for cations with a larger hydrated size. (B-C) Cation effects on CO₂RR at Ag in 0.1 M KHCO₃/NaHCO₃/LiHCO₃ solutions: (B) CO₂ concentration at the reaction plane; (C) model-derived CO current density. (D) Schematic of the difference between the most probable reaction zone and the accessible zone in experimental measurements. (E) Distribution of CO₂ concentration in solutions at -1.2 V versus reversible hydrogen electrode (RHE). Panels B, C and E are adapted with permission from ref ³. Copyright 2021 American Chemical Society.

Various experimental techniques have been employed to detect the local reactant concentration or the local pH, such as surface enhanced infrared absorption spectroscopy, Raman spectroscopy, scanning electrochemical microscopy.^{34–37} However, it is essential to acknowledge that in these experiments, the term "surface" typically refers to somewhere within the diffusion layer. The distance between the catalyst surface and the probe position varies from hundreds of nanometers to hundreds of micrometers,³⁴ which is still far out of the reaction region within the EDL.⁶⁷ This discrepancy in the designation of the "surface" concentration, as depicted in Figure 4D, may lead to confusion. For instance, Malkani et al. observed that the 'surface' CO2 concentration follows the sequence of $Li^+ > Na^+ > K^+$. At first glance, this shows the opposite trend to our simulations in Figure 4B. This superficial inconsistency can be resolved by distinguishing the "surface" concentration in experiments and our simulations. As shown in Figure 4E, our simulations show that the CO₂ concentration in the diffusion layer, which corresponds to the "surface" in experiments, follows the order of Li⁺ > Na⁺ > K⁺. The concentration in this diffusion region is determined by mass transport effects; the above concentration sequence is a direct consequence of the fact that the current density of the CO₂RR follows the sequence $Li^+ < Na^+ <$ K⁺. However, electrostatic interactions and the cation overcrowding effect dominate within the EDL, leading to the inverse order of CO₂ concentration.

PH EFFECTS

The influence of solution pH on electrocatalytic reactions is multifaceted, including intrinsic pH effects and local pH effects. In broad terms, changes in solution pH impact reaction kinetics by inducing shifts in both proton activity and absolute potential of the electrode (*i.e.*, versus the SHE). Given that many electrocatalytic reactions involve proton and electron transfers, variations

in pH play a pivotal role. Moreover, the proton donor or oxidant involved in the reaction may transition from proton/hydroxyl to water molecules when pH varies in a wide range. Additionally, for reactants engaged in acid-alkaline equilibrium, such as formic acid and formate, the concentration of the reactant is intrinsically influenced by the solution pH. These influences are termed as intrinsic pH effects as they collectively shape the overall properties of electrocatalytic reactions. These intrinsic effects have been widely employed to understand the pH effects in various electrocatalytic reactions, including CO₂RR,^{25,62} electrochemical carbon monoxide reduction,^{62,83} HER,⁵³ ORR,⁸⁴ OER,^{52,85} and FAOR.^{51,86,87}

In addition to these intrinsic pH effects, we have emphasized the importance of considering the local pH effects, namely, the pH effects on the LRE.^{2,4,88} On one hand, the local pH shifts with the reaction rate due to the production/consumption of protons, and this pH shift is more pronounced in the intermediate pH range than in very acidic or very alkaline contions.⁸⁹ On the other hand, the pzc on the reversible hydrogen electrode (RHE) scale increases with pH,

$$E_{\rm pzc,RHE} = E_{\rm pzc,SHE} + 0.0592 \rm{pH}.$$
 (16)

Here, $E_{pzc,SHE}$ is the pzc on the SHE scale. Consequently, the surface charge is more negative at higher pH at the same potential versus RHE, resulting the change of EDL properties.

Thermodynamic equilibrium conditions predict that the OER activity should be independent of pH on the RHE scale since it is a proton-coupled electron transfer (PCET) reaction.^{52,90} However, experiments show that the activity increases with pH.⁸⁵ This discrepancy can be understood by considering the EDL effects.



Figure 5. (A) Schematic of the Frumkin theory for electrocatalytic reactions. (B-F) pH effects on FAOR at Pt electrode: (B) pH-activity relations of FAOR observed in experiments, which are bell-shaped in phosphate solutions and trapezoidal-shaped in perchlorate solutions;⁵¹ (C) intrinsic activity-pH relation without considering the LRE effects, and activity-pH relation accounting for the mass transport effects in perchlorate solutions; (D) comparison of the pH in bulk solution and the pH at the most probable reaction plane; (E) model-derived activity-

pH relations in perchlorate solutions and phosphate solutions accounting for the mass transport effects; (G) comparison between the experiments and the simulations with the full-level model in perchlorate solutions. Panels C-F are adapted with permission from ref⁴. Copyright 2023 American Chemical Society.

For the electrochemical oxidation of anions, such as OH⁻ in OER, the negative surface charge induces two competing effects, as per Frumkin effects (Figure 5A): it increases the driving force and decreases the surface concentration of anions (opposite for positive surface charge). The outcome of these competing effects determines the promotion or inhibition of activity. Furthermore, Frumkin effects depend on the pH, as it modulates the surface charge, *i.e.*, the surface charge is more negative at higher pH. For the case of OER at NiOOH, the effect of increasing the driving force is more pronounced. As a result, the activity exhibits an increase as the surface charge becomes more negative, and thus at higher pH.²

However, Frumkin effects have been revealed as being insignificant in the case of FAOR, as the competing effects more or less cancel each. Instead, the mass transport-induced local pH shift emerges as a crucial factor in influencing the observed pH effects.⁴ Although the FAOR has been studied for many decades as a model reaction, the relation between its activity and the pH remains controversial. Joo *et al.* firstly reported that the activity-pH relation of FAOR at Pt exhibits a bell shape with the peak at the pK_a of formic acid (~ 4).⁸⁶ Their study considered phosphate solutions with pH ranging from 0 to 12. It was explained that the activity increases with pH when pH < pK_a since the concentration of HCOO⁻ increases, which is the main reactant. The siteblocking effect of OH adsorption becomes significant when pH > pK_a; therefore, the activity decreases with pH in this range. However, a trapezoidal-shaped activity-pH relation with a plateau between pH 5 and 10 was observed when perchlorate solutions were used (Figure 5B).⁵¹ This observation challenged the previously proposed mechanism.

The complexity of pH effects in this model system arises from multiple interacting factors, including pH-dependent thermodynamics and reaction kinetics of multiple steps, and pHdependent LRE effects. This situation has motivated us to build a hierarchical model in an incremental manner allowing different factors that control the overall pH effect to be disentangled. Our analysis began with exclusive consideration of the microkinetics in perchlorate solutions, in which the specific adsorption of electrolyte anions can be avoided. On this L2 modeling, we obtained the intrinsic activity-pH relation without accounting for the LRE. As shown in Figure 5C, the intrinsic activity-pH relation is bell-shaped with a peak at pH = 6, which is inconsistent with the observed trapezoidal shape. We then added mass transport effects to the model, namely, modeling on the L3. Figure 5D indicates that the pH at the reaction plane (pH_{RP}) is much lower than the pH in the bulk solution (pH_{bulk}), as the FAOR generates protons. Moreover, the pH_{RP} remains almost constant at $pH_{RP} = 4$ in the range of 5 < pH_{bulk} <11. This local pH shift induces a transformation of the activity-pH relation from bell shape to trapezoidal shape, yielding qualitative agreement with the experimental trend (Figure 5C).⁵¹ For the activity-pH relation in phosphate solutions, there are two additional electrolyte effects, *i.e.*, the buffering effect and the specific adsorption of phosphate anions. By incorporating both effects, we captured the experimental trend in phosphate solution with the activity being lower than that in perchlorate solution and the activity-pH relation being bell-shaped (Figure 5E). Furthermore, the site-blocking effect of the specific adsorption of phosphate anions was revealed to be the determining factor. However, we noticed that the simulated activity is approximately three times higher than the experimental data, which cannot be explained by Frumkin effects. Therefore, we suggested that specific EDL effects beyond Frumkin corrections are likely responsible for this. By incorporating

the surface charging effect on adsorption energies of formate, the model captures the experiments quantitatively in both perchlorate solutions (Figure 5F) and phosphate solutions.⁴

For the H₂O₂ redox reaction, the pH effects were shown to arise from the pH-dependent surface charging effect, which were studied using AIMD at electrified Pt(111)-water interfaces.⁸⁸ The negative and positive surface charge conditions were simulated by introducing a lithium ion and a fluorine ion in the water layer, respectively. It was revealed that the negative surface charge repels the O–O bond of H_2O_2 farther away from the electrode surface, leading to a higher activation barrier for breaking the O–O bond. When the applied potential shifts negatively, the driving force of HPRR increases, which leads to the decrease of the activation barrier, promoting the activity. Concurrently, the surface charge becomes more negative, increasing the activation barrier and suppressing the reaction. These two competing effects cause the nonmonotonic (first increasing and then decreasing) activity of HPRR with the negative shift of electrode potential. The activity suppression effect caused by negative surface charge is also responsible for the pH effects of HPRR. As the surface charge becomes more negative with increasing pH, the onset of the suppression effect shifts to more positive potential for higher pH. Consequently, the activity decreases at more positive potential at higher pH, which is consistent with experimental observations.91

Given the above analysis, we underscore the importance of considering the variation of LRE when the solution pH changes. Fluctuations in local pH and surface charging relation induced by pH changes could be the determining factors of apparent pH effects.

SUMMARY AND OUTLOOK

Various kinetic phenomena in electrocatalytic reactions, such as potential-dependent Tafel slopes, cation effects, and pH effects, are influenced by multiple interrelated factors, including thermodynamics, multistep kinetics, mass transport, and EDL charging. In this Account, we have presented a hierarchical framework integrating two essential modules: a microkinetic model that incorporates thermodynamics and kinetics of all elementary steps and a LRE model that accounts for the microscopic EDL structure and macroscopic mass transport in a unified manner. Our applications of this framework to various electrocatalytic reactions have yielded vital insights into potential-dependent Tafel slopes, cation effects, and pH effects. From our perspective, it is crucial to start from a holistic, unbiased view when deciphering the physical origins behind various reaction phenomena.

Until now, our framework has been applied to planar electrodes with a static structure under steady-state conditions. Several important extensions to the framework should be made in the stride towards realism. Firstly, time-dependent methods, *e.g.*, pulsed electrolysis, have been acknowledged to be effective in improving the activity and selectivity of CO₂RR⁹² and ORR.⁹³ Secondly, the catalyst has been revealed to dynamically reconstruct, instead of being static, during reactions.^{94,95} Thirdly, supported nanoparticle catalysts are widely employed in electrochemical energy conversion technologies,⁹⁶ requiring a proper consideration of synergistic effects due to the overlap of EDLs at catalytic nanoparticles and at support material.⁹⁷ Future endeavours in addressing these complexities could take the advantage of recent developments in theory and modelling of electrochemical phenomena. For instance, the thermodynamics and kinetics of elementary steps involved in the microkinetic model can be calculated with increasing

accuracy using grand-canonical DFT.⁹⁸ In addition, the mean field EDL model can be refined and complemented by incorporating the atomistic and molecular details obtained from first-principles calculations.^{24,99} Finally, development of high-performance computation infrastructure and rapidly emerging machine learning techniques pave the way towards handling complexities of real-world electrocatalytic systems.¹⁰⁰

NOTES

The authors declare no competing financial interest.

BIOGRAPHIES

Xinwei Zhu is a fourth-year Ph.D. student under the supervision of Prof. Michael Eikerling. He obtained his B.Sc. and M.Sc. at the Hunan University (China). In his Ph.D. research, he has focused on understanding electrocatalytic reactions with theory and simulation, specifically considering multistep kinetics and the effects of local reaction environment.

Jun Huang is currently a Helmholtz Young Investigator Group leader at Juelich Research Center, Germany, after a Humboldt Fellowship in Ulm University, Germany, and Alicante University, Spain. He obtained his bachelor (2012) and doctoral (2017) degrees from Tsinghua University, China. During 2017–2019, he led an independent research group at Central South University, China. Trained as an engineer, he turned to theoretical electrochemistry during his Ph.D. under the supervision of Profs Jianbo Zhang and Michael Eikerling. Since then, he is pursuing his passion in theoretical and conceptual electrochemistry, with the emphasis put on impedance response of electrochemical elements, electric double layer, and electrocatalysis.

Michael Eikerling is Professor at RWTH Aachen University and Director of the Institute of Energy and Climate Research in Forschungszentrum Jülich, heading the sub-Institute for Theory and Computation of Energy Materials (IEK-13). Moreover, he is the Scientific Coordinator of the Centre for Advanced Simulation and Analytics (CASA) in Jülich. In 2017, he was awarded the Alexander Kuznetsov Prize for Theoretical Electrochemistry of the International Society of Electrochemistry, in recognition of his groundbreaking work on modeling polymer electrolyte

fuel cells. In 2024, he was selected as ISE fellow for his contribution to theoretical electrochemistry, namely, to simulations of electrocatalytic reactions at interfaces.

ACKNOWLEDGEMENT

X.Z. and M.E. acknowledge the financial support from the Forschungszentrum Jülich GmbH and from the German-Canadian Materials Acceleration Centre (GC-MAC), which is funded by the Federal Ministry of Education and Research (BMBF) in Germany. J.H. is supported by the Initiative and Networking Fund of the Helmholtz Association (no. VH-NG-1709). The presented work was carried out within the framework of the Helmholtz program Materials and Technologies for the Energy Transition in the topic Chemical Energy Carriers and the subtopic Power-based Fuels and Chemicals.

REFERENCES

- (1) Huang, J.; Zhu, X.; Eikerling, M. The Rate-Determining Term of Electrocatalytic Reactions with First-Order Kinetics. *Electrochimica Acta* **2021**, *393*, 139019. https://doi.org/10.1016/j.electacta.2021.139019.
- (2) Huang, J.; Li, M.; Eslamibidgoli, M. J.; Eikerling, M.; Groß, A. Cation Overcrowding Effect on the Oxygen Evolution Reaction. JACS Au 2021, jacsau.1c00315. https://doi.org/10.1021/jacsau.1c00315.
- (3) Zhu, X.; Huang, J.; Eikerling, M. Electrochemical CO2 Reduction at Silver from a Local Perspective. ACS Catal. 2021, 11 (23), 14521–14532. https://doi.org/10.1021/acscatal.1c04791.
- (4) Zhu, X.; Huang, J.; Eikerling, M. pH Effects in a Model Electrocatalytic Reaction Disentangled. *JACS Au* **2023**, *3* (4), 1052–1064. https://doi.org/10.1021/jacsau.2c00662.
- (5) Seh, Z. W.; Kibsgaard, J.; Dickens, C. F.; Chorkendorff, I.; Nørskov, J. K.; Jaramillo, T. F. Combining Theory and Experiment in Electrocatalysis: Insights into Materials Design. *Science* **2017**, *355* (6321), eaad4998. https://doi.org/10.1126/science.aad4998.
- (6) Xia, R.; Overa, S.; Jiao, F. Emerging Electrochemical Processes to Decarbonize the Chemical Industry. *JACS Au* **2022**, *2* (5), 1054–1070. https://doi.org/10.1021/jacsau.2c00138.
- (7) Su, D.-J.; Xiang, S.-Q.; Gao, S.-T.; Jiang, Y.; Liu, X.; Zhang, W.; Zhao, L.-B.; Tian, Z.-Q. Kinetic Understanding of Catalytic Selectivity and Product Distribution of Electrochemical Carbon Dioxide Reduction Reaction. JACS Au 2023, 3 (3), 905–918. https://doi.org/10.1021/jacsau.3c00002.
- (8) Eslamibidgoli, M. J.; Huang, J.; Kadyk, T.; Malek, A.; Eikerling, M. How Theory and Simulation Can Drive Fuel Cell Electrocatalysis. *Nano Energy* **2016**, *29*, 334–361. https://doi.org/10.1016/j.nanoen.2016.06.004.
- (9) Hammer, B.; Norskov, J. K. Why Gold Is the Noblest of All the Metals. *Nature* **1995**, *376* (6537), 238–240. https://doi.org/10.1038/376238a0.
- (10) Hammer, B.; Nørskov, J. K. Electronic Factors Determining the Reactivity of Metal Surfaces. *Surf. Sci.* **1995**, *343* (3), 211–220. https://doi.org/10.1016/0039-6028(96)80007-0.
- Nørskov, J. K.; Rossmeisl, J.; Logadottir, A.; Lindqvist, L.; Kitchin, J. R.; Bligaard, T.; Jónsson, H. Origin of the Overpotential for Oxygen Reduction at a Fuel-Cell Cathode. *J. Phys. Chem. B* 2004, *108* (46), 17886–17892. https://doi.org/10.1021/jp047349j.
- (12) Calle-Vallejo, F.; Tymoczko, J.; Colic, V.; Vu, Q. H.; Pohl, M. D.; Morgenstern, K.; Loffreda, D.; Sautet, P.; Schuhmann, W.; Bandarenka, A. S. Finding Optimal Surface Sites on Heterogeneous Catalysts by Counting Nearest Neighbors. *Science* 2015, *350* (6257), 185–189. https://doi.org/10.1126/science.aab3501.
- (13) Calle-Vallejo, F.; Loffreda, D.; Koper, M. T. M.; Sautet, P. Introducing Structural Sensitivity into Adsorption–Energy Scaling Relations by Means of Coordination Numbers. *Nat. Chem.* 2015, 7 (5), 403–410. https://doi.org/10.1038/nchem.2226.
- (14) Zeradjanin, A. R.; Narangoda, P.; Masa, J.; Schlögl, R. What Controls Activity Trends of Electrocatalytic Hydrogen Evolution Reaction?–Activation Energy Versus Frequency Factor. ACS Catal. 2022, 12 (19), 11597–11605. https://doi.org/10.1021/acscatal.2c02964.

- (15) Motagamwala, A. H.; Dumesic, J. A. Microkinetic Modeling: A Tool for Rational Catalyst Design. *Chem. Rev.* **2021**, *121* (2), 1049–1076. https://doi.org/10.1021/acs.chemrev.0c00394.
- (16) Exner, K. S. A Universal Descriptor for the Screening of Electrode Materials for Multiple-Electron Processes: Beyond the Thermodynamic Overpotential. ACS Catal. 2020, 10 (21), 12607–12617. https://doi.org/10.1021/acscatal.0c03865.
- (17) Exner, K. S. Is Thermodynamics a Good Descriptor for the Activity? Re-Investigation of Sabatier's Principle by the Free Energy Diagram in Electrocatalysis. *ACS Catal.* **2019**, *9* (6), 5320–5329. https://doi.org/10.1021/acscatal.9b00732.
- (18) Zhang, Y.; Huang, J.; Eikerling, M. Criterion for Finding the Optimal Electrocatalyst at Any Overpotential. *Electrochimica Acta* 2021, 400, 139413. https://doi.org/10.1016/j.electacta.2021.139413.
- Gómez-Marín, A. M.; Rizo, R.; Feliu, J. M. Oxygen Reduction Reaction at Pt Single Crystals:
 A Critical Overview. *Catal. Sci. Technol.* 2014, 4 (6), 1685–1698. https://doi.org/10.1039/C3CY01049J.
- (20) Dunwell, M.; Luc, W.; Yan, Y.; Jiao, F.; Xu, B. Understanding Surface-Mediated Electrochemical Reactions: CO₂ Reduction and Beyond. ACS Catal. **2018**, 8 (9), 8121–8129. https://doi.org/10.1021/acscatal.8b02181.
- (21) Shinagawa, T.; Garcia-Esparza, A. T.; Takanabe, K. Insight on Tafel Slopes from a Microkinetic Analysis of Aqueous Electrocatalysis for Energy Conversion. *Sci. Rep.* **2015**, *5* (1), 13801. https://doi.org/10.1038/srep13801.
- (22) Koper, M. T. M. Analysis of Electrocatalytic Reaction Schemes: Distinction between Rate-Determining and Potential-Determining Steps. *J. Solid State Electrochem.* **2013**, *17* (2), 339– 344. https://doi.org/10.1007/s10008-012-1918-x.
- (23) Frumkin, A. Wasserstoffüberspannung und Struktur der Doppelschicht. *Z. Für Phys. Chem.* **1933**, *164A* (1), 121–133. https://doi.org/10.1515/zpch-1933-16411.
- (24) Li, P.; Jiao, Y.; Huang, J.; Chen, S. Electric Double Layer Effects in Electrocatalysis: Insights from Ab Initio Simulation and Hierarchical Continuum Modeling. *JACS Au* **2023**. https://doi.org/10.1021/jacsau.3c00410.
- Xu, A.; Govindarajan, N.; Kastlunger, G.; Vijay, S.; Chan, K. Theories for Electrolyte Effects in CO2 Electroreduction. *Acc. Chem. Res.* 2022, 55 (4), 495–503. https://doi.org/10.1021/acs.accounts.1c00679.
- (26) Ringe, S.; Morales-Guio, C. G.; Chen, L. D.; Fields, M.; Jaramillo, T. F.; Hahn, C.; Chan, K. Double Layer Charging Driven Carbon Dioxide Adsorption Limits the Rate of Electrochemical Carbon Dioxide Reduction on Gold. *Nat. Commun.* 2020, *11* (1), 33. https://doi.org/10.1038/s41467-019-13777-z.
- (27) Ringe, S.; Clark, E. L.; Resasco, J.; Walton, A.; Seger, B.; Bell, A. T.; Chan, K. Understanding Cation Effects in Electrochemical CO 2 Reduction. *Energy Environ. Sci.* 2019, *12* (10), 3001– 3014. https://doi.org/10.1039/C9EE01341E.
- (28) Huang, J. Mixed Quantum-Classical Treatment of Electron Transfer at Electrocatalytic Interfaces: Theoretical Framework and Conceptual Analysis. J. Chem. Phys. 2020, 153 (16), 164707. https://doi.org/10.1063/5.0009582.
- (29) Pinto, L. M. C.; Spohr, E.; Quaino, P.; Santos, E.; Schmickler, W. Why Silver Deposition Is so Fast: Solving the Enigma of Metal Deposition. *Angew. Chem. Int. Ed.* **2013**, *52* (30), 7883– 7885. https://doi.org/10.1002/anie.201301998.

- (30) Veniamin Grigorievich Levich. Theory of the Nonequilibrium Double Layer. *Dokl. Akad. Nauk SSSR* **1949**, *67* (2), 309–312.
- (31) Li, X.-Y.; Wang, T.; Cai, Y.-C.; Meng, Z.-D.; Nan, J.-W.; Ye, J.-Y.; Yi, J.; Zhan, D.-P.; Tian, N.; Zhou, Z.-Y.; Sun, S.-G. Mechanism of Cations Suppressing Proton Diffusion Kinetics for Electrocatalysis. Angew. Chem. Int. Ed. 2023, 62 (14), e202218669. https://doi.org/10.1002/anie.202218669.
- (32) Gu, J.; Liu, S.; Ni, W.; Ren, W.; Haussener, S.; Hu, X. Modulating Electric Field Distribution by Alkali Cations for CO2 Electroreduction in Strongly Acidic Medium. *Nat. Catal.* **2022**, *5* (4), 268–276. https://doi.org/10.1038/s41929-022-00761-y.
- (33) Weber, A. Z.; Newman, J. Modeling Transport in Polymer-Electrolyte Fuel Cells. *Chem. Rev.* **2004**, *104* (10), 4679–4726. https://doi.org/10.1021/cr020729l.
- (34) Monteiro, M. C. O.; Koper, M. T. M. Measuring Local pH in Electrochemistry. *Curr. Opin. Electrochem.* **2021**, *25*, 100649. https://doi.org/10.1016/j.coelec.2020.100649.
- Monteiro, M. C. O.; Mirabal, A.; Jacobse, L.; Doblhoff-Dier, K.; Barton, S. C.; Koper, M. T. M. Time-Resolved Local pH Measurements during CO2 Reduction Using Scanning Electrochemical Microscopy: Buffering and Tip Effects. *JACS Au* 2021, *1* (11), 1915–1924. https://doi.org/10.1021/jacsau.1c00289.
- (36) Malkani, A. S.; Anibal, J.; Xu, B. Cation Effect on Interfacial CO2 Concentration in the Electrochemical CO2 Reduction Reaction. *ACS Catal.* **2020**, *10* (24), 14871–14876. https://doi.org/10.1021/acscatal.0c03553.
- (37) Botz, A.; Clausmeyer, J.; Öhl, D.; Tarnev, T.; Franzen, D.; Turek, T.; Schuhmann, W. Local Activities of Hydroxide and Water Determine the Operation of Silver-Based Oxygen Depolarized Cathodes. *Angew. Chem. Int. Ed.* **2018**, *57* (38), 12285–12289. https://doi.org/10.1002/anie.201807798.
- (38) Trasatti, S. Work Function, Electronegativity, and Electrochemical Behaviour of Metals: III. Electrolytic Hydrogen Evolution in Acid Solutions. J. Electroanal. Chem. Interfacial Electrochem. 1972, 39 (1), 163–184. https://doi.org/10.1016/S0022-0728(72)80485-6.
- Man, I. C.; Su, H.-Y.; Calle-Vallejo, F.; Hansen, H. A.; Martínez, J. I.; Inoglu, N. G.; Kitchin, J.; Jaramillo, T. F.; Nørskov, J. K.; Rossmeisl, J. Universality in Oxygen Evolution Electrocatalysis on Oxide Surfaces. *ChemCatChem* 2011, 3 (7), 1159–1165. https://doi.org/10.1002/cctc.201000397.
- (40) Zhou, D.; Wei, J.; He, Z.-D.; Xu, M.-L.; Chen, Y.-X.; Huang, J. Combining Single Crystal Experiments and Microkinetic Modeling in Disentangling Thermodynamic, Kinetic, and Double-Layer Factors Influencing Oxygen Reduction. J. Phys. Chem. C 2020, 124 (25), 13672– 13678. https://doi.org/10.1021/acs.jpcc.0c01621.
- (41) Limaye, A. M.; Zeng, J. S.; Willard, A. P.; Manthiram, K. Bayesian Data Analysis Reveals No Preference for Cardinal Tafel Slopes in CO2 Reduction Electrocatalysis. *Nat. Commun.* 2021, 12 (1), 703. https://doi.org/10.1038/s41467-021-20924-y.
- Kozuch, S.; Martin, J. M. L. The Rate-Determining Step Is Dead. Long Live the Rate-Determining State! *ChemPhysChem* 2011, 12 (8), 1413–1418. https://doi.org/10.1002/cphc.201100137.
- (43) Sepa, D. B.; Vojnovic, M. V.; Vracar, Lj. M.; Damjanovic, A. Different Views Regarding the Kinetics and Mechanisms of Oxygen Reduction at Pt and Pd Electrodes. *Electrochimica Acta* **1987**, *32* (1), 129–134. https://doi.org/10.1016/0013-4686(87)87021-4.

- (44) Holewinski, A.; Linic, S. Elementary Mechanisms in Electrocatalysis: Revisiting the ORR Tafel Slope. J. Electrochem. Soc. **2012**, 159 (11), H864. https://doi.org/10.1149/2.022211jes.
- (45) Marshall, A. T.; Vaisson-Béthune, L. Avoid the Quasi-Equilibrium Assumption When Evaluating the Electrocatalytic Oxygen Evolution Reaction Mechanism by Tafel Slope Analysis. *Electrochem. Commun.* **2015**, *61*, 23–26. https://doi.org/10.1016/j.elecom.2015.09.019.
- (46) Hansen, H. A.; Viswanathan, V.; Nørskov, J. K. Unifying Kinetic and Thermodynamic Analysis of 2 e– and 4 e– Reduction of Oxygen on Metal Surfaces. J. Phys. Chem. C 2014, 118 (13), 6706–6718. https://doi.org/10.1021/jp4100608.
- (47) Resasco, J.; Chen, L. D.; Clark, E.; Tsai, C.; Hahn, C.; Jaramillo, T. F.; Chan, K.; Bell, A. T. Promoter Effects of Alkali Metal Cations on the Electrochemical Reduction of Carbon Dioxide. *J. Am. Chem. Soc.* 2017, 139 (32), 11277–11287. https://doi.org/10.1021/jacs.7b06765.
- (48) Xue, S.; Garlyyev, B.; Watzele, S.; Liang, Y.; Fichtner, J.; Pohl, M. D.; Bandarenka, A. S. Influence of Alkali Metal Cations on the Hydrogen Evolution Reaction Activity of Pt, Ir, Au, and Ag Electrodes in Alkaline Electrolytes. *ChemElectroChem* **2018**, *5* (17), 2326–2329. https://doi.org/10.1002/celc.201800690.
- Singh, M. R.; Kwon, Y.; Lum, Y.; Ager, J. W.; Bell, A. T. Hydrolysis of Electrolyte Cations Enhances the Electrochemical Reduction of CO₂ over Ag and Cu. J. Am. Chem. Soc. 2016, 138 (39), 13006–13012. https://doi.org/10.1021/jacs.6b07612.
- (50) Michael, J. D.; Demeter, E. L.; Illes, S. M.; Fan, Q.; Boes, J. R.; Kitchin, J. R. Alkaline Electrolyte and Fe Impurity Effects on the Performance and Active-Phase Structure of NiOOH Thin Films for OER Catalysis Applications. *J. Phys. Chem. C* 2015, *119* (21), 11475–11481. https://doi.org/10.1021/acs.jpcc.5b02458.
- (51) Perales-Rondón, J. V.; Brimaud, S.; Solla-Gullón, J.; Herrero, E.; Jürgen Behm, R.; Feliu, J.
 M. Further Insights into the Formic Acid Oxidation Mechanism on Platinum: pH and Anion Adsorption Effects. *Electrochimica Acta* 2015, 180, 479–485. https://doi.org/10.1016/j.electacta.2015.08.155.
- (52) Giordano, L.; Han, B.; Risch, M.; Hong, W. T.; Rao, R. R.; Stoerzinger, K. A.; Shao-Horn, Y. pH Dependence of OER Activity of Oxides: Current and Future Perspectives. *Catal. Today* 2016, 262, 2–10. https://doi.org/10.1016/j.cattod.2015.10.006.
- (53) Lamoureux, P. S.; Singh, A. R.; Chan, K. pH Effects on Hydrogen Evolution and Oxidation over Pt(111): Insights from First-Principles. *ACS Catal* **2019**, 8.
- (54) Marcandalli, G.; Monteiro, M. C. O.; Goyal, A.; Koper, M. T. M. Electrolyte Effects on CO2 Electrochemical Reduction to CO. *Acc. Chem. Res.* **2022**, *55* (14), 1900–1911. https://doi.org/10.1021/acs.accounts.2c00080.
- (55) Fuller, T. F.; Newman, J. Water and Thermal Management in Solid-Polymer-Electrolyte Fuel Cells. *J. Electrochem. Soc.* **1993**, *140* (5), 1218. https://doi.org/10.1149/1.2220960.
- (56) Eikerling, M.; Kornyshev, A. A. Modelling the Performance of the Cathode Catalyst Layer of Polymer Electrolyte Fuel Cells. *J. Electroanal. Chem.* **1998**, *453* (1), 89–106. https://doi.org/10.1016/S0022-0728(98)00214-9.
- (57) Eikerling, M.; Kornyshev, A. A. Electrochemical Impedance of the Cathode Catalyst Layer in Polymer Electrolyte Fuel Cells. *J. Electroanal. Chem.* **1999**, *475* (2), 107–123. https://doi.org/10.1016/S0022-0728(99)00335-6.
- (58) Singh, M. R.; Goodpaster, J. D.; Weber, A. Z.; Head-Gordon, M.; Bell, A. T. Mechanistic Insights into Electrochemical Reduction of CO ₂ over Ag Using Density Functional Theory and

Transport Models. *Proc. Natl. Acad. Sci.* **2017**, *114* (42), E8812–E8821. https://doi.org/10.1073/pnas.1713164114.

- (59) Sheng, W.; Gasteiger, H. A.; Shao-Horn, Y. Hydrogen Oxidation and Evolution Reaction Kinetics on Platinum: Acid vs Alkaline Electrolytes. *J. Electrochem. Soc.* **2010**, *157* (11), B1529. https://doi.org/10.1149/1.3483106.
- (60) Fornaciari, J. C.; Weng, L.-C.; Alia, S. M.; Zhan, C.; Pham, T. A.; Bell, A. T.; Ogitsu, T.; Danilovic, N.; Weber, A. Z. Mechanistic Understanding of pH Effects on the Oxygen Evolution Reaction. *Electrochimica Acta* 2022, 405, 139810. https://doi.org/10.1016/j.electacta.2021.139810.
- (61) Huang, B.; Rao, R. R.; You, S.; Hpone Myint, K.; Song, Y.; Wang, Y.; Ding, W.; Giordano, L.; Zhang, Y.; Wang, T.; Muy, S.; Katayama, Y.; Grossman, J. C.; Willard, A. P.; Xu, K.; Jiang, Y.; Shao-Horn, Y. Cation- and pH-Dependent Hydrogen Evolution and Oxidation Reaction Kinetics. JACS Au 2021, 1 (10), 1674–1687. https://doi.org/10.1021/jacsau.1c00281.
- (62) Kastlunger, G.; Wang, L.; Govindarajan, N.; Heenen, H. H.; Ringe, S.; Jaramillo, T.; Hahn,
 C.; Chan, K. Using pH Dependence to Understand Mechanisms in Electrochemical CO Reduction. ACS Catal. 2022, 12 (8), 4344–4357. https://doi.org/10.1021/acscatal.1c05520.
- (63) Frumkin, A. N.; Nikolaeva-Fedorovich, N. V.; Berezina, N. P.; Keis, Kh. E. The Electroreduction of the S2O82– Anion. *J. Electroanal. Chem. Interfacial Electrochem.* **1975**, *58* (1), 189–201. https://doi.org/10.1016/S0022-0728(75)80352-4.
- Monteiro, M. C. O.; Dattila, F.; Hagedoorn, B.; García-Muelas, R.; López, N.; Koper, M. T. M. Absence of CO2 Electroreduction on Copper, Gold and Silver Electrodes without Metal Cations in Solution. *Nat. Catal.* 2021, *4* (8), 654–662. https://doi.org/10.1038/s41929-021-00655-5.
- (65) Qin, H.-G.; Li, F.-Z.; Du, Y.-F.; Yang, L.-F.; Wang, H.; Bai, Y.-Y.; Lin, M.; Gu, J. Quantitative Understanding of Cation Effects on the Electrochemical Reduction of CO2 and H+ in Acidic Solution. *ACS Catal.* **2023**, *13* (2), 916–926. https://doi.org/10.1021/acscatal.2c04875.
- (66) Johnson, E. F.; Boutin, E.; Liu, S.; Haussener, S. Pathways to Enhance Electrochemical CO2 Reduction Identified through Direct Pore-Level Modeling. *EES Catal.* **2023**, *1* (5), 704–719. https://doi.org/10.1039/D3EY00122A.
- (67) Nazmutdinov, R. R.; Glukhov, D. V.; Petrii, O. A.; Tsirlina, G. A.; Botukhova, G. N. Contemporary Understanding of the Peroxodisulfate Reduction at a Mercury Electrode. *J. Electroanal. Chem.* **2003**, *552*, 261–278. https://doi.org/10.1016/S0022-0728(03)00221-3.
- (68) Huang, J.; Zhang, J.; Eikerling, M. Unifying Theoretical Framework for Deciphering the Oxygen Reduction Reaction on Platinum. *Phys. Chem. Chem. Phys.* **2018**, *20* (17), 11776–11786. https://doi.org/10.1039/C8CP01315B.
- (69) Bohra, D.; Ledezma-Yanez, I.; Li, G.; de Jong, W.; Pidko, E. A.; Smith, W. A. Lateral Adsorbate Interactions Inhibit HCOO– While Promoting CO Selectivity for CO2 Electrocatalysis on Silver. *Angew. Chem. Int. Ed.* **2019**, *58* (5), 1345–1349. https://doi.org/10.1002/anie.201811667.
- (70) Chen, L. D.; Urushihara, M.; Chan, K.; Nørskov, J. K. Electric Field Effects in Electrochemical CO₂ Reduction. ACS Catal. 2016, 6 (10), 7133–7139. https://doi.org/10.1021/acscatal.6b02299.

- (71) Zhang, L.; Cai, J.; Chen, Y.; Huang, J. Modelling Electrocatalytic Reactions with a Concerted Treatment of Multistep Electron Transfer Kinetics and Local Reaction Conditions. *J. Phys. Condens. Matter* **2021**, *33* (50), 504002. https://doi.org/10.1088/1361-648X/ac26fb.
- (72) Koutecky, J.; Levich, V. The Use of a Rotating Disk Electrode in the Studies of Electrochemical Kinetics and Electrolytic Processes. *Zh Fiz Khim* **1958**, *32*, 1565–1575.
- (73) Guo, J.; Brimley, P.; Liu, M. J.; Corson, E. R.; Muñoz, C.; Smith, W. A.; Tarpeh, W. A. Mass Transport Modifies the Interfacial Electrolyte to Influence Electrochemical Nitrate Reduction. *ACS Sustain. Chem. Eng.* **2023**, *11* (20), 7882–7893. https://doi.org/10.1021/acssuschemeng.3c01057.
- (74) Johnson, E. F.; Boutin, E.; Haussener, S. Surface Charge Boundary Condition Often Misused in CO2 Reduction Models. J. Phys. Chem. C 2023, 127 (37), 18784–18790. https://doi.org/10.1021/acs.jpcc.3c05364.
- (75) Huang, J. Zooming into the Inner Helmholtz Plane of Pt(111)–Aqueous Solution Interfaces: Chemisorbed Water and Partially Charged Ions. *JACS Au* **2023**, *3* (2), 550–564. https://doi.org/10.1021/jacsau.2c00650.
- (76) Huang, J. Surface Charging Behaviors of Electrocatalytic Interfaces with Partially Charged Chemisorbates. *Curr. Opin. Electrochem.* **2022**, 100938.
- Guidelli, R.; Compton, R. G.; Feliu, J. M.; Gileadi, E.; Lipkowski, J.; Schmickler, W.; Trasatti,
 S. Defining the Transfer Coefficient in Electrochemistry: An Assessment (IUPAC Technical Report). *Pure Appl. Chem.* 2014, *86* (2), 245–258. https://doi.org/10.1515/pac-2014-5026.
- (78) Laborda, E.; Henstridge, M. C.; Batchelor-McAuley, C.; Compton, R. G. Asymmetric Marcus–Hush Theory for Voltammetry. *Chem. Soc. Rev.* **2013**, *42* (12), 4894–4905. https://doi.org/10.1039/C3CS35487C.
- (79) Hübner, J. L.; Lucchetti, L. E. B.; Nong, H. N.; Sharapa, D. I.; Paul, B.; Kroschel, M.; Kang, J.; Teschner, D.; Behrens, S.; Studt, F.; Knop-Gericke, A.; Siahrostami, S.; Strasser, P. Cation Effects on the Acidic Oxygen Reduction Reaction at Carbon Surfaces. ACS Energy Lett. 2024, 1331–1338. https://doi.org/10.1021/acsenergylett.3c02743.
- (80) Yang, C.; Fontaine, O.; Tarascon, J.-M.; Grimaud, A. Chemical Recognition of Active Oxygen Species on the Surface of Oxygen Evolution Reaction Electrocatalysts. *Angew. Chem. Int. Ed.* **2017**, *56* (30), 8652–8656. https://doi.org/10.1002/anie.201701984.
- Qin, X.; Hansen, H. A.; Honkala, K.; Melander, M. M. Cation-Induced Changes in the Innerand Outer-Sphere Mechanisms of Electrocatalytic CO2 Reduction. *Nat. Commun.* 2023, 14 (1), 7607. https://doi.org/10.1038/s41467-023-43300-4.
- (82) Feaster, J. T.; Shi, C.; Cave, E. R.; Hatsukade, T.; Abram, D. N.; Kuhl, K. P.; Hahn, C.; Nørskov, J. K.; Jaramillo, T. F. Understanding Selectivity for the Electrochemical Reduction of Carbon Dioxide to Formic Acid and Carbon Monoxide on Metal Electrodes. ACS Catal. 2017, 7 (7), 4822–4827. https://doi.org/10.1021/acscatal.7b00687.
- Wang, L.; Nitopi, S. A.; Bertheussen, E.; Orazov, M.; Morales-Guio, C. G.; Liu, X.; Higgins, D. C.; Chan, K.; Nørskov, J. K.; Hahn, C.; Jaramillo, T. F. Electrochemical Carbon Monoxide Reduction on Polycrystalline Copper: Effects of Potential, Pressure, and pH on Selectivity toward Multicarbon and Oxygenated Products. ACS Catal **2018**, 10.
- (84) Li, M. F.; Liao, L. W.; Yuan, D. F.; Mei, D.; Chen, Y.-X. pH Effect on Oxygen Reduction Reaction at Pt(111) Electrode. *Electrochimica Acta* 2013, 110, 780–789. https://doi.org/10.1016/j.electacta.2013.04.096.

- (85) Grimaud, A.; Diaz-Morales, O.; Han, B.; Hong, W. T.; Lee, Y.-L.; Giordano, L.; Stoerzinger, K. A.; Koper, M. T. M.; Shao-Horn, Y. Activating Lattice Oxygen Redox Reactions in Metal Oxides to Catalyse Oxygen Evolution. *Nat. Chem.* 2017, *9* (5), 457–465. https://doi.org/10.1038/nchem.2695.
- (86) Joo, J.; Uchida, T.; Cuesta, A.; Koper, M. T. M.; Osawa, M. Importance of Acid–Base Equilibrium in Electrocatalytic Oxidation of Formic Acid on Platinum. J. Am. Chem. Soc. 2013, 135 (27), 9991–9994. https://doi.org/10.1021/ja403578s.
- (87) Zhu, X.; Huang, J. Modeling Electrocatalytic Oxidation of Formic Acid at Platinum. J. *Electrochem. Soc.* **2019**, *167* (1), 013515. https://doi.org/10.1149/2.0152001JES.
- (88) Huang, J.; Climent, V.; Groß, A.; Feliu, J. Understanding Surface Charge Effects in Electrocatalysis. Part 2: Hydrogen Peroxide Reactions at Platinum. *Chin. J. Catal.* **2022**, 220617. https://doi.org/10.1016/S1872-2067(22)64138-X.
- (89) Zhang, M.-K.; Wei, Z.; Chen, W.; Xu, M.-L.; Cai, J.; Chen, Y.-X. Bell Shape vs Volcano Shape pH Dependent Kinetics of the Electrochemical Oxidation of Formic Acid and Formate, Intrinsic Kinetics or Local pH Shift? *Electrochimica Acta* 2020, 363, 137160. https://doi.org/10.1016/j.electacta.2020.137160.
- (90) Koper, M. T. M. Theory of Multiple Proton–Electron Transfer Reactions and Its Implications for Electrocatalysis. *Chem. Sci.* **2013**, *4* (7), 2710–2723. https://doi.org/10.1039/C3SC50205H.
- (91) Briega-Martos, V.; Herrero, E.; Feliu, J. M. The Inhibition of Hydrogen Peroxide Reduction at Low Potentials on Pt(111): Hydrogen Adsorption or Interfacial Charge? *Electrochem. Commun.* **2017**, *85*, 32–35. https://doi.org/10.1016/j.elecom.2017.10.016.
- (92) Casebolt, R.; Levine, K.; Suntivich, J.; Hanrath, T. Pulse Check: Potential Opportunities in Pulsed Electrochemical CO2 Reduction. *Joule* **2021**, *5* (8), 1987–2026. https://doi.org/10.1016/j.joule.2021.05.014.
- (93) Ding, Y.; Zhou, W.; Li, J.; Wang, J.; Xie, L.; Meng, X.; Gao, J.; Sun, F.; Zhao, G.; Qin, Y. Revealing the In Situ Dynamic Regulation of the Interfacial Microenvironment Induced by Pulsed Electrocatalysis in the Oxygen Reduction Reaction. ACS Energy Lett. 2023, 8 (7), 3122– 3130. https://doi.org/10.1021/acsenergylett.3c00758.
- (94) Jiang, H.; He, Q.; Zhang, Y.; Song, L. Structural Self-Reconstruction of Catalysts in Electrocatalysis. Acc. Chem. Res. 2018, 51 (11), 2968–2977. https://doi.org/10.1021/acs.accounts.8b00449.
- (95) Xu, L.; Papanikolaou, K. G.; Lechner, B. A. J.; Je, L.; Somorjai, G. A.; Salmeron, M.; Mavrikakis, M. Formation of Active Sites on Transition Metals through Reaction-Driven Migration of Surface Atoms. *Science* **2023**, *380* (6640), 70–76. https://doi.org/10.1126/science.add0089.
- (96) Kameya, Y.; Hayashi, T.; Motosuke, M. Stability of Platinum Nanoparticles Supported on Surface-Treated Carbon Black. *Appl. Catal. B Environ.* **2016**, *189*, 219–225. https://doi.org/10.1016/j.apcatb.2016.02.049.
- (97) Binninger, T.; Schmidt, T. J.; Kramer, D. Capacitive Electronic Metal-Support Interactions: Outer Surface Charging of Supported Catalyst Particles. *Phys. Rev. B* **2017**, *96* (16), 165405. https://doi.org/10.1103/PhysRevB.96.165405.

- (98) Melander, M. M. Grand Canonical Ensemble Approach to Electrochemical Thermodynamics, Kinetics, and Model Hamiltonians. *Curr. Opin. Electrochem.* **2021**, *29*, 100749. https://doi.org/10.1016/j.coelec.2021.100749.
- (99) Magnussen, O. M.; Groß, A. Toward an Atomic-Scale Understanding of Electrochemical Interface Structure and Dynamics. *J. Am. Chem. Soc.* **2019**, *141* (12), 4777–4790. https://doi.org/10.1021/jacs.8b13188.
- (100) Mou, T.; Pillai, H. S.; Wang, S.; Wan, M.; Han, X.; Schweitzer, N. M.; Che, F.; Xin, H. Bridging the Complexity Gap in Computational Heterogeneous Catalysis with Machine Learning. *Nat. Catal.* 2023, 6 (2), 122–136. https://doi.org/10.1038/s41929-023-00911-w.