


The Intricacies of Computational Electrochemistry

Nitish Govindarajan,^{△△} Georg Kastlunger,^{△△} Joseph A. Gauthier,^{△△} Jun Cheng, Ivo Filot, Arthur Hagopian, Heine Anton Hansen, Jun Huang, Piotr M. Kowalski, Jinwen Liu, Juan M. Lombardi, Mikael Maraschin, Andrew Peterson, Hemanth S. Pillai, Hector Prats, Conor J. Price, René van Roij, Jan Rossmeisl, Ranga Rohit Seemakurthi, Seung-Jae Shin, Audrey Smith, Jia-Xin Zhu, and Katharina Doblhoff-Dier*

 Cite This: *ACS Energy Lett.* 2025, 10, 4277–4288

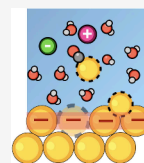
 Read Online

ACCESS |

 Metrics & More

 Article Recommendations

ABSTRACT: Computational electrochemistry is hard—anybody who has ever tried will know. We argue that the reasons for its complexity lie not only in the multiscale nature of electrochemical processes but also in the rapid, ongoing method development in the field. This has resulted in a lack of clear guidelines and many open discussions in the community. These issues were also the topic of a recent Lorentz Center workshop, the key take-away messages of which are highlighted in this Perspective. In particular, we discuss why the choice between constant potential and constant charge simulations is less trivial than it may seem, why interpreting electrochemical reaction free energy diagrams can be challenging, why the Poisson–Nernst–Planck equation is not all there is, and why we desperately need more benchmarking in the field.



Constant charge *and* constant potential methods
Interpreting electrochemical free energy diagrams
Beyond Poisson–Nernst–Planck models
Need for benchmarking studies

In the past few decades, there has been a rapid development of new computational methods in the field of electrochemistry. This development is driven by the important role of electrochemical processes in the transition toward a fossil-carbon free economy. Rapid method development is also inherently driven by the necessity of tackling the complex and dynamic nature of electrochemical processes.

To date, one cannot capture all aspects of the complexity of electrochemical systems in a single simulation. Consequently, one and the same electrochemical system is often addressed from various angles, with each approach offering distinct advantages and limitations. However, our current approaches generally rely on so many assumptions and approximations that our understanding of their true limitations can remain blurred. The lack of clarity in the best practices to study electrochemical processes, the inherent (multiscale) complexity of the problem, and the rapid development of methods make computational electrochemistry difficult and increases the likelihood that methods are used in situations where they are not appropriate.

To discuss the aforementioned issues, we organized a Lorentz center workshop on *Multiscale modeling of electrochemical processes*¹ where 46 primarily computational electrochemists with modeling expertise across different length and time scales came together to discuss pressing issues and new developments in the field. We would like to highlight key discussion points that emerged throughout the workshop. In particular, we will discuss

why the choice between constant potential and constant charge ensembles in atomistic simulations is less trivial than it may seem (see highlight 1), why interpreting electrochemical reaction free energy diagrams can be challenging (see highlight 2), why the Poisson–Nernst–Planck equation is not all there is to model transport (see highlight 3), and why there is an urgent need for more benchmarking in the field (see highlight 4). For each of these points, we also provide a perspective on developments required to move the field forward.

Electrochemical Processes Are Inherently Multiscale in Nature. In electrochemistry, experimental observations are often complex to interpret, as the physical origin of an observed effect can be the result of various physicochemical phenomena occurring across a wide range of length and time scales (Figure 1): mass transport, double layer effects, surface diffusion, adsorption/desorption, and electrode restructuring can each have their own influence on electrochemical processes.

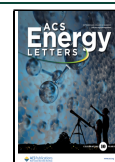
It is currently not feasible to capture all the relevant length- and time-scales in a single simulation. The general practice is

Received: April 3, 2025

Revised: June 2, 2025

Accepted: June 4, 2025

Published: August 8, 2025



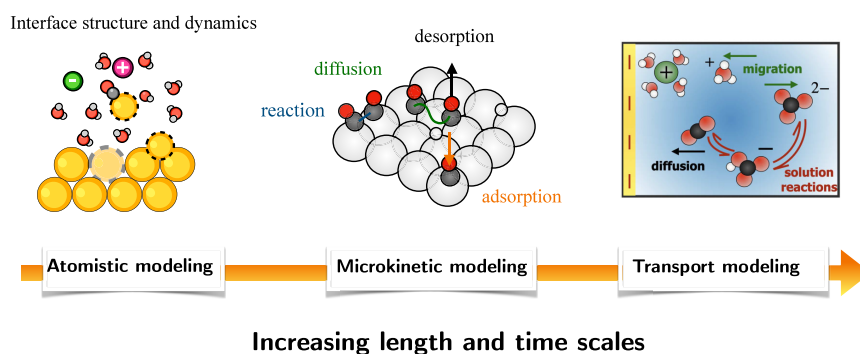


Figure 1. Schematic of the various simulation types (atomistic, microkinetic, and transport modeling) with increasing length and time scales needed to study electrochemical processes.

therefore to focus on a single length/time scale and to leverage knowledge from one scale to the next, resulting in information flow both up and down the spatiotemporal scales. However, due to the convoluted nature of effects across the different scales, separating scales can lead to erroneous predictions and insights.

In the following, we will gradually ascend the space and time scales. This discussion will form a framework in which we highlight some of the key points that were raised during the workshop and some key take-away messages.

Electrochemical Interfaces at the Atomic Scale. To obtain mechanistic insights into (electro)chemical reactions occurring at the electrode surface, we generally have to resort to simulations at the atomic level. Two main challenges for atomistic simulations discussed during the workshop were (a) identifying the atomic structure of the electrode surface under *operando* conditions and (b) identifying appropriate approaches to treat charge transfer reactions in electronic structure simulations of the electrochemical interface and understanding their restrictions.

Operando Electrode Structure. Electrochemical reactions strongly depend on the *operando* structure of the electrode (catalyst). Unfortunately, this (dynamic) structure is often hard to characterize using experimental techniques.

In modeling, thermodynamic stability descriptors are often used to identify the most stable state of the electrode^{2–7} or the structure of a nanoparticle under potential control.^{8–10} The *operando* structure of an electrode is, however, not uniquely defined by thermodynamic quantities (pressure, temperature, pH, bulk ion concentration, and potential). Instead, the entire (experimental) history plays a role. For example, surface reconstruction can be influenced by the potential range during cycling,¹¹ requiring a kinetic description of the surface reconstruction.

In modeling, these kinetic factors are often not taken into account. This issue was discussed several times during the workshop and triggered interesting discussions as to whether the most stable state obtained using thermodynamic descriptors represents an appropriate starting point for further investigations. Additionally, it was mentioned that, when accounting only for the most stable structure(s), one might overlook the presence of minority surface sites, which can dominate the overall activity of a catalyst.⁷

In addition to the surface structure, leaching, corrosion, and the incorporation of solution-phase species can also affect the interfacial composition and the reactivity of an electrocatalyst. A good example is SrIrO₃, which is one of the best reported catalysts for oxygen evolution—but only after selective leaching

of Sr, leading to the formation of a highly active IrO_x/SrIrO₃ phase.¹² To investigate the thermodynamic stability of a catalyst, traditional Pourbaix diagrams can be used. In the context of electrochemistry, the thermodynamic driving force for leaching and corrosion of charged species is generally computed via a Born–Haber cycle, relying on experimental equilibrium potentials.^{13,14}

Unfortunately, traditional Pourbaix diagrams do not account for the presence of an interface, which can affect the stability of a catalyst. A well-known example, in which the sole consideration of bulk stability is insufficient, is aluminum. Aluminum would corrode (and ultimately dissolve) unless passivated by a stabilizing surface oxide layer. To bridge the gap between understanding the stability of the bulk and the surface of an electrode, the concept of a “surface Pourbaix diagram” was developed. Surface Pourbaix diagrams consider a constrained equilibrium surface coverage of intermediates at a given potential and pH¹⁵ but generally do not consider leaching and corrosion, limiting their predictive power. Additionally, and as mentioned above, reconstruction, adsorption, leaching, and corrosion are ultimately driven by kinetic considerations that are not captured in thermodynamic descriptors.

Despite advances in understanding the stability of catalytic materials in electrochemical environments, identifying and modeling the true active sites and reconstruction pathways of dynamic electrocatalyst surfaces under reaction conditions remain critical challenges. We anticipate that machine learning procedures will play an important role in improving this situation.^{16,17}

Reaction Thermodynamics. The main force driving an electrochemical reaction is the applied potential. Atomistic models of a catalytic surface alone are not sufficient to account for the potential. Therefore, any computational method would *a priori* require the description of the entire double layer. This requirement is circumvented by the computational hydrogen electrode (CHE) method that uses an elegant thermodynamic framework to account for the applied potential.¹⁸ Unfortunately, the CHE method cannot deal with situations involving partial charge transfer as commonly encountered in multistep electrochemical reactions. In addition, the electrolyte can also have a direct influence on electrochemical reactions.^{19–23} To date, electrolyte effects and the explicit buildup of a potential are mostly addressed via mean-field approaches. In this case, local effects and specific interactions are lost. Alternatively, one can explicitly include a fraction of the electrolyte. To fully account for the liquid nature of the electrolyte, *ab initio* molecular dynamics and free energy sampling are required, leading to a

	constant potential	constant charge
fully explicit	<ul style="list-style-type: none"> - Cell size limitations due to high computational cost - Requires counter electrode or charging of electrolyte; may not correctly replicate the double layer - Charges cannot be brought into field-free region (shielding occurs in the entire cell) 	<ul style="list-style-type: none"> + No unphysical transitions - Continuous charging not possible - Charges cannot be rigorously brought into field-free region due to periodic images
hybrid	<ul style="list-style-type: none"> + reduced computational cost - Possibly unphysical transition from expl. to impl. region. - Capacitance mismatch between explicit and implicit charging region can lead to the grand canonical free energy being poorly defined. 	<ul style="list-style-type: none"> + Continuous charging possible
expl. electrode + expl. reactant (+ expl. microsolv.) implicit electrolyte	<ul style="list-style-type: none"> + No corrections needed for constant U ensemble + Continuous charging possible - Most codes: no micro-scale U fluctuations 	<ul style="list-style-type: none"> - Requires a posteriori corrections for constant U + Simple a posteriori correction schemes available + No "add-ons" needed in codes

Figure 2. An overview of the advantages and limitations of the various constant potential and constant charge approaches available to compute electrochemical barriers. “fully explicit” and “implicit” refer to an atomistic and mean-field description of the electrolyte, respectively. See text for details.

high computational cost, often necessitating harsh approximations. Computationally less expensive, quantum mechanics/molecular mechanics (QM/MM) based approaches have also been used²⁴ but come with their own challenges.⁴

Overall, the correct incorporation of electrolyte effects, including specific interactions, local electric field effects, and sufficient sampling under the correct thermodynamic conditions (see below), remain a challenge though—a fact that triggered critical questions throughout the workshop. We will discuss this issue in more detail in the next section.

Electrochemical Barriers. In the community, there is no consensus on the correct (or optimal) approach to estimate electrochemical reaction barriers. Although we cannot resolve the issue here, we want to summarize some of the key points driving this ongoing discussion.

Similar to reaction thermodynamics, electrochemical barriers depend on the applied potential (or, equivalently, the corresponding interfacial electric field). Changes to barrier energies $G^{\ddagger}(U_{\text{abs}})$ with potential are often quantified in terms of a symmetry factor, β in a linear-like manner relative to the barrier obtained at an absolute reference potential U_{abs}^1 as

$$G^{\ddagger}(U_{\text{abs}}) = G^{\ddagger}(U_{\text{abs}}^1) + \beta(U_{\text{abs}}) \cdot (U_{\text{abs}} - U_{\text{abs}}^1) \quad (1)$$

Nonlinearities are captured by allowing β to be potential dependent. The symmetry factor $\beta(U_{\text{abs}})$ is, however, *a priori* not known, and can vary (typically between 0 and 1). This can lead to large errors in the estimate of $G^{\ddagger}(U_{\text{abs}})$ —in particular when $(U_{\text{abs}} - U_{\text{abs}}^1)$ is large. Therefore, separate barrier calculations should be performed in the range of potentials of interest to estimate β .^{25,26}

To compute potential-dependent electrochemical reaction barriers, various approaches are available as summarized in Figure 2. Constant potential methods^{27–31} are often preferred over constant charge or constant electric field methods.³² The reason may be that constant potential methods do not require extrapolation to the infinite cell size limit in order to account for the applied (and thus constant) potential.^{33–35} However, constant potential approaches also have their own limitations.

First, one should ask whether individual electrochemical reaction events truly occur at constant potential. Santos and Schmickler³⁶ have recently challenged this assertion based on

the fact that time scales for double layer relaxation and the response time of the potentiostat can be much larger than the reaction time scale. Consequently, they argue that the reaction should proceed under constant charge conditions. It is debatable whether a single reaction event should actually change the potential—a macroscopic observable—or whether such a reaction-induced change in potential is an artifact of the periodic, relatively small unit cells used in DFT simulations. However, one fact remains: if the relaxation of solvent and ions are slow compared to the reaction time scale, reaction kinetics will be nonergodic,^{37,38} suggesting that, in these cases, the electrolyte should not be treated in thermodynamic equilibrium. As discussed in more detail in refs 37 and 39, this should not typically be an issue for activated processes with barriers above 0.2–0.3 eV in aqueous solvents but may play a role for non- or weakly activated reactions (as can be achieved by tuning the potential), large solutes, or in ionic liquids. Under these circumstances, conditions of thermodynamic equilibrium, as typically assumed in constant potential calculations (e.g., in JDFTx³⁰ or the reference interaction site method⁴⁰), are not necessarily met.

Second, and somewhat related to the issue above, at the microscopic scale, the potential (between a microscopic subpart of the surface and any position in space) as well as the surface charge fluctuate.⁴¹ This has to do with the RC-time scales of the capacitor and is similar to the temperature in an NVT ensemble, which should also fluctuate in small simulation cells. Potential fluctuations are not accounted for in most constant potential simulations. Adding them via a thermpotentiostat⁴² is possible but has restrictions as the time-scales of the fluctuations present in the real system are generally unknown. Additionally, in real systems, several physical effects causing fluctuations will play a role (e.g., surface conductivity, solvent fluctuations, ion diffusion, response of the potentiostat), causing fluctuations at different time-scales. To date, it is still an open question whether these fluctuations will affect relevant electrochemical reactions in an important way, but one may expect some influence, in particular, when reactions proceed fast enough to be able to react to the fluctuations.

Third, while constant potential methods guarantee the overall potential drop to be constant, the corresponding potential

profile may be incorrect. In particular, most (fully) implicit solvation schemes grossly underestimate the double layer capacitance,^b neglect its potential dependence,⁴⁵ and inaccurately predict the impact of electrolyte on the work function, as demonstrated in ref 44. This may contribute to an incorrect description of the interfacial electric field, which in turn can be expected to lead to inaccurate reaction energetics for adsorbed species with sizable dipole moments and for electrochemical barriers.

To obtain an improved description of the potential profile at the interface and to improve the description of the hydration of (species at) the interface, hybrid explicit + implicit (e+i) solvation schemes have been proposed.⁴⁴ In e+i models, the implicit solvation and countercharge are used to keep the potential constant. The explicit electrolyte molecules, on the other hand, hydrate the interface. This can be done statically, by combining microsolvation with implicit solvation,^{46,47} or dynamically, by allowing the explicit solvent to move via molecular dynamics simulations.⁴⁸ However, even in e+i schemes, certain caveats remain: (i) Depending on the solvation model, there may be an artificial potential drop at the explicit/implicit interface, either caused by artificial solvent alignment or a “gap” region. Such a potential drop will distort the relation between applied potential and surface electric field. The fact that e+i schemes often have a capacitance that is much lower ($\sim 10 \mu\text{F}/\text{cm}^2$)^{49–52} than that found in fully explicit models^{53,54} is an important indication that such an effect could play a role. (ii) In e+i schemes, double layer screening occurs only in the implicit solvent region. In particular for a wide explicit solvent region, this can be an important restriction. As a consequence, an electric field is also present in the entire explicit region, and any charged species in this region cannot move into the field-free region, possibly requiring the use of pseudo-initial or pseudo-final states when describing electrochemical reactions (see next section). (iii) Depending on the solvation model, implicit electrolyte may unphysically “leak” in between explicit electrolyte molecules. Some commonly used polarizable continuum models have recently introduced “solvent aware” cavity formation definitions which largely mitigate this issue.⁵⁵ (iv) Capacitance mismatch between the explicit and implicit electrolyte can lead to the grand canonical free energy being a poorly defined quantity at a given potential, manifesting as a finite cell-size effect.⁵⁶

The above-mentioned issues explain why fully explicit interface models, which are intrinsically at constant charge, are sometimes preferred. Unfortunately, these methods come with their own challenges, as summarized in Figure 2: (i) The use of a constant charge ensemble in small supercells requires approximate correction schemes that rely on the extraction of the (quantum-mechanically ill-defined) surface charge⁵⁷ or on the assumption that the charge rearrangement in the cell due to the reaction is equivalent to the recharging of the double layer.^{33,51} (ii) The computational cost for such simulations is excessively large, resulting in the use of harsh approximations in the computational setups as discussed later in this article. And (iii), even in these approaches, a charged particle cannot be rigorously brought into a field-free region due to the periodic repetition of a (typically small) unit cell, leading to an effective capacitive charging between the charged species and the surface, which in turn results in an incorrect electrostatic energy response.^c

To summarize, while constant charge approaches and constant potential approaches are equivalent in the infinite size limit,^{33–35} each approach comes with its own approx-

imations when used in practice. To date, it often remains unclear which of the approximations/omissions of a given model has the largest impact on the outcome of our simulations. It is our firm belief that, to ultimately find a consensus within the community as to the strengths and limitations of various methods, fundamental studies and (more)⁵⁷ rigorous method comparisons are needed.

Highlight 1: Overall, we believe that it is not so much a matter of constant potential vs constant charge methods, but rather the matter of constant potential and constant charge methods, as both approaches have their strengths and limitations (see Figure 2).

We believe that future work should provide a better understanding of (i) how the (local or mean-field) surface electric field or potential affect the energetics, (ii) when the (approximate) correction schemes for constant charge simulations in finite system sizes⁵⁷ break down, and (iii) which artifacts are caused by the use of small unit cells (e.g., overstructuring of water, unrealistic ion density profiles). The computational challenge or “hackathon” that was held during the Lorentz workshop was aimed at highlighting the need for such fundamental investigations, and raising awareness on issues related to the various approaches.

Interpreting Electrochemical Free Energy Diagrams. Once the reaction barriers are known, reaction rates can be predicted using microkinetic modeling. A qualitative analysis can also be obtained directly by analyzing free energy diagrams. However, we observed during the workshop that this is not as simple as it might seem. Part of the difficulty stems from the fact that free energy diagrams of electrochemical reactions are presented in different ways, depending on the approach used and the preferences of the authors involved in the study.

Another issue is that the variables included in the Gibbs free energy are often not clearly defined, and the differentiation between Gibbs free energies and standard Gibbs free energies is not clearly made. Results obtained from a CHE-based approach are generally reported as the Gibbs free energy (ΔG) of the different elementary reaction steps at 0 V vs RHE (i.e., versus the reversible hydrogen electrode) or at the U_{RHE} value corresponding to equilibrium conditions (i.e., when the overall reaction free energy $\Delta G_{\text{rxn}} = 0$). For barriers, however, one often plots the standard Gibbs free energy profile ($\Delta G^\circ(x)$) profile, i.e., the Gibbs free energy at standard conditions of all reactants and products as a function of the reaction coordinate x . This is a logical choice as this quantity is what “drops out” of a nudged-elastic band calculation^d and free energy sampling. However, the choice of G vs G° is often not clearly indicated. In addition, one should also distinguish between electronically grand canonical ($G(\mu_{\text{el}})$) and electronically canonical ($G(N_{\text{el}})$) energies. Various constant potential methods provide electronically grand-canonical energies as output, and the CHE and constant charge methods (with and without using correction schemes, such as the one proposed by Chan and Nørskov⁵⁷)^e are also consistent with electronically grand canonical energies, but the distinction between $G(\mu_{\text{el}})$ and $G(N_{\text{el}})$ is not always clearly made in papers. Finally, for electrochemical reactions or reactions containing species with a strong dipole, the (standard) Gibbs free energy profile will depend crucially on the applied potential versus vacuum or (equivalently) the initial surface charge. It should therefore go without saying that these conditions should be clearly indicated, which is, unfortunately, not always the case, and often such diagrams are (incorrectly) assigned to $U = 0$ V vs RHE or SHE (by the reader).

Highlight 2: Electrochemical literature would benefit from a clearer nomenclature: Clear distinctions between Gibbs free energies G , standard Gibbs free energies G° , and electronically grand canonical energies $G(\mu_e)$ vs electronically canonical energies $G(N_e)$ are needed. Additionally, the potential dependence of electrochemical free energy diagrams should be recognized and the potential (or surface charge), which they are estimated at, should be clearly stated.

An additional challenge in correctly interpreting Gibbs free energies obtained directly from barrier calculations is that charged reactants or products in solution (e.g., H^+ or OH^-) are generally not accurately captured in current computational approaches, as they often cannot be brought into a “bulk solution” region. Instead, calculations often suffer from (i) charge transfer to and from species that reside (too) close to the interface (offsetting the chemical energy at this “initial” (or “final” state) and (ii) the fact that the charged species do not reside in a field-free region (offsetting the electrostatic energy of the species) (see Figure 3). We refer to such states with residual

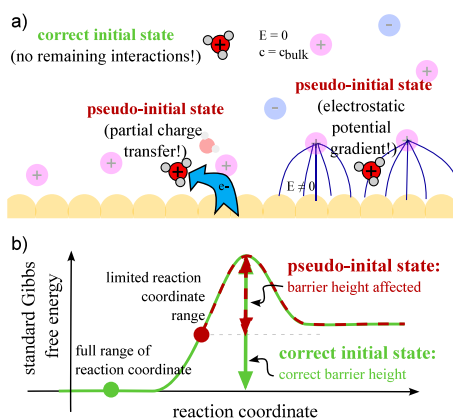


Figure 3. a) Schematic of possible causes for pseudo-initial states in simulations. The true initial state is characterized by the ion residing in a region where it does not interact with the electrode and the electric field is zero. For particles residing (too) close to the interface, charge transfer and electrostatic energy gradients can affect the reactant state and its energy. b) Sketch of a free energy diagram when using a correct initial state (green) vs a pseudo-initial state (red). The use of a pseudo-initial state will lead to incorrect barrier predictions and incorrect reaction free energies.

interactions to the catalyst surface as “pseudo-initial” or “pseudo-final” states. Considering such a pseudo-state as the initial or final state is equivalent to restricting the range of the reaction coordinate, such that the full elementary step will not be captured (see Figure 3b). This can lead to incorrect reaction barrier predictions (see Figure 3b) and reaction free energies that generally do not scale correctly with the applied potential, U . Unfortunately, when presenting free energy diagrams, this possible issue is often not considered: In typical AIMD simulation setups it is, strictly speaking, not even possible to bring a charged species into a field-free region (see also Figure 2). Similarly, in hybrid explicit + implicit methods, bringing charges into a field-free region is difficult because it would require moving the charged species from the explicit region to the implicit region. This would likely introduce other errors due to an unbalanced description of the solvation in the explicit and implicit regions. In how far the resulting pseudo-initial/final states will affect the actual result will depend on the exact computational setup. We assert that good practice requires one

to check for the possible presence of pseudo-initial or pseudo-final states. This can be achieved by studying a reaction that is expected to be well described by the CHE. By comparing reaction free energies and their dependence on the potential and pH as obtained using the CHE framework and the computational scheme in question, one should be able to identify issues arising from the presence of pseudo-states.

If a simulation is affected by the presence of a pseudo-state, one can choose to correct for it *a posteriori* by adjusting the initial or final states to those obtained from the CHE-model or, generally speaking, from a Born–Haber cycle. As an example, the Gibbs free energy of the pseudo-initial state $G(H^+@int|_{U_{abs}})$ in an acidic Volmer step should be replaced by

$$G(H^+_{(bulksol)} + int|_{U_{abs}}) = G^\circ(int|_{U_{abs}}) + \frac{1}{2}G^\circ(H_2) - eU_{RHE}$$

where $U_{RHE} = U_{abs} - U_{SHE,abs} + \frac{k_B T}{e} \ln(10)pH$ and $U_{SHE,abs} \approx 4.44$ V is the absolute potential of the standard hydrogen electrode.^f This has been done, for example, in refs 25 and 59–62.^g Obviously, this method will lead to errors whenever a reaction is ill-described within the CHE method. However, depending on whether the charged state is the reactant or product, such a shortcoming might not necessarily impact the magnitude of the barrier.

Interpreting Multistep Reactions. While reaction barriers are typically extracted in plots showing the standard free energy (see above), reaction networks and multistep reactions are often easier to analyze when plotting ΔG^\ddagger rather than $\Delta G^{\circ\ddagger}$. Using ΔG^\ddagger , the reaction rate of elementary steps involving bulk species can be written without explicit reference to the bulk concentrations

$$r = A \cdot \prod_i [i]^{u_i} \cdot e^{-\Delta G^{\circ\ddagger}/k_B T} = A \cdot e^{-\Delta G^\ddagger/k_B T} \quad (2)$$

which facilitates the identification of an “effective” barrier ΔG_{eff}^\ddagger that can be used to approximate the overall reaction rate (r) of a multistep reaction as

$$r \propto e^{-\Delta G_{eff}^\ddagger/k_B T} \quad (3)$$

It follows from textbook kinetics that ΔG_{eff}^\ddagger can be approximated by the largest free energy difference between any transition state (TS) and the Gibbs free energy of the resting state prior to this TS. This approximation will be reasonable as long as the adsorbate coverage in the resting state is stable. By comparing ΔG_{eff}^\ddagger for different reaction pathways, the most probable reaction pathways can be identified directly from the free energy diagrams. Figure 4 illustrates how to determine ΔG_{eff}^\ddagger using the example of an electrocatalytic oxidation reaction. As can be seen, it is not (necessarily) the elementary step with the highest activation energy that defines the rate of a reaction. Instead, it may be a series of steps that determine the effective barrier. The traditional limiting potential analysis,^{18,63} which is still widely used, does not account for this possible combined effect of several reaction steps. As a consequence, the limiting potential analysis is also unable to explain certain trends in product selectivity, for example in the oxygen reduction reaction^{48,64} and CO_2 reduction.⁶⁵ Although extremely simple and powerful, traditional limiting potential analysis should therefore be used with caution.^g

A characteristic of electrochemical free energy diagrams is not only that they can be used to predict effective barriers and the

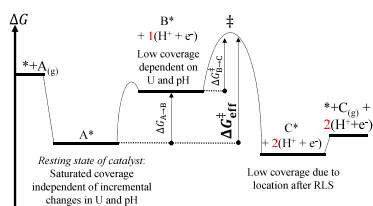


Figure 4. A sample free energy profile for a two-step electrocatalytic oxidation of $A_{(g)}$ to $C_{(g)}$ with the effective barrier $\Delta G_{\text{eff}}^{\ddagger}$ approximated as the largest free energy difference between the transition state and the resting state (A^*). The exergonic adsorption of $A_{(g)}$ results in a sizable coverage of A^* , making it the resting state of the catalyst. The free energy of B^* is irrelevant to the rate of the reaction as long as $\Delta G_{A \rightarrow B} > 0$ and its barrier is not as high as that of the next step. Finally, the free energy of C^* also does not affect r , as it is located after rate-limiting step of the reaction.

most probable reaction pathways but also that the same diagrams can also be used to predict Tafel slopes and pH dependencies of the reaction rate.^{52,66}

Within the effective-barrier approximations, the Tafel slope is given by

$$\left(\frac{\partial \log(r/r_0)}{\partial U} \right)^{-1} \Bigg|_{\text{pH}} = \frac{\ln(10)k_B T}{N_{\text{ec}} + \beta_{\text{RLS}}} \quad (4)$$

where N_{ec} is the number of equilibrated steps involving the creation or annihilation of an ion–electron pair (including proton–electron pairs) between the resting state and the rate-limiting step, and β_{RLS} is the symmetry factor.^{52,66}

The pH dependence is given by

$$\frac{\partial \log(r)}{\partial \text{pH}} \Bigg|_{U_{\text{abs}}} = \pm N_{\text{pe}} + N_{\text{OH}^-, \text{ini}} - N_{\text{H}^+, \text{ini}} \quad (5)$$

where \pm refers to oxidation (+) or reduction (−), N_{pe} is the number of equilibrated steps involving the creation or annihilation of proton–electron pair *only* between the resting state and the rate-limiting step, and $N_{\text{OH}^-, \text{ini}}$ ($N_{\text{H}^+, \text{ini}}$) are the number of OH^- (H^+) ions involved as reactants in the rate limiting step.⁵²

These relations can, on the one hand, be used to verify theoretically predicted reaction mechanisms by comparing them to experimental results where available but can, on the other hand, also serve to extract mechanistic insight (e.g., the number of involved ion–electron transfer pairs vs the number of involved proton–electron transfer pairs and the symmetry factor) directly from experimental results. In this regard we note, though, that experimental Tafel slopes should be treated with care as they are relatively prone to errors due to mass transport limitations and bubble formation.⁶⁹

Overall, it is clear that even such a qualitative analysis of free energy diagrams can provide important insights into electrochemical reaction kinetics. To allow for a reuse and reanalysis of data provided in papers, we repeat, however, our earlier statement that care should be taken to clearly indicate what is plotted [e.g., G° vs G and $G(\mu_{\text{el}})$ vs $G(N_{\text{el}})$]. Additionally, it is important to ensure consistency throughout the free energy profile (i.e., keeping the number of particles involved constant throughout the entire free energy diagram).

Microkinetic Modeling. Whenever a qualitative assessment outlined in the previous section is not sufficient to predict

reaction rates or understand reaction mechanisms,ⁱ one needs to resort to microkinetic (MK) modeling.

In spite of the difficulty in obtaining reliable reaction barriers from first-principles based approaches, both “bottom-up” models^{52,60,70–72} (using barriers obtained from first-principles calculations) and “top-down” models (in which certain model parameters are fitted to reproduce experimental results) are used to understand reaction kinetics.^{70,73} The latter approach goes back more than half a century⁷⁴ and has been used successfully to rationalize various experimental observations in electrocatalysis.^{75–78} A difficulty, however, is to make a decision on the complexity of the model employed. A fundamental choice lies in the description of the reaction network (e.g., as one, overall reaction with an effective barrier, or using individual reaction steps), and the description of the potential dependency (e.g., via Butler–Volmer type relations, Marcus theory, or by including potential-dependent barriers from DFT calculations). Another choice in the complexity of the model lies in whether parallel reaction networks are considered to account for multiple active sites or (mean-field) lateral interactions between adsorbates. Deciding on the choice of the MK model without detailed insights from first-principles calculations is nontrivial, and it seems to be “best practice” to keep the model as simple as possible so that they are computationally tractable and to avoid potential overfitting.^{79,80}

Mean-field MK models typically struggle in systems where spatial correlations play an important role. Examples include island formation, steric exclusion effects (including those caused by multidentate species), complex reaction patterns involving adsorbates in specific arrangements or oscillatory dynamics, such as the formation of complex, long-range spatiotemporal patterns.⁸¹ Accounting for such effects requires moving beyond mean-field approaches toward kinetic Monte Carlo based methods.^{82,83}

Mass Transport and Electrokinetic Phenomena. Measured current densities during electrochemical processes often depend on the mass transport properties of the reactor. The simplest model to account for mass transport effects is a (1D) reaction–diffusion model that accounts for Fickian diffusion of species across a boundary layer. To further account for electromigration of charged species (e.g., ions) that are relevant in the formation of the electrical double layer, Poisson–Nernst–Planck (PNP) and its size-modified version (GMPNP) have been used in a number of studies.^{84,85} These models can further be coupled to reaction fluxes obtained from ab initio based microkinetic models and include solution phase reactions (e.g., buffer reactions in CO_2R) in a self-consistent manner to develop “bottom-up” multiscale models.^{85,86} Although diffusion and electromigration have been accounted for in previous studies, discussions during the workshop highlighted that electrokinetic phenomena are not generally considered.

Highlight 3: In computational electrochemistry, electrokinetic transport phenomena are often neglected despite their potential relevance.

Electrokinetic phenomena include electro-osmotic flow (fluid flow due to a body force on the nonzero charge density of mobile ions in the electric double layer) and streaming currents (electric currents caused by a pressure-induced flow of mobile charges in the electric double layer). These effects could play a significant role in transport-dominated regimes of electrochemical processes. Recent studies show that fluid flow can directly couple to the chemical processes at the surface,⁸⁷ resulting in initially homogeneous surfaces to become heterogeneous with a

charge-density gradient in the flow direction.^{88,89} Similarly, an applied potential drop across cone-shaped channels (which are omnipresent in many porous materials) can yield ionic accumulation and depletion in the channel depending on the polarity of the applied voltage,^{90,91} and can thereby affect the surface chemistry.⁹² Exploring these electrokinetic and iontronic effects might thus be important in the development of multiscale models.

To ultimately compare the results from modeling studies to experiments and develop accurate insights into electrochemical processes, it is essential to transition from modeling reaction kinetics to *reactor kinetics* that requires the consideration of complex mass transport and electrokinetic phenomena in multiscale models of electrochemical processes.

Benchmarking Computational Approaches. To identify the similarities, differences, strengths, and weaknesses of the various (multiscale) modeling approaches currently available, thorough method comparisons are urgently needed. During the workshop, the possibility of curating a standardized test set was discussed. However, we identified several issues with the idea of a “universal benchmark”.

First, for most electrochemical processes, the “ground truth” is unknown. Experimental studies are often unsuitable as benchmarks due to the convolution of several effects (e.g., surface restructuring, impurities at the electrode surface or in the electrolyte, mass transport effects, double layer effects, etc.). Therefore, using typical experimental results to validate simulations would require the consideration of all these effects, increasing the complexity of the model beyond what is currently possible. Perhaps an easier option would be to compare results with more accurate, albeit more expensive methods. However, in computational electrochemistry, such methods generally do not exist. For example, there is no atomic scale model that can accurately capture charge transfer processes within a realistic representation of the double layer. In fact, we do not even fully understand all the effects relevant to double layers.⁹³

A second issue in defining a universal benchmark set is that different methods make substantially different approximations and often target different effects. Developing a balanced test set that all methods should pass therefore seems hard, if not impossible. Yet, it is exactly this wealth of different approximations that makes thorough benchmarking all the more important: otherwise the implications of certain approximations may not be recognized. The development of a universal test set may thus be ambitious, but there are good examples of tests/checks that could be performed for a wide class of methods used in computational electrochemistry. One example would be to check for the presence of pseudo-states that impact the computed reaction thermodynamics as described in the previous section.

At the workshop, it was broadly recognized that we as a community often fail to perform a thorough validation of methods used. We believe that this is a result of our strive to provide chemical insight into relevant processes and the societal urgency of these insights.

Highlight 4: To develop computational electrochemistry into a mature field and to avoid misinterpretations and incorrect conclusions, better method comparisons are needed—with benchmarks between different groups and to experiment whenever possible.

In particular, we believe that collaborative efforts in which different research groups approach the same question using different techniques (as sometimes published in the past) are

extremely valuable. Such efforts, together with pedagogical studies that highlight the successes, failures, pitfalls, and opportunities of the different methods would serve as valuable guides for practitioners in the field.

Similar considerations also pertain to the computational setups used. In particular in atomistic modeling studies, we tend to make harsh practical decisions based on the computational cost. While this is often necessary, it is sometimes done without sufficient testing and without reporting the expected errors incurred due to these practical decisions.

For example, simulations aimed at estimating the potential of zero charge (PZC) of electrode–electrolyte interfaces are typically performed in small unit cells using the Γ -point only when sampling the Brillouin zone. For small (4×4) unit cells, this can lead to errors of several hundred meV in the work function (see Figure 5). These errors will directly translate into

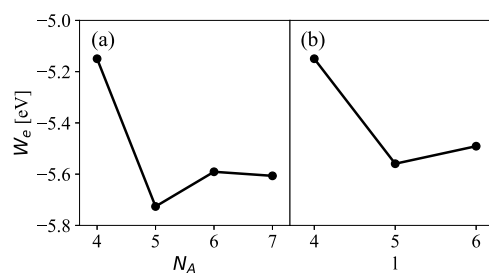


Figure 5. Dependence of the negative of the workfunction, W_e , of Pt(100) on (a) the number of atoms, N_A , in a $N_A \times N_A$ atom unit cell and (b) as a function of the number of layers l in the slab when only the Γ -point is considered during k-point averaging. The workfunction can change dramatically (several hundreds of meV) depending on the exact setup and can hence differ strongly from the true value. ($l = 4$ in panel a, and $N_A = 4$ in panel b.) This figure is reproduced from the Supporting Information of ref 94.

errors in the computed PZC but are often not discussed. Similarly, it is telling that it took until 2022 until the hot solvent–cold solute problem was discussed in the community.⁹⁵ This thermostatting issue (that can occur for certain thermostats/thermostat settings) can cause the solvent to be hotter than the more rigid solute. Since the catalytic region can be considered as a “solute”, this problem can impact interface simulations. Overall, we believe that some more rigor in the use of methods could be beneficial.

To close on a positive note, we would like to highlight some studies that do discuss such epistemic errors (i.e., errors caused by limited or inaccurate knowledge of the system). At the atomic scale, Calle-Vallejo et al.⁹⁶ discussed errors in energies of gas-phase species incurred when using commonly used DFT exchange-correlation functionals and their influence on activity-volcano relationships of electrocatalysts. Kastlunger et al.³³ and Hörmann et al.³⁴ independently derived the equivalence of constant potential vs constant charge in the infinite cell size limit and identified various practical limitations in both approaches. Deißbeck et al.⁴¹ compared the dynamics under constant potential conditions with that obtained when including charge-potential fluctuations. For microkinetic modeling, Reiher and co-workers investigated the uncertainties in complex reaction networks.⁹⁷ Finally, the uncertainty in transport models has mainly been addressed in the fields of lithium-ion batteries^{98,99} and polymer electrolyte fuel cells.¹⁰⁰ This list is far from exhaustive but highlights the valuable contribution of systematic studies on model uncertainties, as

well as the impact of these uncertainties on the prediction of key properties. In the future, we anticipate that there will (and should) be more studies on epistemic errors in computational electrochemistry.

Concluding Remarks. In summary, we have discussed the existing challenges and ongoing discussions in computational approaches to study electrochemical processes and, where appropriate, suggested a path forward.

The field of computational electrochemistry is relatively young and marked by a proliferation of methods. However, for computational electrochemistry to evolve toward a mature field, the strengths and limitations of the various methods need to be thoroughly understood, and clear guidelines for the various approaches need to be established. In doing so, we strongly believe that computational electrochemistry will play a crucial role in developing a thorough understanding of electrochemical processes from the atomistic to the system level.

AUTHOR INFORMATION

Corresponding Author

Katharina Doblhoff-Dier – *Leiden Institute of Chemistry, Leiden University, 2300RA Leiden, The Netherlands;* orcid.org/0000-0002-5981-9438; Email: k.doblhoff-dier@lic.leidenuniv.nl

Authors

Nitish Govindarajan – *School of Chemistry, Chemical Engineering and Biotechnology, Nanyang Technological University, Singapore 637371, Singapore;* orcid.org/0000-0003-3227-5183

Georg Kastlunger – *Catalysis Theory Center, Department of Physics, Technical University of Denmark (DTU), 2800 Kgs. Lyngby, Denmark;* orcid.org/0000-0002-3767-8734

Joseph A. Gauthier – *Department of Chemical Engineering, Texas Tech University, Lubbock, Texas 79409, United States;* orcid.org/0000-0001-9542-0988

Jun Cheng – *State Key Laboratory of Physical Chemistry of Solid Surfaces, iChEM, College of Chemistry and Chemical Engineering and Institute of Artificial Intelligence, Xiamen University, Xiamen 361005, China; Laboratory of AI for Electrochemistry (AI4EC), IKKEM, Xiamen 361005, China;* orcid.org/0000-0001-6971-0797

Ivo Filot – *Laboratory of Inorganic Materials and Catalysis, Department of Chemistry and Chemical Engineering, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands;* orcid.org/0000-0003-1403-8379

Arthur Hagopian – *Leiden Institute of Chemistry, Leiden University, 2300RA Leiden, The Netherlands*

Heine Anton Hansen – *Department of Energy Conversion and Storage, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark;* orcid.org/0000-0001-7551-9470

Jun Huang – *Forschungszentrum Jülich GmbH, Institute of Energy Technologies, 52425 Jülich, Germany;* orcid.org/0000-0002-1668-5361

Piotr M. Kowalski – *Forschungszentrum Jülich GmbH, Institute of Energy Technologies, 52425 Jülich, Germany;* orcid.org/0000-0001-6604-3458

Jinwen Liu – *Leiden Institute of Chemistry, Leiden University, 2300RA Leiden, The Netherlands*

Juan M. Lombardi – *Fritz-Haber-Institut der Max-Planck-Gesellschaft, 14195 Berlin, Germany*

Mikael Maraschin – *Department of Chemical Engineering, Texas Tech University, Lubbock, Texas 79409, United States*

Andrew Peterson – *School of Engineering, Brown University, Providence, Rhode Island 02912, United States; Department of Energy Conversion and Storage, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark;* orcid.org/0000-0003-2855-9482

Hemanth S. Pillai – *Fritz-Haber-Institut der Max-Planck-Gesellschaft, 14195 Berlin, Germany*

Hector Prats – *Department of Chemistry, Physical and Theoretical Chemistry Laboratory, University of Oxford, Oxford OX1 3QZ, U.K.;* orcid.org/0000-0003-4991-253X

Conor J. Price – *Forschungszentrum Jülich GmbH, Institute of Energy Technologies, 52425 Jülich, Germany;* orcid.org/0000-0002-1430-3294

René van Roij – *Institute for Theoretical Physics, Utrecht University, Utrecht 3584, The Netherlands*

Jan Rossmesl – *Center for High Entropy Alloy Catalysis, Department of Chemistry, University of Copenhagen, Copenhagen DK-2100, Denmark;* orcid.org/0000-0001-7749-6567

Ranga Rohit Seemakurthi – *Institute of Chemical Research of Catalonia (ICIQ-CERCA), The Barcelona Institute of Science and Technology, Tarragona 43007, Spain;* orcid.org/0000-0001-8523-4129

Seung-Jae Shin – *School of Energy and Chemical Engineering, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Republic of Korea;* orcid.org/0000-0002-5530-4453

Audrey Smith – *School of Engineering, Brown University, Providence, Rhode Island 02912, United States*

Jia-Xin Zhu – *State Key Laboratory of Physical Chemistry of Solid Surfaces, iChEM, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China;* orcid.org/0000-0002-3471-4728

Complete contact information is available at: <https://pubs.acs.org/10.1021/acsenerylett.5c00748>

Author Contributions

△△N.G., G.K., and J.A.G. contributed equally to this work.

Notes

The authors declare no competing financial interest.

Biographies

Nitish Govindarajan is an Assistant Professor at NTU Singapore. His group (DELI Lab) is interested in using atomistic simulations to understand electrochemical interfaces for applications in energy storage and conversion.

Georg Kastlunger is an Associate Professor at the Technical University of Denmark. Following research at the University of Vienna and Brown University, he founded his group in 2023. He seeks to enhance the atomic-scale understanding of electrocatalysis via density functional and transition state theory, addressing CO₂, waste, and biomass valorization.

Joseph A. Gauthier is an Assistant Professor of Chemical Engineering at Texas Tech University. He received his Ph.D. from Stanford University in 2020 under Professor Jens Nørskov and spent one year as a postdoctoral scholar with Professors Alex Bell and Martin Head-Gordon at UC Berkeley/LBNL before joining TTU in 2021.

Jun Cheng is Professor in Chemistry at Xiamen University. His group develops computational methods to simulate electrochemical interfaces and catalyst dynamics. He is a Deputy Editor of The Journal of Chemical Physics and has received the Alexander Kuznetsov Prize for

Theoretical Electrochemistry of the International Society of Electrochemistry.

Ivo Filot focuses on multiscale modeling of heterogeneous catalysts, with a particular emphasis on supported nanoparticle systems. His research seeks to bridge atomic-scale structure and macroscopic performance, enabling the rational design of advanced catalytic materials. Through predictive computational chemistry, he contributes to the development of sustainable chemical technologies.

Arthur Hagopian is a Postdoctoral Researcher at Leiden University specializing in computational electrochemistry. His work focuses on *ab initio* simulations of electrochemical interfaces, including double-layer capacitance, hydrogen adsorption, and solvation phenomena within the electrochemical double-layer region.

Heine Anton Hansen is an Associate Professor at DTU Energy. He did his Ph.D. at DTU and was a post doc at Northwestern University and at Stanford University. His work focuses on atomic scale modeling of processes at electrochemical interfaces in fuel cells and electrolyzers.

Jun Huang leads a Helmholtz Young Investigators Group in Juelich Research Center and teaches as a Junior Professor at RWTH Aachen University, Germany. His team works mainly on developing density-potential functional theoretic methods for understanding thermodynamics and nonequilibrium dynamics of electrocatalytic double layers, especially on the mesoscale.

Piotr M. Kowalski is the head of Computational Materials Modelling division in IET-3 institute at Forschungszentrum Jülich. He obtained his Ph.D. from Vanderbilt U./LANL. His research focuses on atomistic simulations of energy materials. He has published >100 papers in variety of research fields, including electrochemistry, geoscience, nuclear materials and astrophysics.

Jinwen Liu holds a B.Sc. in chemical engineering (2019) and a M.Sc. degree in physical chemistry (2022). He is currently a Ph.D. student at Leiden University, supervised by Marc Koper and Katharina Doblhoff-Dier. His research interest is theoretical understanding of electrochemical double layer and its impact on electrocatalysis.

Juan M. Lombardi is a Postdoctoral Researcher at the Max Planck Institute for Solid State Research. He earned his Ph.D. in Physics from the University of Rosario, Argentina. His research encompasses electrochemical modeling, machine-learning methods, and computational materials design.

Mikael Maraschin is a Ph.D. candidate in Chemical Engineering at Texas Tech University, working under the guidance of Assistant Professor Joe Gauthier.

Andrew Peterson is an Associate Professor in the School of Engineering at Brown University in Providence, Rhode Island. His research focuses on the theory of reactions at electrified interfaces.

Hemanth S. Pillai earned his Ph.D. in Chemical Engineering from Virginia Tech, where he worked with Dr. Hongliang Xin on leveraging machine learning to accelerate catalyst discovery. He is now a postdoc at the Fritz Haber Institute's theory department, studying how catalyst morphology affects selectivity in electrocatalysis with Dr. Vanessa Bukas.

Hector Prats is a Postdoctoral Fellow at TU Wien with expertise in density functional theory and Kinetic Monte Carlo simulations. He develops and applies computational tools to investigate surface reaction mechanisms and design improved catalytic materials for sustainable processes.

Conor J. Price is a Postdoctoral Researcher at Forschungszentrum Jülich. He obtained his Ph.D. in physics from the University of Exeter in

2023. His research interest is in using high performance computing and atomistic modelling to investigate electrochemical processes in materials for energy applications."

René van Roij, professor of Soft-Matter Theory at Utrecht University, has a background in developing theories for equilibrium thermodynamics and structure of liquid crystals, colloidal dispersions, and electrolytes, often using classical DFT. Recent extensions include theories for nonequilibrium phenomena such as iontronics, microfluidics, blue energy, neuromorphic computing, and electrochemistry.

Jan Rossmel is Professor at Department of Chemistry at University of Copenhagen. Since 2020 he is heading a Danish National Research Foundation center, Center for High Entropy Alloy Catalysis and in 2024 he received an ERC synergy grant together with three others. Jan is coauthor on more than 250 papers.

Ranga Rohit Seemakurthi obtained his Ph.D. in 2021 from Purdue University under the supervision of Prof. Jeffrey Greeley. He is currently a Postdoctoral Fellow with Prof. Núria López at the Institute of Chemical Research of Catalonia (ICIQ), Tarragona. His research focuses on developing multiscale models for heterogeneous catalytic processes.

Seung-Jae Shin is an Assistant Professor at Ulsan-National-Institute-of-Science and Technology (UNIST). His research interests include electrochemical catalysis, energy storage, and materials chemistry with physical chemistry theory and multiscale simulation. He was a postdoctoral researcher at Yonsei university and Imperial college london. He obtained his Ph.D. in Chemistry from Korea-Advanced-Institute-of- Science and Technology (KAIST).

Audrey Smith is PhD student in the group of Andrew Peterson, where she is also a Draper Scholar. She received her undergraduate degree at the University of Maine.

Jia-Xin Zhu is a Ph.D. student at the college of chemistry and chemical engineering, Xiamen University, under the supervisor of Prof. Jun Cheng. Her research interest is to investigate the electrochemical interfaces based on molecular dynamics simulations with machine learning potentials.

Katharina Doblhoff-Dier is Assistant Professor at Leiden University. Her group exploits a wide range of computational and theoretical approaches to study processes occurring at solid/liquid interfaces on the atomic and micro-scale. The webpage of her group can be found at <https://www.universiteitleiden.nl/en/staffmembers/katharina-doblhoff-dier>.

ACKNOWLEDGMENTS

The organizers of the 2024 Lorentz center workshop on *Multiscale modeling of electrochemical processes* (Katharina Doblhoff-Dier, Nitish Govindarajan and Georg Kastlunger) thank the Lorentz center for financial support and an excellent organization of the workshop. They also thank all workshop participants for their contributions. The organizers furthermore gratefully acknowledge financial support for the workshop by Leiden University, the Technical University of Denmark, and the Software for Chemistry & Materials B.V. (SCM) (Amsterdam, The Netherlands). This work was sponsored by NWO - Domain Science for the use of supercomputer facilities. Generative AI tools (<https://chatgpt.com/>) were used to suggest improvements of some of the phrasings in the paper.

ADDITIONAL NOTES

"E.g., a double-layer capacitance that is typically much lower than in experiments or in *ab initio* molecular dynamics

simulations, the difficulty of smoothly connecting QM and MM water molecules, and the difficulty of charging up the QM cluster in response to changes in the MM part of the simulation cell.

^bNote that some recent works show ESM-RISM⁴⁰ to correctly predict the measured double layer capacitance.^{43,44}

^cNote that the magnitude of errors might be small, depending on the distance of the charged particle from the surface and the potential profile generated. We are unaware of rigorous tests published in this regard.

^dAfter accounting for vibrational and rotational enthalpy and entropy effects.

^eI.e., there is no need to subtract an additional term $\Delta n\mu_e(U)$ to account for the effective change in number of electrons Δn required to keep the potential constant. In the CHE and constant charge methods, this is done by accounting for the electrons as reactants/products.

^fWe note that this scheme cannot be rigorously applied for barriers obtained from free energy sampling (e.g., slow-growth, metadynamics, etc.), as, in this case, the Gibbs free energy of the interface is unknown. Accessing it would require the use of computationally expensive insertion–deletion methods.⁵⁸ One may, however, expect the influence of pseudo-states to be somewhat reduced as charges species can be brought further away from the surface. A rigorous proof for this statement is, to the authors knowledge, however missing to date.

^gNote that the y -axis labels in several studies read G° . It should, however, be G for any species related to bulk concentrations and G° for adsorbed species, leading to a somewhat mixed representation.

^hThe symmetry factor is often approximated to be 0.5 but can also be estimated following a plethora of schemes.^{56,57,66–68}

ⁱE.g., if the coverage of reactants in the resting state is not constant or the resting state cannot be unambiguously identified.

REFERENCES

- (1) Center for Scientific Workshops in All Disciplines - Multiscale Modeling of Electrochemical Processes. <https://www.lorentzcenter.nl/multiscale-modeling-of-electrochemical-processes.html>, Accessed: 2025-05-13.
- (2) Hibbitts, D.; Dybeck, E.; Lawlor, T.; Neurock, M.; Iglesia, E. Preferential Activation of CO near Hydrocarbon Chains during Fischer–Tropsch Synthesis on Ru. *J. Catal.* **2016**, *337*, 91–101.
- (3) Papanikolaou, K. G.; Shi, Y.; Schimmenti, R.; Xia, Y.; Mavrikakis, M. The Role of Coverage Effects on the Structure–Sensitivity of Formic Acid Electrooxidation on Pd Surfaces. *J. Catal.* **2023**, *417*, 408–420.
- (4) Li, Y.-F.; Li, J.-L.; Liu, Z.-P. Structure and Catalysis of NiOOH: Recent Advances on Atomic Simulation. *J. Phys. Chem. C* **2021**, *125*, 27033–27045.
- (5) Chen, B. W. J.; Mavrikakis, M. How Coverage Influences Thermodynamic and Kinetic Isotope Effects for H₂/D₂ Dissociative Adsorption on Transition Metals. *Catalysis Science & Technology* **2020**, *10*, 671–689.
- (6) Neurock, M.; Pallassana, V.; van Santen, R. A. The Importance of Transient States at Higher Coverages in Catalytic Reactions. *J. Am. Chem. Soc.* **2000**, *122*, 1150–1153.
- (7) Dahl, S.; Logadottir, A.; Egeberg, R. C.; Larsen, J. H.; Chorkendorff, I.; Törnqvist, E.; Nørskov, J. K. Role of Steps in N₂ Activation on Ru(0001). *Phys. Rev. Lett.* **1999**, *83*, 1814–1817.
- (8) Opalka, D.; Scheurer, C.; Reuter, K. Ab Initio Thermodynamics Insight into the Structural Evolution of Working IrO₂ Catalysts in Proton-Exchange Membrane Electrolyzers. *ACS Catal.* **2019**, *9*, 4944–4950.
- (9) Huang, J.; Hörmann, N.; Oveisi, E.; Loidice, A.; De Gregorio, G. L.; Andreussi, O.; Marzari, N.; Buonsanti, R. Potential-Induced Nanoclustering of Metallic Catalysts during Electrochemical CO₂ Reduction. *Nat. Commun.* **2018**, *9*, 3117.
- (10) Yu, H.; Govindarajan, N.; Weitzner, S. E.; Serra-Maia, R. F.; Akhade, S. A.; Varley, J. B. Theoretical Investigation of the Adsorbate and Potential-Induced Stability of Cu Facets During Electrochemical CO₂ and CO Reduction. *ChemPhysChem* **2024**, *25*, No. e202300959.
- (11) Strbac, S.; Hamelin, A.; Adžić, R. R. Electrochemical Indication of Surface Reconstruction of (100), (311) and (111) Gold Faces in Alkaline Solutions. *J. Electroanal. Chem.* **1993**, *362*, 47–53.
- (12) Seitz, L. C.; Dickens, C. F.; Nishio, K.; Hikita, Y.; Montoya, J.; Doyle, A.; Kirk, C.; Vojvodic, A.; Hwang, H. Y.; Nørskov, J. K.; Jaramillo, T. F. A Highly Active and Stable IrO_x/SrIrO₃ Catalyst for the Oxygen Evolution Reaction. *Science* **2016**, *353*, 1011–1014.
- (13) Greeley, J. Structural Effects on Trends in the Deposition and Dissolution of Metal-Supported Metal Adstructures. *Electrochim. Acta* **2010**, *55*, 5545–5550.
- (14) Greeley, J.; Nørskov, J. K. Electrochemical Dissolution of Surface Alloys in Acids: Thermodynamic Trends from First-Principles Calculations. *Electrochim. Acta* **2007**, *52*, 5829–5836.
- (15) Hansen, H. A.; Rossmeisl, J.; Nørskov, J. K. Surface Pourbaix Diagrams and Oxygen Reduction Activity of Pt, Ag and Ni(111) Surfaces Studied by DFT. *Phys. Chem. Chem. Phys.* **2008**, *10*, 3722–3730.
- (16) Ulissi, Z. W.; Singh, A. R.; Tsai, C.; Nørskov, J. K. Automated Discovery and Construction of Surface Phase Diagrams Using Machine Learning. *J. Phys. Chem. Lett.* **2016**, *7*, 3931–3935.
- (17) Bang, K.; Hong, D.; Park, Y.; Kim, D.; Han, S. S.; Lee, H. M. Machine Learning-Enabled Exploration of the Electrochemical Stability of Real-Scale Metallic Nanoparticles. *Nat. Commun.* **2023**, *14*, 3004.
- (18) 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*, 17886–17892.
- (19) Murata, A.; Hori, Y. Product Selectivity Affected by Cationic Species in Electrochemical Reduction of CO₂ and CO at a Cu Electrode. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 123–127.
- (20) Goyal, A.; Koper, M. T. M. The Interrelated Effect of Cations and Electrolyte pH on the Hydrogen Evolution Reaction on Gold Electrodes in Alkaline Media. *Angew. Chem., Int. Ed.* **2021**, *60*, 13452–13462.
- (21) Govindarajan, N.; Kastlunger, G.; Heenen, H. H.; Chan, K. Improving the Intrinsic Activity of Electrocatalysts for Sustainable Energy Conversion: Where Are We and Where Can We Go? *Chemical Science* **2021**, *13*, 14–26.
- (22) Bender, J. T.; Petersen, A. S.; Østergaard, F. C.; Wood, M. A.; Heffernan, S. M. J.; Milliron, D. J.; Rossmeisl, J.; Resasco, J. Understanding Cation Effects on the Hydrogen Evolution Reaction. *ACS Energy Letters* **2023**, *8*, 657–665.
- (23) Bender, J. T.; Sanspeur, R. Y.; Valles, A. E.; Uvodich, A. K.; Milliron, D. J.; Kitchin, J. R.; Resasco, J. The Potential of Zero Total Charge Predicts Cation Effects for the Oxygen Reduction Reaction. *ACS Energy Letters* **2024**, *9*, 4724–4733.
- (24) Shin, S.-J.; Choi, H.; Ringe, S.; Won, D. H.; Oh, H.-S.; Kim, D. H.; Lee, T.; Nam, D.-H.; Kim, H.; Choi, C. H. A Unifying Mechanism for Cation Effect Modulating C1 and C2 Productions from CO₂ Electroreduction. *Nat. Commun.* **2022**, *13*, 5482.
- (25) Lindgren, P.; Kastlunger, G.; Peterson, A. A Challenge to the $G \sim 0$ Interpretation of Hydrogen Evolution. *ACS Catal.* **2020**, *10*, 121–128.
- (26) Chen, X.; Kastlunger, G.; Peterson, A. A. Fundamental Drivers of Electrochemical Barriers. *Phys. Rev. Lett.* **2023**, *131*, 238003.
- (27) Kastlunger, G.; Lindgren, P.; Peterson, A. A. Controlled-Potential Simulation of Elementary Electrochemical Reactions: Proton Discharge on Metal Surfaces. *J. Phys. Chem. C* **2018**, *122*, 12771–12781.
- (28) Rezwanul Islam, S. M.; Khezeli, F.; Ringe, S.; Plaisance, C. An implicit electrolyte model for plane wave density functional theory exhibiting nonlinear response and a nonlocal cavity definition. *J. Chem. Phys.* **2023**, No. 234117.

- (29) Hörmann, N. G.; Andreussi, O.; Marzari, N. Grand Canonical Simulations of Electrochemical Interfaces in Implicit Solvation Models. *J. Chem. Phys.* **2019**, *150*, 041730.
- (30) Sundararaman, R.; Letchworth-Weaver, K.; Schwarz, K. A.; Gunceler, D.; Ozhables, Y.; Arias, T. A. JDFTx: Software for Joint Density-Functional Theory. *SoftwareX* **2017**, *6*, 278–284.
- (31) Islam, S. M. R.; Khezeli, F.; Ringe, S.; Plaisance, C. An Implicit Electrolyte Model for Plane Wave Density Functional Theory Exhibiting Nonlinear Response and a Nonlocal Cavity Definition. *J. Chem. Phys.* **2023**, *159*, 234117.
- (32) Luan, D.; Xiao, J. Adaptive Electric Fields Embedded Electrochemical Barrier Calculations. *J. Phys. Chem. Lett.* **2023**, *14*, 685–693.
- (33) Kastlunger, G.; Vijay, S.; Chen, X.; Sharma, S.; Peterson, A. On the Thermodynamic Equivalence of Grand Canonical, Infinite-Size, and Capacitor-Based Models in First-Principle Electrochemistry. *ChemPhysChem* **2024**, *25*, No. e202300950.
- (34) Hörmann, N. G.; Beinlich, S. D.; Reuter, K. Converging Divergent Paths: Constant Charge vs Constant Potential Energetics in Computational Electrochemistry. *J. Phys. Chem. C* **2024**, *128*, 5524–5531.
- (35) Domínguez-Flores, F.; Melander, M. M. Approximating Constant Potential DFT with Canonical DFT and Electrostatic Corrections. *J. Chem. Phys.* **2023**, *158*, 144701.
- (36) Santos, E.; Schmickler, W. On the Timescale of Electrochemical Processes. *Electrochim. Acta* **2024**, *498*, 144659.
- (37) Matyushov, D. V.; Newton, M. D. Electrode Reactions in Slowly Relaxing Media. *J. Chem. Phys.* **2017**, *147*, 194506.
- (38) Matyushov, D. V. Nonergodic Activated Kinetics in Polar Media. *J. Chem. Phys.* **2009**, *130*, 164522.
- (39) Melander, M. M. Frozen or Dynamic? — An Atomistic Simulation Perspective on the Timescales of Electrochemical Reactions. *Electrochim. Acta* **2023**, *446*, 142095.
- (40) Nishihara, S.; Otani, M. Hybrid Solvation Models for Bulk, Interface, and Membrane: Reference Interaction Site Methods Coupled with Density Functional Theory. *Phys. Rev. B* **2017**, *96*, 115429.
- (41) Deißbeck, F.; Wippermann, S. Dielectric Properties of Nanoconfined Water from Ab Initio Thermopotentiostat Molecular Dynamics. *J. Chem. Theory Comput.* **2023**, *19*, 1035–1043.
- (42) Deißbeck, F.; Freysoldt, C.; Todorova, M.; Neugebauer, J.; Wippermann, S. Dielectric Properties of Nanoconfined Water: A Canonical Thermopotentiostat Approach. *Phys. Rev. Lett.* **2021**, *126*, 136803.
- (43) Kowalski, P. M.; Bornhake, T.; Cheong, O.; Dohrmann, N.; Koch Liston, A. L.; Potts, S. K.; Shad, A.; Tesch, R.; Ting, Y.-Y. Fundamentals of Energy Storage from First Principles Simulations: Challenges and Opportunities. *Frontiers in Energy Research* **2023**, *10*, 1096190.
- (44) Tesch, R.; Kowalski, P. M.; Eikerling, M. H. Properties of the Pt(111)/Electrolyte Electrochemical Interface Studied with a Hybrid DFT–Solvation Approach. *J. Phys.: Condens. Matter* **2021**, *33*, 444004.
- (45) Sundararaman, R.; Schwarz, K. Evaluating Continuum Solvation Models for the Electrode-Electrolyte Interface: Challenges and Strategies for Improvement. *J. Chem. Phys.* **2017**, *146*, 084111.
- (46) Goodpaster, J. D.; Bell, A. T.; Head-Gordon, M. Identification of Possible Pathways for C–C Bond Formation during Electrochemical Reduction of CO₂: New Theoretical Insights from an Improved Electrochemical Model. *J. Phys. Chem. Lett.* **2016**, *7*, 1471–1477.
- (47) Gauthier, J. A.; Ringe, S.; Dickens, C. F.; Garza, A. J.; Bell, A. T.; Head-Gordon, M.; Nørskov, J. K.; Chan, K. Challenges in Modeling Electrochemical Reaction Energetics with Polarizable Continuum Models. *ACS Catal.* **2019**, *9*, 920–931.
- (48) Zhao, X.; Liu, Y. Origin of Selective Production of Hydrogen Peroxide by Electrochemical Oxygen Reduction. *J. Am. Chem. Soc.* **2021**, *143*, 9423–9428.
- (49) Sechi, R.; Kastlunger, G.; Bhowmik, A.; Hansen, H. A. First-Principles Molecular Dynamics with Potential and Charge Fluctuations Applied to Au(111) in Alkaline Solutions. *J. Chem. Theory Comput.* **2025**, *21*, 5279.
- (50) Goldsmith, K.; Andrade, M. F. C.; Selloni, A. Effects of Applied Voltage on Water at a Gold Electrode Interface from Ab Initio Molecular Dynamics. *Chemical Science* **2021**, *12*, 5865–5873.
- (51) Gauthier, J. A.; Dickens, C. F.; Ringe, S.; Chan, K. Practical Considerations for Continuum Models Applied to Surface Electrochemistry. *ChemPhysChem* **2019**, *20*, 3074–3080.
- (52) 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*, 4344–4357.
- (53) Le, J.-B.; Fan, Q.-Y.; Li, J.-Q.; Cheng, J. Molecular Origin of Negative Component of Helmholtz Capacitance at Electrified Pt(111)/Water Interface. *Science Advances* **2020**, *6*, No. eabb1219.
- (54) Le, J.-B.; Chen, A.; Li, L.; Xiong, J.-F.; Lan, J.; Liu, Y.-P.; Iannuzzi, M.; Cheng, J. Modeling Electrified Pt(111)-Had/Water Interfaces from Ab Initio Molecular Dynamics. *JACS Au* **2021**, *1*, 569–577.
- (55) Andreussi, O.; Hörmann, N. G.; Nattino, F.; Fisicaro, G.; Goedecker, S.; Marzari, N. Solvent-Aware Interfaces in Continuum Solvation. *J. Chem. Theory Comput.* **2019**, *15*, 1996–2009.
- (56) Gauthier, J. A.; Dickens, C. F.; Heenen, H. H.; Vijay, S.; Ringe, S.; Chan, K. Unified Approach to Implicit and Explicit Solvent Simulations of Electrochemical Reaction Energetics. *J. Chem. Theory Comput.* **2019**, *15*, 6895–6906.
- (57) Chan, K.; Nørskov, J. K. Electrochemical Barriers Made Simple. *J. Phys. Chem. Lett.* **2015**, *6*, 2663–2668.
- (58) Cheng, J.; Liu, X.; VandeVondele, J.; Sulpizi, M.; Sprik, M. Redox Potentials and Acidity Constants from Density Functional Theory Based Molecular Dynamics. *Acc. Chem. Res.* **2014**, *47*, 3522–3529.
- (59) Lindgren, P.; Kastlunger, G.; Peterson, A. A. Electrochemistry from the Atomic Scale, in the Electronically Grand-Canonical Ensemble. *J. Chem. Phys.* **2022**, *157*, 180902.
- (60) 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**, *9*, 6194–6201.
- (61) Liu, X.; Xiao, J.; Peng, H.; Hong, X.; Chan, K.; Nørskov, J. K. Understanding Trends in Electrochemical Carbon Dioxide Reduction Rates. *Nat. Commun.* **2017**, *8*, 15438.
- (62) Liu, X.; Schlexer, P.; Xiao, J.; Ji, Y.; Wang, L.; Sandberg, R. B.; Tang, M.; Brown, K. S.; Peng, H.; Ringe, S.; Hahn, C.; Jaramillo, T. F.; Nørskov, J. K.; Chan, K. pH Effects on the Electrochemical Reduction of CO(2) towards C₂ Products on Stepped Copper. *Nat. Commun.* **2019**, *10*, 32.
- (63) 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*, 6706–6718.
- (64) Diesen, E.; Dudzinski, A. M.; Reuter, K.; Bukas, V. J. Origin of Electrocatalytic Selectivity during the Oxygen Reduction Reaction on Au(111). *ACS Catal.* **2025**, *15*, 5403–5411.
- (65) Kastlunger, G.; Heenen, H. H.; Govindarajan, N. Combining First-Principles Kinetics and Experimental Data to Establish Guidelines for Product Selectivity in Electrochemical CO₂ Reduction. *ACS Catal.* **2023**, *13*, 5062–5072.
- (66) Guidelli, R.; Compton, R. G.; Feliu, J. M.; Gileadi, E.; Lipkowsky, J.; Schmickler, W.; Trasatti, S. Defining the Transfer Coefficient in Electrochemistry: An Assessment (IUPAC Technical Report). *Pure Appl. Chem.* **2014**, *86*, 245–258.
- (67) Björketun, M. E.; Tripkovic, V.; Skúlason, E.; Rossmeisl, J. Modeling of the Symmetry Factor of Electrochemical Proton Discharge via the Volmer Reaction. *Catal. Today* **2013**, *202*, 168–174.
- (68) Vijay, S.; Kastlunger, G.; Gauthier, J. A.; Patel, A.; Chan, K. Force-Based Method to Determine the Potential Dependence in Electrochemical Barriers. *J. Phys. Chem. Lett.* **2022**, *13*, 5719–5725.
- (69) van der Heijden, O.; Park, S.; Eggebeen, J. J. J.; Koper, M. T. M. Non-Kinetic Effects Convolute Activity and Tafel Analysis for the Alkaline Oxygen Evolution Reaction on NiFeOOH Electrocatalysts. *Angew. Chem., Int. Ed.* **2023**, *62*, No. e202216477.
- (70) Baz, A.; Dix, S. T.; Holewinski, A.; Linic, S. Microkinetic Modeling in Electrocatalysis: Applications, Limitations, and Recom-

mentations for Reliable Mechanistic Insights. *J. Catal.* **2021**, *404*, 864–872.

(71) Dickens, C. F.; Kirk, C.; Nørskov, J. K. Insights into the Electrochemical Oxygen Evolution Reaction with Ab Initio Calculations and Microkinetic Modeling: Beyond the Limiting Potential Volcano. *J. Phys. Chem. C* **2019**, *123*, 18960–18977.

(72) Zheng, T.; Liu, C.; Guo, C.; Zhang, M.; Li, X.; Jiang, Q.; Xue, W.; Li, H.; Li, A.; Pao, C.-W.; Xiao, J.; Xia, C.; Zeng, J. Copper-Catalysed Exclusive CO₂ to Pure Formic Acid Conversion via Single-Atom Alloying. *Nat. Nanotechnol.* **2021**, *16*, 1386–1393.

(73) Jung, O.; Jackson, M. N.; Bisbey, R. P.; Kogan, N. E.; Surendranath, Y. Innocent Buffers Reveal the Intrinsic pH- and Coverage-Dependent Kinetics of the Hydrogen Evolution Reaction on Noble Metals. *Joule* **2022**, *6*, 476–493.

(74) Bockris, J. O.; Potter, E. C. The Mechanism of the Cathodic Hydrogen Evolution Reaction. *J. Electrochem. Soc.* **1952**, *99*, 169.

(75) Mefford, J. T.; Zhao, Z.; Bajdich, M.; Chueh, W. C. Interpreting Tafel Behavior of Consecutive Electrochemical Reactions through Combined Thermodynamic and Steady State Microkinetic Approaches. *Energy Environ. Sci.* **2020**, *13*, 622–634.

(76) Blom, M. J. W.; van Swaaij, W. P. M.; Mul, G.; Kersten, S. R. A. Mechanism and Micro Kinetic Model for Electroreduction of CO₂ on Pd/C: The Role of Different Palladium Hydride Phases. *ACS Catal.* **2021**, *11*, 6883–6891.

(77) Oppel, N.; Röse, P.; Heuser, S.; Prokein, M.; Apfel, U.-P.; Krewer, U. Unveiling the Kinetics of CO₂ Reduction in Aprotic Electrolyte: The Critical Role of Adsorption. *Electrochim. Acta* **2024**, *490*, 144270.

(78) Hori, Y.; Takahashi, R.; Yoshinami, Y.; Murata, A. Electrochemical Reduction of CO at a Copper Electrode. *J. Phys. Chem. B* **1997**, *101*, 7075–7081.

(79) Corpus, K. R. M.; Bui, J. C.; Limaye, A. M.; Pant, L. M.; Manthiram, K.; Weber, A. Z.; Bell, A. T. Coupling Covariance Matrix Adaptation with Continuum Modeling for Determination of Kinetic Parameters Associated with Electrochemical CO₂ Reduction. *Joule* **2023**, *7*, 1289–1307.

(80) Chung, M.; Maalouf, J. H.; Adams, J. S.; Jiang, C.; Román-Leshkov, Y.; Manthiram, K. Direct Propylene Epoxidation via Water Activation over Pd-Pt Electrocatalysts. *Science* **2024**, *383*, 49–55.

(81) Savva, G. D.; Benson, R. L.; Christidi, I. A.; Stamatakis, M. Large-Scale Benchmarks of the Time-Warp/Graph-Theoretical Kinetic Monte Carlo Approach for Distributed on-Lattice Simulations of Catalytic Kinetics. *Phys. Chem. Chem. Phys.* **2023**, *25*, 5468–5478.

(82) Andersen, M.; Panosetti, C.; Reuter, K. A Practical Guide to Surface Kinetic Monte Carlo Simulations. *Frontiers in Chemistry* **2019**, *7*, 202.

(83) Pineda, M.; Stamatakis, M. Kinetic Monte Carlo Simulations for Heterogeneous Catalysis: Fundamentals, Current Status, and Challenges. *J. Chem. Phys.* **2022**, *156*, 120902.

(84) Bohra, D.; Chaudhry, J. H.; Burdyny, T.; Pidko, E. A.; Smith, W. A. Modeling the Electrical Double Layer to Understand the Reaction Environment in a CO₂ Electrocatalytic System. *Energy Environ. Sci.* **2019**, *12*, 3380–3389.

(85) 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*, 33.

(86) Govindarajan, N.; Lin, T. Y.; Roy, T.; Hahn, C.; Varley, J. B. Coupling Microkinetics with Continuum Transport Models to Understand Electrochemical CO₂ Reduction in Flow Reactors. *PRX Energy* **2023**, *2*, 033010.

(87) Lis, D.; Backus, E. H. G.; Hunger, J.; Parekh, S. H.; Bonn, M. Liquid Flow along a Solid Surface Reversibly Alters Interfacial Chemistry. *Science* **2014**, *344*, 1138–1142.

(88) Werkhoven, B. L.; Everts, J. C.; Samin, S.; van Roij, R. Flow-Induced Surface Charge Heterogeneity in Electrokinetics Due to Stern-Layer Conductance Coupled to Reaction Kinetics. *Phys. Rev. Lett.* **2018**, *120*, 264502.

(89) Ober, P.; Boon, W. Q.; Dijkstra, M.; Backus, E. H. G.; van Roij, R.; Bonn, M. Liquid Flow Reversibly Creates a Macroscopic Surface Charge Gradient. *Nat. Commun.* **2021**, *12*, 4102.

(90) Jubin, L.; Poggioli, A.; Siria, A.; Bocquet, L. Dramatic Pressure-Sensitive Ion Conduction in Conical Nanopores. *Proc. Natl. Acad. Sci. U. S. A.* **2018**, *115*, 4063–4068.

(91) Boon, W. Q.; Veenstra, T. E.; Dijkstra, M.; van Roij, R. Pressure-Sensitive Ion Conduction in a Conical Channel: Optimal Pressure and Geometry. *Phys. Fluids* **2022**, *34*, 101701.

(92) Kamsma, T. M.; Klop, M. S.; Boon, W. Q.; Spitoni, C.; Rueckauer, B.; van Roij, R. Chemically Regulated Conical Channel Synapse for Neuromorphic and Sensing Applications. *Physical Review Research* **2025**, *7*, 013328.

(93) Doblhoff-Dier, K.; Koper, M. T. M. Electric Double Layer of Pt(111): Known Unknowns and Unknown Knowns. *Current Opinion in Electrochemistry* **2023**, *39*, 101258.

(94) Zhu, J.-X.; Le, J.-B.; Koper, M. T. M.; Doblhoff-Dier, K.; Cheng, J. Effects of Adsorbed OH on Pt(100)/Water Interfacial Structures and Potential. *J. Phys. Chem. C* **2021**, *125*, 21571–21579.

(95) Korpelin, V.; Kiljunen, T.; Melander, M. M.; Caro, M. A.; Kristoffersen, H. H.; Mammen, N.; Apaja, V.; Honkala, K. Addressing Dynamics at Catalytic Heterogeneous Interfaces with DFT-MD: Anomalous Temperature Distributions from Commonly Used Thermostats. *J. Phys. Chem. Lett.* **2022**, *13*, 2644–2652.

(96) Urrego-Ortiz, R.; Builes, S.; Illas, F.; Calle-Vallejo, F. Gas-Phase Errors in Computational Electrocatalysis: A Review. *EES Catalysis* **2024**, *2*, 157–179.

(97) Proppe, J.; Husch, T.; Simm, G. N.; Reiher, M. Uncertainty Quantification for Quantum Chemical Models of Complex Reaction Networks. *Faraday Discuss.* **2016**, *195*, 497–520.

(98) Escalante, J. M.; Sahu, S.; Foster, J. M.; Protas, B. On Uncertainty Quantification in the Parametrization of Newman-Type Models of Lithium-Ion Batteries. *J. Electrochem. Soc.* **2021**, *168*, 110519.

(99) Alipour, M.; Yin, L.; Tavallaey, S. S.; Andersson, A. M.; Brandell, D. A. Surrogate-Assisted Uncertainty Quantification and Sensitivity Analysis on a Coupled Electrochemical–Thermal Battery Aging Model. *J. Power Sources* **2023**, *579*, 233273.

(100) Karyofylli, V.; Danner, Y.; Ashoke Raman, K.; Kungl, H.; Karl, A.; Jodat, E.; Eichel, R.-A. Sensitivity Analysis and Uncertainty Quantification in Predictive Modeling of Proton-Exchange Membrane Electrolytic Cells. *J. Power Sources* **2024**, *600*, 234209.