

# Challenges in the modeling of elementary steps in electrocatalysis

Axel Groß<sup>1,2</sup>

## Abstract

The full understanding of electrocatalytic reactions requires a complete knowledge of the elementary steps occurring in these reactions together with the corresponding rate constants as a function of the parameters controlling the electrochemical environment. Given the complexity of electrochemical electrode/electrolyte interfaces, the modeling of elementary steps in electrocatalysis represents a substantial challenge, and there is still a need for reliable benchmark studies. Nevertheless, tremendous progress has been made in this field in recent years. Here, the current status of this field will be briefly sketched, possible routes to meet the challenges will be suggested and open questions will be discussed.

## Addresses

<sup>1</sup> Institute of Theoretical Chemistry, Ulm University, 89069 Ulm, Germany

<sup>2</sup> Helmholtz Institute Ulm (HIU), Electrochemical Energy Storage, 89081 Ulm, Germany

Email address: [axel.gross@uni-ulm.de](mailto:axel.gross@uni-ulm.de) (A. Groß)

## Keywords

Electrocatalysis, Interfaces, Electrode potential, Quantum chemistry, Kinetic modeling.

## Introduction

Electrocatalytic reactions play an increasingly important role. They are the central processes occurring in electrochemical energy conversion and storage [1] which are critical for the energy transition towards a more sustainable future of our society. For example, hydrogen and oxygen evolution are the basic reactions underlying water splitting, whereas the reverse processes, hydrogen oxidation and oxygen reduction, are crucial in proton exchange membrane fuel cells. In spite of the importance of these reactions and intensive research, in particular the oxygen reduction (ORR) and the oxygen evolution reaction (OER) are

still hindered by substantial overpotentials which limit the efficiency of fuel cells and water electrolysis, respectively. Although the origin of the overpotentials in the ORR and OER appears to be well understood [2,3], mechanistic details of electrocatalytic processes at electrolyte/electrode interfaces are often still not known in detail due to the complexity of these interfaces [4].

In the study of processes in interfacial chemistry, theoretical considerations and numerical modeling have been playing an increasingly important role due to the development of more efficient algorithms and the increase in the computer power, in particular as far as solid-gas interfaces are concerned [5]. However, the presence of an electrolyte and the appropriate description of the electrode potential add considerable complexity to the theoretical modeling of structures and processes at electrochemical interfaces. In spite of rather promising progress in this field [6], it is certainly fair to say that there are still considerable challenges ahead before a truly reliable computational modeling of electrochemical interfaces will be achieved.

In this opinion, I will particularly address the challenges in the modeling of elementary steps in electrocatalysis. This task can be subdivided into three levels, as reflected in a recent ORR study [7] of the editors of the electrocatalysis section of this journal in which this contribution appears. The first level corresponds to the identification of possible reaction intermediates and the elementary reaction steps connecting these intermediates. Experiments can only detect rather long-lived species; hence, chemical intuition or computational tools are required to suggest complete reaction schemes. Next, the minimum energy paths connecting these intermediates need to be determined which also yields the activation barriers for the elementary processes. Finally, these barriers will then enter the kinetic modeling of the complete electrocatalytic reaction for which ideally also the preexponential factors and the influence of the adsorbate coverage should have been reliably derived.

In the following, I will address these three levels separately. The first two levels in principle require calculations based on quantum-chemical approaches, as adsorption and reactions are associated with bond-making and bond-breaking processes. I will concentrate

on these two first levels, because in my opinion the most severe challenges in the modeling of elementary steps in electrocatalysis are connected to the appropriate quantum-chemical evaluation of adsorption energies and reaction barriers at electrochemical electrolyte/electrode interfaces. I will then only briefly touch the kinetic modeling of electrocatalytic reactions, before I will give a personal perspective on the challenges lying ahead for a truly reliable modeling of electrocatalytic reactions.

### Quantum-chemical modeling of adsorbates at electrochemical interfaces

From a quantum chemical perspective, the positions of the atoms define any chemical systems, be it a molecule, a solid or an interface. The electronic distribution then follows from solving the many-body quantum chemical equations for this system. Periodic density functional theory (DFT) calculations represent the working horse with respect to the quantum chemical modeling of interfaces, as they combine numerical efficiency with an acceptable reliability. There are short-comings of this approach from a quantum-chemical perspective [8], but typically these short-comings are known and can be controlled.

Note that in this section we only consider equilibrium scenarios. It is important to realize that the adsorbed reaction intermediates originate from solvated species. Using grand-canonical concepts [9], such as the computational hydrogen electrode [2,10,11], the electrochemical potential of the proton can be expressed with respect to the chemical potential of the hydrogen molecule in gas phase  $\mu(\text{H}_2(\text{g}))$ ,

$$\tilde{\mu}(\text{H}^+(\text{aq})) + \mu(e^-) = \frac{1}{2}\mu(\text{H}_2(\text{g})) - eU_{\text{SHE}} - k_{\text{B}}T\ln(10)\text{pH}, \quad (1)$$

where, the electrode potential  $U_{\text{SHE}}$  is given with respect to standard hydrogen electrode (SHE). This expression then enters the free energy of hydrogen adsorption per surface area according to [12].

$$\Delta\gamma_{\text{H}}(T, U, \text{pH}, N_{\text{H}}) = \frac{N_{\text{H}}}{A_{\text{S}}} \left( \Delta G_{\text{H}}^{\text{ads}}(T, U, \text{pH}) + eU_{\text{SHE}} + k_{\text{B}}T\ln(10)\text{pH} \right), \quad (2)$$

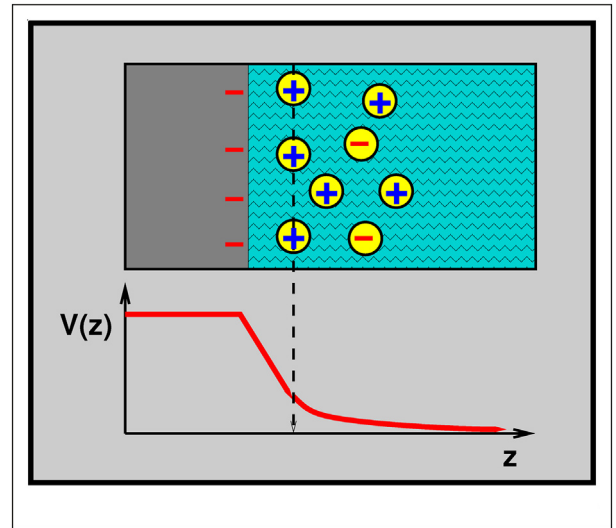
where,

$$\Delta G_{\text{H}}^{\text{ads}}(T, U, \text{pH}) = \frac{1}{N_{\text{H}}} \left( G_{A_{\text{S}}}^{\text{interf}}(T, U, \text{pH}, N_{\text{H}}) - G_{A_{\text{S}}}^{\text{interf}}(T, U, \text{pH}, 0) \right) - \frac{1}{2}\mu_{\text{H}_2(\text{g})} \quad (3)$$

corresponds to the free adsorption energy per hydrogen atom in the structure with  $N_{\text{H}}$  adsorbed hydrogen atoms per surface area  $A_{\text{S}}$  with respect to the hydrogen molecule in the gas phase.  $G_{A_{\text{S}}}^{\text{interf}}(T, U, \text{pH}, N_{\text{H}})$  is the free energy per surface area  $A_{\text{S}}$  of an in principle sufficiently large region perpendicular to the interface encompassing the electric double layer (EDL) [12]. For other adsorbates such as, e.g., halides  $A^-$ , corresponding expressions for the electrochemical potential enter the determination of the adsorption energy [13].

Thus the main problem lies in the appropriate evaluation of the free energy  $G_{A_{\text{S}}}^{\text{interf}}(T, U, \text{pH}, N_{\text{H}})$  in Eq. (3). The crucial challenge in the quantum-chemical determination of free energies at electrochemical interfaces is associated with a proper presentation of the electrochemical environment and the electrochemical control parameters. Typically, electrocatalytic processes occur at the interface between a solid catalyst and a liquid electrolyte, often an aqueous electrolyte which contains solvated ions. At such an interface, an electric double layer (EDL) is formed [15] which is sketched in Figure 1. Usually, the structure of the EDL is discussed using concepts that have been developed about 100 years ago. The Stern model [14] combines a Helmholtz layer consisting of a charged electrode together with a layer of counter ions with a diffuse layer of anions and cations according to the Gouy-Chapman model. It is important to note that the electric double layer is overall charge-neutral. Otherwise there would be a remaining electric field outside of the EDL which would lead to a

Figure 1



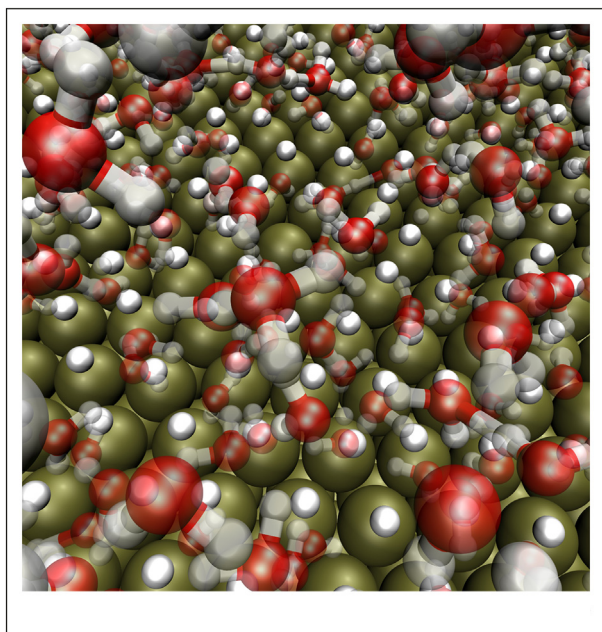
Schematic illustration of the structure of electric double layers in the Stern model [14] combining the Helmholtz model consisting of a charged electrode together with a layer of counter ions with the Gouy-Chapman model in which additionally the presence of a diffuse layer of anions and cations is taken into account.

charge rearrangement until the EDL has become charge neutral. Likewise, the electrolyte has to be macroscopically charge-neutral, i.e., any concentration of, say, anions is compensated by the corresponding amount of cations.

The Stern model has for example been intensively used to estimate the double-layer capacitance, which has been divided into a Helmholtz and a Guy-Chapman capacitance. This model is certainly based on valid physical arguments. Still it is important to realize that the Stern model corresponds to an idealization, and there is to the best of my knowledge no experimental or theoretical validation that the structure of the EDL really follows the simple arrangement illustrated in [Figure 1](#).

The theoretical or numerical identification of the structure of the EDL is hampered by the fact that a proper modeling requires an adequate consideration of the statistical nature of the liquid electrolyte. In principle, such a statistical modeling could be achieved by averaging over sufficiently long molecular dynamics runs based on the ergodic theorem. A snapshot of such an *ab initio* molecular dynamics (AIMD) simulation of a six-layer water film on a hydrogen-covered Pt(111) simulation [16] is shown in [Figure 2](#). This picture illustrates the complexity of the interface of an aqueous electrolyte with a metal electrode which requires, first, to use adequately large unit cells in periodic calculations and, second, to average over sufficiently long times.

**Figure 2**



Snapshot of a AIMD simulation of six water layers on a hydrogen-covered Pt(111) within a  $(6 \times 6)$  periodicity with in total 144 water molecules [16] (courtesy of Sung Sakong).

However, it is fair to say that running AIMD simulations is still too time-consuming to faithfully model the EDL. It is true that AIMD simulations of water/metal interfaces can now routinely take about 200 water molecules into account [17]. Still, this is not sufficient to model the whole EDL. In particular this is not sufficient to model typical ion concentrations in electrochemistry. Note that for example a 0.01 M ion concentration corresponds to one ion in 5500 water molecules. Yet, it is important to realize that periodic DFT calculations are still able to correctly model adsorbate layers on electrode surfaces due to the strong ion-electrode interaction which for example leads to halide coverages of up to about 0.5 even for mM concentrations in the electrolyte [18].

Molecular dynamics simulations based on classical force fields are in principle capable of considering sufficiently large systems to model electric double layers [19]. However, typically such force fields cannot properly take into account long-range electrostatic and electrode potential effects which are crucial for electrochemical interfaces. Instead of an explicit atomistic modeling of the electrolyte, implicit solvent models can be used [20] in which the electrolyte is described as a polarizable dielectric continuum. Such models have been extensively used in the description of solvated molecules [21], but they are now also used routinely in the modeling of electrochemical interfaces [20]. Interestingly enough, this approach is best-suited for the description of non-polar molecules, so that its reliability in the description of strong polar solvents such as water is not clear. And indeed, a computational study comparing the adsorption energies of small molecules and radicals at water/metal interfaces derived from AIMD simulations and from implicit solvent calculations [22] found not only relatively large quantitative differences, but also qualitative differences with respect to the order of the adsorption energy of the considered adsorbates. Hence, the appropriate modeling of the EDL certainly still poses a problem in the description of electrocatalytic reactions at electrolyte/electrode interfaces.

Furthermore, electrochemical equilibrium systems are characterized by the electrode potential and the concentrations or rather activities of the solvated ions which all enter the electrochemical potentials of the solvated species. For example, the electrode potential plays a similar role in cyclic voltammograms as the temperature in temperature-programmed desorption in surface science. In equilibrium, the electrode potential is an intensive property of the electrolyte which means that it should be uniform. In quantum chemical approaches, it can be calculated from bulk properties of the electrolyte film [23,24]. However, the electrode potential can also be determined from the work function of the electrode

covered by a sufficiently thick electrolyte film [25], which is widely used [17,16,26].

In periodic electronic structure calculations, electrodes are typically regarded as a charged system whose charge needs to be balanced by counter charges. Based on the seminal work by Lozovoi et al. [27], several different flavors of the approach have been developed [23,28,29]. While these approaches have certainly provided important insights into the potential dependence of electrochemical interfaces, they almost entirely focused on the charging of the electrode. The counter charge has only been introduced in order to guarantee the charge neutrality of the periodic unit cell. However, at real electrochemical interfaces, charge neutrality is guaranteed by the presence of the EDL. Hence, a proper representation of the EDL is key to a reliable modeling of electrochemical interfaces.

A more realistic approach to model electrochemical interfaces was introduced by Skulason et al. [30]. By adding hydrogen atoms to or removing them from the water layer above a metal electrode, the charge distribution at the electrolyte/electrode interface becomes altered. In detail, upon adding a hydrogen atom to the water layer, a  $\text{H}_3\text{O}^+$  hydronium cation spontaneously forms, and the remaining electron is transferred to the electron reservoir of the interface system which means that the electron moves to the metal surface to a state at the Fermi energy. Conversely, if a hydrogen atom is taken away from a water molecule, spontaneously an  $\text{OH}^-$  hydroxide anion is formed with the electron being transferred from the Fermi level of the metal electrode. The charge transfer changes the dipole moment at the electrolyte/electrode interface and thus also its work function, thereby altering the electrode potential. This approach preserves the charge neutrality of the electrochemical interface. Instead of adding or removing hydrogen atoms, alternatively alkali or halogen atoms can be added to the water layer, causing an decrease or increase, respectively, of the electrode potential. This method automatically guarantees that in equilibrium any change of the electronic charge distribution in the electrode is accompanied by a corresponding structural change of the EDL and *vice versa*. This is obviously the reason why this approach is nowadays also widely used in *ab initio* molecular dynamics simulations of electrochemical water/metal interfaces [17,16,31]. However, typically rather large concentrations of atoms have to be added to achieve relatively small changes in the electrode potential. On the other hand, our knowledge of the concentration of solvated ions in the electrolyte close to the electrode surface is still limited, so that we do not really know whether these necessary concentrations are unrealistically large.

Still the question arises whether it is really necessary to explicitly include a sufficiently thick electrolyte layer in

the quantum chemical determination of adsorption energies. Indeed, the fact whether the electrochemical control parameters affect the adsorption energies can be derived from phase diagrams of adsorbate structures at electrolyte/electrode interfaces as a function of these electrochemical control parameters [12], so-called Pourbaix diagrams. Let us take hydrogen adsorption as an example. Any adsorption energy corresponds to a difference of two energies. First of all, there is the energy change of the interface upon adsorbing the species of interest which correspond to the difference in brackets in Eq. (3). Then there is the energy it takes to remove the species from their respective reservoir which in electrochemical system is given by the electrochemical potential (Eq. (1)). First of all, the electrochemical potential depends on the electrode potential  $U$  and on pH. If the energy difference in Eq. (3) is independent of  $U$  and pH, then the boundaries of pure hydrogen adsorption phases in Pourbaix diagrams will exhibit a slope of 59 mV/pH. As this slope follows from the Nernst equation, systems that follow this trend are said to exhibit Nernstian behavior [12].

However, also the energy difference in Eq. (3) depends on the same electrochemical control parameters. Upon changes in the electrode potential  $U$  and in pH, the EDL might rearrange and thus also modify local electric fields which affect the energy difference in Eq. (3). Conversely, if hydrogen adsorption phases exhibit true Nernstian behavior, then the presence of the EDL would either not affect the energetics at the interface or lead to a  $U$ - and pH-independent shift. Equivalently, if the stability of adsorbate phases that do not contain any hydrogen does not depend on pH, this also means that changes in the EDL apparently do not influence the adsorption energy.

In fact, there are some adsorbate phases on metal electrodes that do exhibit such a Nernstian behavior, as far as their stability is concerned [12,32,33], in particular small adsorbates such as hydrogen and halogen atoms. And indeed, the corresponding Pourbaix diagrams can be semi-quantitatively reproduced by periodic DFT calculations in which the presence of the aqueous electrolyte and the varying electrode potential is entirely neglected [12,13]. However, for larger adsorbates such as sulfate, this is no longer true [34,35], so that the appropriate consideration of the electrochemical control parameters in the determination of adsorption energies is crucial.

### Determination of activation barriers in electrocatalytic reactions

The determination of activation barriers in electrocatalytic reactions represents a much higher theoretical and computational challenge as the evaluation of adsorption energies. First of all, activation barriers correspond to saddle points in the multidimensional potential energy surface and not to minima, as the

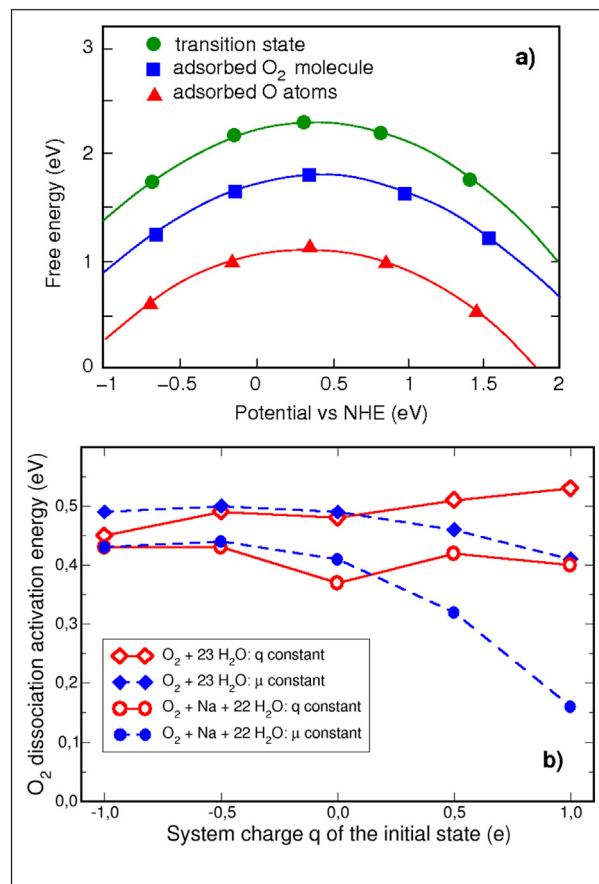


adsorption configurations. This requires to perform saddle-point searches [34,35] which are computationally much more demanding than the identification of minima. Furthermore, adsorbates on single-crystal surfaces often form periodic structures which can be faithfully presented in periodic structure calculations. However, reactions usually correspond to rare events which do not occur in a periodic fashion. Still, in periodic DFT calculations, only relatively small surface unit cells are computationally feasible, so that an infinite array of the same reaction is modeled. These reactions are usually associated with some charge rearrangement along their reaction path. This causes a change of the local dipole moment, which in an periodic presentation of these reactions alters the work function of the electrochemical interface and thus also the corresponding electrode potential [36].

In a realistic situation in which the reaction corresponds to a rare event, a single reaction within a sufficiently large surface area typically does not change the work function. To model this correctly in periodic calculations with necessarily small surface unit cells, keeping the electrode potential constant along the reaction path then requires some charge transfer to compensate for the intrinsic charge rearrangement along the reaction path. In fact, it might still be a matter of debate whether this is really the correct way to simulate electrocatalytic reactions in an array of small unit cells. Still, reaction barriers in electrocatalytic reactions can vary substantially depending on whether they are derived at constant charge or at constant potential.

This is illustrated in Figure 3 where the barrier of  $O_2$  dissociation on solvated Pt(111) is addressed, both for a pure water film and for a water film with on solvated Na ion [37]. These calculations have been performed using the so-called double-reference method [23], which is an *a posteriori* method with respect to potential control. This means that in this method the charge of the electrode is an input parameter with the counter charge being realized through an homogeneous background, and then the corresponding electrode potential for the particular configuration is derived. As shown in Figure 3, for five different system electrode charge states, the energies of the initial state in  $O_2$  dissociation, adsorbed  $O_2$ , of the final state, two adsorbed O atoms, and of the transition state are determined and the electrode potentials of the corresponding configurations are derived. These data are represented by the symbols in Figure 3a. For each state, an interpolation of the energy as a function of the electrode potential is obtained. The barriers at constant charge are then given by the difference of the corresponding symbols, whereas the barriers at constant potential can be determined from the difference between the interpolated curves at a given potential.

Figure 3



a) Calculated free energies as a function of potential for the initial, transition and final state of  $O_2$  dissociation on solvated Pt(111) obtained with the double reference method [23]. The symbols correspond to the results obtained for different charge states of the Pt electrode whereas the solid curves are quadratic fits to the results. b) Dissociation barrier of  $O_2$  on solvated Pt(111) without and with Na coadsorption, respectively, for various constant system charges q of the system and for constant potential, kept at the corresponding value of the initial state. Adapted from Wasilewski and Janik 2008 [37] with permission of Royal Society of Chemistry. Reprinted from Groß 2020 [38] with permission of John Wiley and Sons.

The barriers thus determined at constant charge and constant potential can differ quite significantly, as Figure 3b illustrates. In particular at large positive potentials, there are differences of more than 0.2 eV between these two approaches. However, again one has to emphasize that these differences are in principle only a consequence of the small unit cells that need to be used in periodic DFT calculations.

In the previous chapter, we also discussed the ansatz of Skulason et al. [30] to change the electrode potential by adding or removing hydrogen atoms in the water layer. Using this ansatz, Rossmeisl et al. [39] studied the Heyrovsky reaction:  $H_2 \rightarrow H^+ + e^- + H^*$  on Pt(111) as

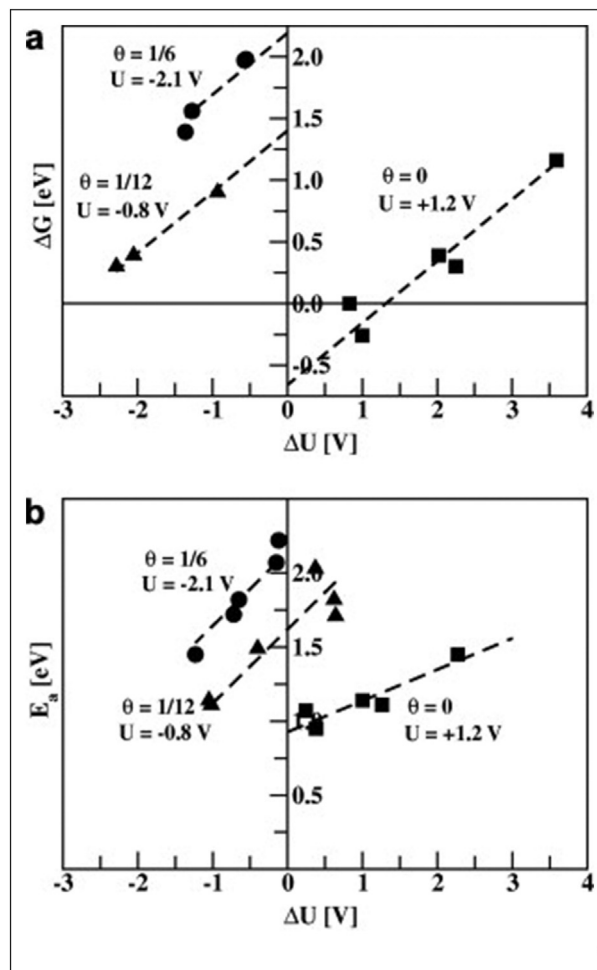
a function of the surface unit cell size with  $(3 \times 2)$ ,  $(3 \times 4)$ ,  $(3 \times 6)$ ,  $(6 \times 2)$ , and  $(6 \times 4)$  surface unit cells being used. This reaction corresponds to a one-electron reaction. Using the analogy to a capacitor, Rossmeisl et al. could show that the reaction energy  $\Delta G$  of a one-electron reaction as a function of the potential difference  $\Delta U$  between final and initial state should scale with  $e\Delta U/2$ , or in other words,  $\Delta G(\Delta U)$  should exhibit a slope of 1/2 when  $\Delta G$  is given in eV in calculations in which the ratio  $\theta$  between the number  $n$  of protons in the double layer and the number  $N$  of surface metal atoms per surface unit cell is kept constant. Recall that by varying the concentration of protons in the double layer, the electrode potential can be varied. Hence, calculations with the same ratio  $\theta = n/N$  should correspond to the same electrode potential.

As Figure 4a shows, indeed the reaction free energies  $\Delta G(\Delta U)$  nicely follow the predicted trend [39]. As discussed above, for a sufficiently large surface unit cell, the electrode potential should remain constant along the reaction path of a single reaction per surface unit cell. Hence, the extrapolation of the curves shown in Figure 4a to  $\Delta U = 0$  should give the reaction free energy in an infinite unit cell. Figure 4a furthermore shows that there is quite a drastic change in the reaction free energy as a function of the surface unit cell size.

Using the same methodology, also the activation barrier of the Heyrovsky reaction has been determined, as illustrated in Figure 4b. As the charge state at the transition state is not a predetermined fixed number, the slope of the curves for different unit cell sizes can be different from 1/2. There is also a considerable dependence of height of the activation barrier on the size of the surface unit cell.

As far as the calculations presented in Figure 4 are concerned, one has to note that they were performed with basically only one water layer present. Furthermore, the calculations have apparently been done for a static water layer. However, particularly at the transition state the statistical nature of the water distribution might significantly influence the barrier height. Hence, the calculated barrier heights should still be considered with caution. In a more recent study [36], a scheme to evaluate the energetics of electrocatalytic reaction steps at constant potential has been proposed that is only based on the a single barrier calculation in the electrochemical environment. Additionally, the surface charge at the initial, transition, and final states enter this formalism. This charge-extrapolation scheme [36] requires a much smaller computationally effort than the cell-extrapolation scheme [39] used for the results shown in Figure 4, but yields rather similar reaction energetics within typical DFT errors [36]. Still it needs to be noted that from a fundamental point of view local charges in an extended system such as atomic or surface charges correspond to ill-defined quantities as there are

Figure 4



(a) Calculated reaction free energies of the Heyrovsky reaction:  $H_2 \rightarrow H^+ + e^- + H^*$  for different surface unit cell sizes which cause different changes  $\Delta U$  in the electrode potential between initial and final state. (b) Activation energy  $E_a$  of the Heyrovsky reaction as a function of the potential change caused by using different surface unit cell sizes. Reprinted from Rossmeisl et al., 2008 [39] with permission of Elsevier.

ambiguities with respect to the integration boundaries necessary for their determination [40].

Basically, we know how to determine reliable reaction barriers for electrocatalytic reactions at the interface between a liquid electrolyte and an electrode: free energy calculations need to be performed for sufficiently large surface unit cells with the electrode potential being fixed by the appropriate structure of the electric double layer. The statistical nature of the water configurations along the reaction path together with the possible reorientation close to the reactants needs to be taken into account via appropriate thermodynamic integration schemes such as the Blue Moon ensemble [41].

First attempts to perform constrained molecular dynamics simulations with thermodynamic integration in

estimating activation and reaction (free) energies have indeed already been performed [42], and substantial changes in reaction energies have been found upon the consideration of solvent dynamics. Unfortunately, such calculations are not routinely feasible at the moment. The modeling of electrocatalytic processes by first-principles electronic structure calculations is very popular at the moment [43–47] due to the importance of electrochemically energy conversion and storage for our future sustainable energy supply [1]. These studies provide valuable insights into the reaction mechanism of electrocatalytic processes. Yet it is fair to say that we still need reliable and realistic free energy studies of elementary reaction steps in electrocatalysis as benchmark systems in order to be able to judge the accuracy of the more approximate approaches that are feasible at the moment.

## Kinetic modeling

In order to do a kinetic modeling of electrocatalytic processes, the activation barriers together with their pre-exponential factors, preferentially as a function of coverage, are the crucial input. The pre-exponential factor can be obtained via transition state theory [48] which requires to take all relevant degrees of freedom, also those of the liquid electrolyte, into account. Once the hopefully complete list of reaction steps together with their rate constants has been determined, the kinetic modeling of electrocatalytic processes itself is in principle not more demanding than the kinetic modeling of any chemical reaction, as only the rate constants enter the kinetic formalism. Indeed, such kinetic simulations have already been done [44]. As an alternative, kinetic Monte Carlo simulations can be performed which do not suffer from the fact that the reacting mixture is treated as an ideal solution [49]. Yet, only relatively few KMC simulations for electrocatalytic reaction have been performed, for example one recent study on CO<sub>2</sub> electroreduction [50], where, however, empirical rate constants have been used. Thus the basic problem in the kinetic modeling of electrocatalytic processes is not related to running the kinetic simulations, but rather to the reliable determination of the rate constants entering these simulations.

## Conclusions

The modeling of elementary steps in electrocatalysis is not only rather interesting from a scientific point of view, but it is also technologically relevant due to the importance of electrocatalytic processes in electrochemical energy conversion and storage. Due to the increase in computer power and the development of appropriate methods, first-principles simulations of electrocatalytic processes have significantly improved our understanding of these reactions. However, electrocatalytic reactions are still modeled in an approximate fashion, as it is numerically too demanding to realistically consider the

complexity of electrochemical electrolyte/electrode interfaces and to appropriately take the role of the electrode potential into account. Thus there are still substantial theoretical and numerical challenges associated with the modeling of electrocatalytic processes which make this research field very demanding, but also highly interesting.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

No data was used for the research described in the article.

## Acknowledgment

This work contributes to the research performed at CELEST (Center for Electrochemical Energy Storage Ulm-Karlsruhe). Support by the German Research Foundation (DFG) through contract GR 1503/39-1 and the POLIS Cluster of Excellence, Project ID 390874152, and by the Dr. Barbara Mez-Starck Foundation is gratefully acknowledged.

## References

- Schlögl R: **The role of chemistry in the energy challenge.** *ChemSusChem* 2010, **3**:209.
- Nørskov JK, Rossmeisl J, Logadottir A, Lindqvist L, Kitchin JR, Bligaard T, Jónsson H: **Origin of the overpotential for oxygen reduction at a fuel-cell cathode.** *J Phys Chem B* 2004, **108**, 17886.
- Man IC, Su HY, Calle-Vallejo F, Hansen HA, Martinez JI, Inoglu NG, Kitchin J, Jaramillo TF, Nørskov JK, Rossmeisl J: **Universality in oxygen evolution electrocatalysis on oxide surfaces.** *ChemCatChem* 2011, **3**:1159.
- Magnussen OM, Groß A: **Toward an atomic-scale understanding of electrochemical interface structure and dynamics.** *J Am Chem Soc* 2019, **141**:4777.
- Groß A: **The virtual chemistry lab for reactions at surfaces: is it possible? Will it be helpful?** *Surf Sci* 2002, **500**:347.
- Koper MTM, Weber AZ, Chan K, Cheng J: **Introduction: computational electrochemistry.** *Chem Rev* 2022, **122**, 10579.
- Poux T, Bonnefont A, Kerangueven G, Tsirlina GA, Savinova ER: **Electrocatalytic oxygen reduction reaction on perovskite oxides: series versus direct pathway.** *ChemPhysChem* 2014, **15**:2108.
- Lejaeghere K, Bihlmayer G, Björkman T, Blaha P, Blügel S, Blum V, Caliste D, Castelli IE, Clark SJ, Corso AD, de Gironcoli S, Deutsch T, Dewhurst JK, Marco ID, Draxl C, Dulak M, Eriksson O, Flores-Livas JA, Garrity KF, Genovese L, Giannozzi P, Giantomassi M, Goedecker S, Gonze X, Grånäs O, Gross EKV, Gulans A, Gygi F, Hamann DR, Hasnip PJ, Holzwarth NAW, Işuşan D, Jochym DB, Jollet F, Jones D, Kresse P, Koepnick K, Küçükbenli E, Kvashnin YO, Loch IL, Lubeck S, Marsman M, Marzari N, Nitzsche U, Nordström L, Ozaki T, Paulatto L, Pickard CJ, Poelmans W, Probert MJ, Refson K, Richter M, Rignanese GM, Saha S, Scheffler M, Schlipf M, Schwarz K,

- Sharma S, Tavazza F, Thunström P, Tkatchenko A, Torrent M, Vanderbilt D, van Setten MJ, Speybroeck VV, Wills JM, Yates JR, Zhang GX, Cottenier S: **Reproducibility in density functional theory calculations of solids**. *Science* 2016, **351**:aad3000.
9. Melander MM, Kuisma MJ, Christensen TEK, Honkala K: **Grand-canonical approach to density functional theory of electro-catalytic systems: thermodynamics of solid-liquid interfaces at constant ion and electrode potentials**. *J Chem Phys* 2019, **150**, 041706.
10. Peterson AA, Abild-Pedersen F, Studt F, Rossmeisl J, Nørskov JK: **How copper catalyzes the electroreduction of carbon dioxide into hydrocarbon fuels**. *Energy Environ Sci* 2010, **3**:1311.
11. Groß A: **Grand-canonical approaches to understand structures and processes at electrochemical interfaces from an atomistic perspective**. *Curr. Opin. Electrochem.* 2021, **27**, 100684.
12. Groß A: **Reversible vs standard hydrogen electrode scale in interfacial electrochemistry from a theoretician's atomistic point of view**. *J Phys Chem C* 2022, **126**, 11439.
13. Gossenberger F, Roman T, Groß A: **Hydrogen and halide co-adsorption on Pt(111) in an electrochemical environment: a computational perspective**. *Electrochim Acta* 2016, **216**:152.
14. Stern O: **Zur theorie der Elektrolytischen doppelschicht**. *Z. Elektrochem. Angew. P.* 1924, **30**:508.
15. Groß A, Sakong S: **Modelling the electric double layer at electrode/electrolyte interfaces**. *Curr. Opin. Electrochem.* 2019, **14**:1.
16. Sakong S, Groß A: **Water structures on a Pt(111) electrode from ab initio molecular dynamic simulations for a variety of electrochemical conditions**. *Phys Chem Chem Phys* 2020, **22**, 10431.
17. Groß A, Sakong S: **Ab initio simulations of water/metal interfaces**. *Chem Rev* 2022, **122**, 10746.
18. Magnussen OM: **Ordered anion adlayers on metal electrode surfaces**. *Chem Rev* 2002, **107**:679.
19. Sundararaman R, Vigil-Fowler D, Schwarz K: **Improving the accuracy of atomistic simulations of the electrochemical interface**. *Chem Rev* 2022, **122**, 10651.
20. Ringe S, Hörmann NG, Oberhofer H, Reuter K: **Implicit solvation methods for catalysis at electrified interfaces**. *Chem Rev* 2022, **122**, 10777.
21. Barone V, Cossi M: **Quantum calculation of molecular energies and energy gradients in solution by a conductor solvent model**. *J Phys Chem A* 1998, **102**:1995.
22. Heenen HH, Gauthier JA, Kristoffersen HH, Ludwig T, Chan K: **Solvation at metal/water interfaces: an ab initio molecular dynamics benchmark of common computational approaches**. *J Chem Phys* 2020, **152**, 144703.
23. Taylor CD, Wasileski SA, Filhol JS, Neurock M: **First principles reaction modeling of the electrochemical interface: consideration and calculation of a tunable surface potential from atomic and electronic structure**. *Phys Rev B* 2006, **73**, 165402.
24. Cheng J, Sulpizi M, Sprk M: **Redox potentials and pKa for benzoquinone from density functional theory based molecular dynamics**. *J Chem Phys* 2009, **131**, 154504.
25. Trasatti S: **The "absolute" electrode potential—the end of the story**. *Electrochim Acta* 1990, **35**:269.
26. Li P, Huang J, Hu Y, Chen S: **Establishment of the potential of zero charge of metals in aqueous solutions: different faces of water revealed by ab initio molecular dynamics simulations**. *J Phys Chem C* 2021, **125**:3972.
27. Lozovoi AY, Alavi A, Kohanoff J, Lynden-Bell RM: **Ab initio simulation of charged slabs at constant chemical potential**. *J Chem Phys* 2001, **115**:1661.
28. Bonnet N, Morishita T, Sugino O, Otani M: **First-principles molecular dynamics at a constant electrode potential**. *Phys Rev Lett* 2012, **109**, 266101.
29. Surendralal S, Todorova M, Finnis MW, Neugebauer J: **First-principles approach to model electrochemical reactions: understanding the fundamental mechanisms behind mg corrosion**. *Phys Rev Lett* 2018, **120**, 246801.
30. Skulason E, Karlberg GS, Rossmeisl J, Bligaard T, Greeley J, Jonsson H, Nørskov JK: **Density functional theory calculations for the hydrogen evolution reaction in an electrochemical double layer on the Pt(111) electrode**. *Phys Chem Chem Phys* 2007, **9**:3241.
31. Li CY, Le JB, Wang YH, Chen S, Yang ZL, Li JF, Cheng J, Tian ZQ: **In situ probing electrified interfacial water structures at atomically flat surfaces**. *Nat Mater* 2019, **18**:697.
32. Sheng W, Zhuang Z, Gao M, Zheng J, Chen JG, Yan Y: **Correlating hydrogen oxidation and evolution activity on platinum at different pH with measured hydrogen binding energy**. *Nat Commun* 2015, **6**:5848.
33. Mello GAB, Briega-Martos V, Climent V, Feliu JM: **Bromide adsorption on Pt(111) over a wide range of pH: cyclic voltammetry and CO displacement experiments**. *J Phys Chem C* 2018, **122**, 18562.
34. Gossenberger F, Juarez F, Groß A: **Sulfate, bisulfate, and hydrogen co-adsorption on Pt(111) and Au(111) in an electrochemical environment**. *Front Chem* 2020, **8**:634.
35. Fang Y, Ding SY, Zhang M, Steinmann SN, Hu R, Mao BW, Feliu JM, Tian ZQ: **Revisiting the atomistic structures at the interface of Au(111) electrode–sulfuric acid solution**. *J Am Chem Soc* 2020, **142**:9439.
36. Chan K, Nørskov JK: **Electrochemical barriers made simple**. *J Phys Chem Lett* 2015, **6**:2663.
37. Wasileski SA, Janik MJ: **A first-principles study of molecular oxygen dissociation at an electrode surface: a comparison of potential variation and coadsorption effects**. *Phys-ChemChemPhys* 2008, **10**:3613.
38. Groß A: *Theory of solid/electrolyte interfaces*. John Wiley & Sons; 2020:471–515, <https://doi.org/10.1002/9783527680603.ch56>. chap. 56.
39. Rossmeisl J, Skúlason E, Björketun ME, Tripkovic V, Nørskov JK: **Modeling the electrified solid–liquid interface**. *Chem Phys Lett* 2008, **466**:68.
40. Huang J: **Surface charging behaviors of electrocatalytic interfaces with partially charged chemisorbates**. *Curr. Opin. Electrochem.* 2022, **33**, 100938.
41. Ciccotti G, Ferrario M: **Blue moon approach to rare events**. *Mol Simulat* 2004, **30**:787.
42. Kronberg R, Lappalainen H, Laasonen K: **Revisiting the Volmer–Heyrovsky mechanism of hydrogen evolution on a nitrogen doped carbon nanotube: constrained molecular dynamics versus the nudged elastic band method**. *Phys Chem Chem Phys* 2020, **22**, 10536.
43. Nahian MS, Jayan R, Kaewmaraya T, Hussain T, Islam MM: **Elucidating synergistic mechanisms of adsorption and electrocatalysis of polysulfides on double-transition metal MXenes for Na–S batteries**. *ACS Appl Mater Interfaces* 2022, **14**, 10298.
44. Kastlunger G, Wang L, Govindarajan N, Heenen HH, Ringe S, Jaramillo T, Hahn C, Chan K: **Using pH dependence to understand mechanisms in electrochemical CO reduction**. *ACS Catal* 2022, **12**:4344.
45. Beinlich SD, Hörmann NG, Reuter K: **Field effects at protruding defect sites in electrocatalysis at metal electrodes?** *ACS Catal* 2022, **12**:6143.



46. Wallace SW, McCrum IT, Janik MJ: **Ammonia electro-oxidation mechanism on the platinum (100) surface.** *Catal Today* 2021, **371**:50.
47. Patel AM, Ringe S, Siahrostami S, Bajdich M, Nørskov JK, Kulkarni AR: **Theoretical approaches to describing the oxygen reduction reaction activity of single-atom catalysts.** *J Phys Chem C* 2018, **122**, 29307.
48. Hänggi P, Talkner P, Borkovec M: **Reaction-rate theory: fifty years after Kramers.** *Rev Mod Phys* 1990, **62**:251.
49. Temel B, Meskine H, Reuter K, Scheffler M, Metiu H: **Does phenomenological kinetics provide an adequate description of heterogeneous catalytic reactions?** *J Chem Phys* 2007, **126**, 204711.
50. Li J, Maresi I, Lum Y, Ager JW: **Effects of surface diffusion in electrocatalytic CO<sub>2</sub> reduction on Cu revealed by kinetic Monte Carlo simulations.** *J Chem Phys* 2021, **155**, 164701.