

Bridging the scales within transport-coupled kinetic models for heterogeneous electrocatalysis

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Abstract

Optimizing reaction rates in heterogeneous electrocatalysis requires a solid, fundamental understanding of the interplay between mass transport and the intrinsic reaction kinetics at the electrode surface. As these processes occur on disparate scales, however, bridging the two into a (single) comprehensive reaction model is a challenging task and active area of research. In this perspective, we give a current overview of transport-coupled kinetic models while making a distinction between those that describe the surface reaction *via* an effective phenomenological or first-principles based kinetic model. This choice tends to be accompanied by a correspondingly more or less elaborate inclusion of mass transport. The two modeling approaches thus generally differ in the scientific questions that they aim to answer; whether focusing on elaborate transport effects and resulting design rules at the device level or more detailed mechanistic insight on a microscopic scale. We first discuss these approaches separately, including their pros and cons through notable studies in the existing literature, and conclude with an outlook view on combining the value of both in future research.

Keywords: mass transport, kinetics, reaction, modeling, electrocatalysis, gas diffusion electrode, density functional theory

1. Introduction

As we strive towards a sustainable energy economy, it becomes increasingly urgent to optimize electrochemical reaction rates at the practical device level. In heteroge-

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neous electrocatalysis, the reaction rate is a direct measure of the overall current which inexorably intertwines the kinetics of the catalytic surface reaction with mass transport. This crucial interplay manifests in a number of different phenomena including the diffusion-limited transfer of reactants to the active surface [1, 2], ion crowding [3, 4] or so-called “local” pH effects [5, 6], as well as the diffusion-controlled desorption/re-adsorption of surface-bound reaction intermediates [7, 8]. While surface kinetics are determined by atomistic processes over nanoscopic active sites, however, transport effects typically emerge over micrometer length scales. Bridging these two disparate scales into a (single) comprehensive reaction model is an ongoing, yet key, challenge both from a conceptual as well as a methodological point of view.

The coupling between surface kinetics and transport is presently largely realized by coupling a reaction kinetic model with a continuum mechanics transport model. The actual coupling is then achieved through a mass flux boundary condition at the electrochemical interface which establishes an interdependence between the two processes. Solving the resulting multi-scale problem thus always requires that near-surface fluxes and concentrations are aligned between the kinetic and transport models. Depending upon how these two models are set up and combined in practice, however, we distinguish two basic modeling approaches in the current literature. The approaches generally differ in their primary focus and, hence, the level of theory used for the individual model components, as illustrated in Figure 1. The first approach uses phenomenological kinetics to approximate the partial current density J_{surf} that is generated through the surface reaction and fed as input into a (usually) rather elaborate transport model. As a result, this approach often addresses more complex transport phenomena and mechanisms (diffusion, migration, convection) or design strategies at the device level through, *e.g.*, simulations of realistic porous electrode morphologies, gas diffusion electrodes (GDEs), and even full electrolyzers (including cathode/anode and membrane) [9]. Alternatively, the second approach is to put the stronger focus on the surface kinetics and couple to transport through a predictive-quality J_{surf} that is computed from a first-principles based microkinetic model (1p-mkm). This approach will thus directly include the free energy profile of elementary surface reaction steps while integrating microscopic details of an assumed catalytic mechanism. At this point, it should be em-

phasized that the above classification simply reflects our view of the prevailing status quo and that there is, in principle, no conceptual limitation to, *e.g.*, coupling a 1p-mkm to a most elaborate mass transport model. This situation is analogous to that observed in the field of thermal heterogeneous catalysis.

This short review aims to give a current overview over corresponding transport-coupled kinetic models for heterogeneous electrocatalysis. We first separately discuss the two aforementioned modeling approaches, distinguished by whether the surface reaction is included *via* a phenomenological or first-principles based kinetic model. Focus is specifically put on some of the main conceptual and methodological differences between these two approaches, while demonstrating the advantages and value of each through notable examples in the recent literature. Finally, we comment upon insights realized, remaining challenges, as well as the prospects of combining the two “schools of thought” in future research.

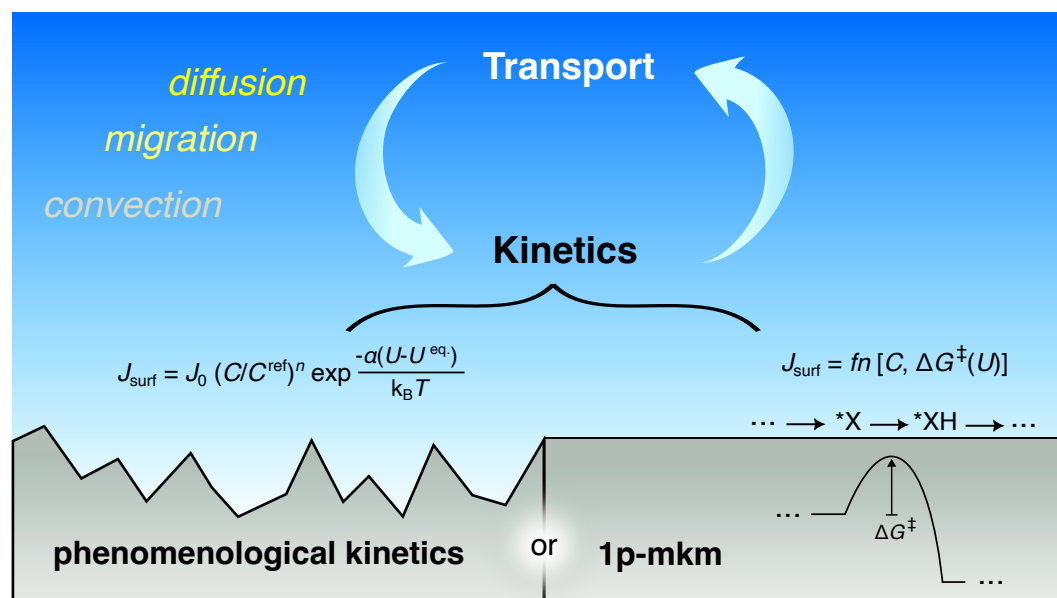


Figure 1: Schematic representation of the two discussed modeling approaches for transport-coupled kinetic models in heterogeneous electrocatalysis. A phenomenological treatment of the surface kinetics, *e.g.* *via* a Butler-Volmer expression, generates an empirical J_{surf} that is (usually) combined with modeling more complex transport phenomena and design strategies at the device level. On the other hand, a first-principles based microkinetic model (1p-mkm) integrates into J_{surf} a predictive-quality description of the free energy reaction path with specific focus on elucidating the underlying microscopic catalytic mechanism.

2. Coupling mass transport to phenomenological surface kinetics

A phenomenological treatment of surface kinetics is meant to provide a simple, yet effective, ansatz for the resulting current density J_{surf} at the surface. Common formulations here include a potential-dependent Butler-Volmer (BV) expression, or just the simple assumption that this J_{surf} is a constant. In the latter case, J_{surf} is simply approximated based on a specific faradaic efficiency and directly fed as input into the transport model with no effect from the applied potential U or interfacial species' concentration C . On the other hand, the BV formalism (which simplifies into a Tafel expression at large overpotentials) represents the more sophisticated ansatz, but comes at the price of relying upon a set of empirical parameters that must be *a priori* defined. These parameters primarily include the exchange current density J_0 and cathodic/anodic transfer (or symmetry) coefficient α within the standard BV formalism. Most often the basic BV formulation is extended by an additional concentration-dependent term that allows for a more advanced, transport-aware model [10]:

$$J_{\text{surf}} = J_0 \left(\frac{C}{C^{\text{ref}}} \right)^n \exp \frac{-\alpha(U-U^{\text{eq}})}{k_{\text{B}}T} \quad (1)$$

where U^{eq} is the equilibrium reaction potential, C^{ref} is a reference concentration (usually set to 1 M), and n represents a specific reaction order which is either taken from the literature or treated as an additional fitted parameter. The typical fitting procedure of above BV parameters generally involves the following steps [11]: a 1D transport-coupled kinetic model is solved first [12], while essentially assuming a planar electrode with J_{surf} set equal to the experimental product J measured in the bulk electrolyte at a given U . This solution gives an initial potential-dependent C profile which is then used to fit the included model parameters. The resulting BV expression is finally solved iteratively within a 2D or 3D set-up (according to the surface geometry of interest), yielding a self-consistent solution for J_{surf} and C as a function of U . Note that, while practical, this approach suffers from its inherent dependence upon the above fitted parameters which have been shown to sensitively change the model's results [13]. Furthermore, both Dunne [13] as well as Biu *et al.* [9] have suggested that (J_0, α) parameter sets are not unique solutions to the BV expression while highlighting a large

variation for very similar systems.

The efficiency of phenomenological surface kinetics is most usually paired with a more elaborate transport model, either in the underlying transport equations themselves, considered electrode geometry, or both. While early such models focused mainly on planar electrodes [14, 15], the approach has since been extended to include also, *e.g.*, macroscale so-called “volume averaged” simulations [12, 16] as well as the simulations of pores [9, 17]. We specifically highlight in Figure 2 two recent studies on GDEs [18, 10]. These examples nicely demonstrate how elaborate transport models, coupled to BV surface kinetics, can predict complex concentration profiles in the diffusion layer; both as a function of electrolyte composition and electrode geometry. Such fundamental insight into transport processes within a GDE is key to its future design and optimization [19, 20, 21].

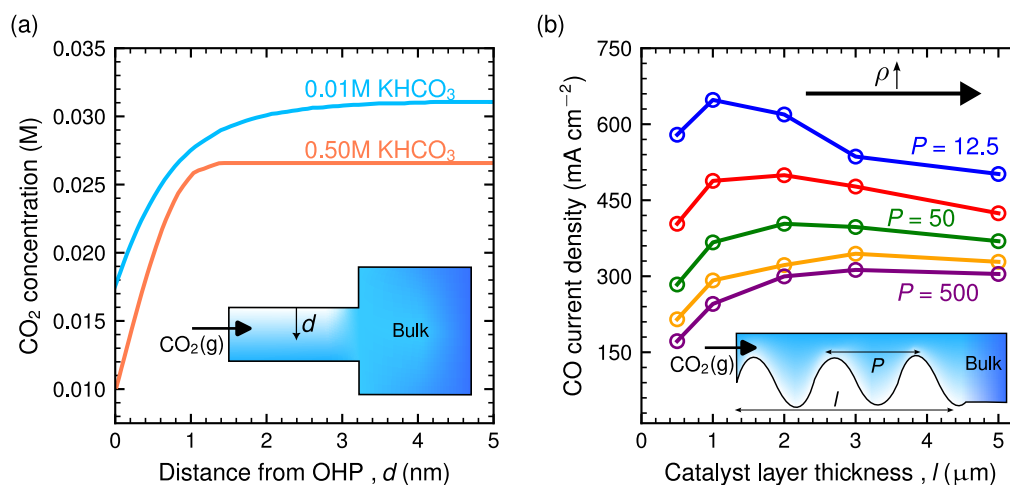


Figure 2: (a) Simulated CO_2 concentration as a function of distance d from the outer Helmholtz plane (OHP) in a GDE catalyst nanopore. The two curves are generated assuming a different buffer KHCO_3 concentration which is predicted to change CO_2 solubility and induce steric hindrance close to the electrode surface. A schematic illustration of the considered pore geometry is shown in the figure’s inset. Adapted from the study by Butt *et al.* [18]. (b) Simulated CO partial current density over a model sinusoidal catalyst geometry, illustrated in the figure’s inset. Increasing the catalyst length l along the x -axis corresponds to higher surface roughness ρ for a given value of the wave period P (represented by the different colored curves). Adapted from the study by Johnson *et al.* [10].

Upon developing an elaborate 2D model for ion migration, Butt *et al.* investigated

the influence of electrolyte composition on the local reaction environment within a GDE catalyst nanopore. Figure 2a) shows simulated concentration profiles for the reactant CO₂ as a function of its distance from the catalyst surface at different KHCO₃ buffer concentrations. Increasing K⁺ concentration predicts lower CO₂ solubility (modeled here through a ‘Sechenov-corrected’ Henry’s constant [22]), but also induces steric hindrance at the electric double layer due to ion crowding. Together these two effects limit the CO₂ that can reach the surface and react, thus affecting catalytic performance. Another factor that can considerably change surface concentration profiles and resulting reaction rates through mass transport is the catalyst morphology. Johnson *et al.* performed a systematic study of how different 2D catalyst layer geometries change the CO product current within a GDE [10]. One such example is shown in Figure 2b) where the catalyst is modeled as a sinusoidal layer of varying thickness (l) and wave periodicity (P). The results show that CO production has a much more complex dependence on catalyst shape than what might be simply expected from estimates of the corresponding surface roughness (ρ), leading to *e.g.* a peculiar activity maximum at intermediate ρ values.

3. Coupling mass transport to a first-principles microkinetic model

A mean-field microkinetic model of the catalytic surface reaction predicts J_{surf} by breaking the process down to a series of consecutive elementary reaction steps, deriving a rate expression for each, and solving the resulting set of ordinary differential equations. Near-surface concentrations and turnover frequencies predicted in this way subsequently serve as boundary conditions when coupling to mass transport. While there are many excellent reviews on recent mkm developments [23, 24, 25], it is clear that the overall approach hinges upon the reliability of the assumed reaction mechanism and input kinetic parameters. The huge benefit, but also cost, of a 1p-mkm is its predictive quality through explicitly calculated reaction energies and barriers at an *ab initio* level. Such calculations are nowadays becoming increasingly tractable within density functional theory (DFT), at least within small simulation cells and simple solvation models. Including a more advanced description of the electrolyte as well as the effect of applied potential at the solid/liquid interface, however, represent the forefront in the

field. The vast majority of studies currently still include U only at the level of thermodynamic reservoirs *via* the so-called computational hydrogen electrode [26] while relying on BEP scaling relations, vanishingly small or fitted barriers for the reaction kinetics [27]. Possibly more critical, however, is the almost standard approximation of a 1D transport-coupled model that assumes uniform concentration profiles regardless of the catalyst's 2D or 3D morphology.

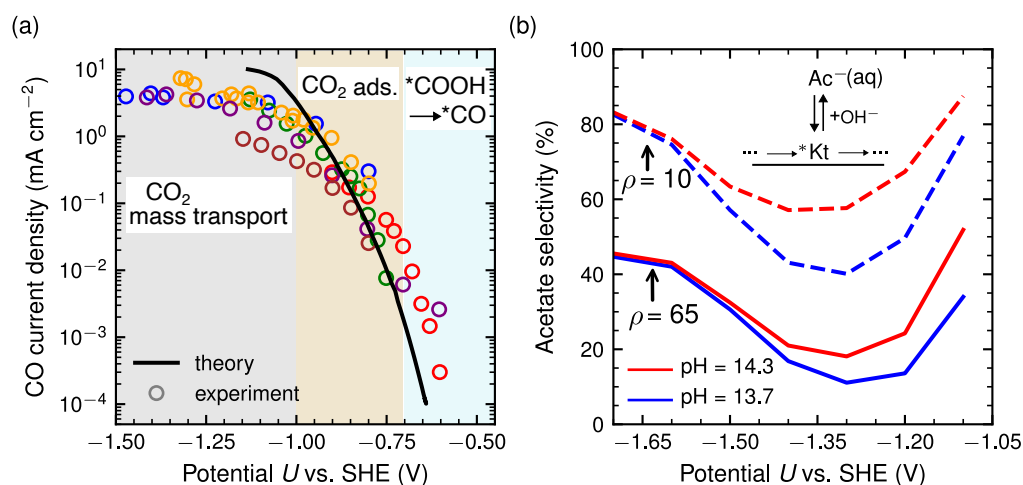


Figure 3: (a) CO partial current density during CO_2 electro-reduction over Au as a function of applied potential U . Different colored regions suggest a changing kinetic regime with the identity of the rate-determining step noted in the figure's labels. The black line shows the prediction of a transport-coupled 1p-mkm including field-dependent DFT barriers, while different colored markers correspond to independent sets of experimental data. Adapted from the study by Ringe *et al.* [2]. (b) Simulated selectivity towards acetate during CO electro-reduction over Cu. The selectivity is measured against further reduced carbon-coupled products and plotted as a function of applied potential U . Key here is the kinetic competition between the surface- and solution-reaction of a ketene (Kt) intermediate to form acetate (Ac^-), as illustrated in the figure's inset. This competition is resolved *via* a diffusion-coupled 1p-mkm, predicting a complex "U-shaped" selectivity profile with U that shifts with pH and catalyst roughness (ρ). Adapted from the study by Heenen *et al.* [28].

Because of their predictive-quality description of the surface kinetics, transport-coupled 1p-mkm models can provide us with valuable (atomically-resolved) mechanistic insights. Early such coupled models, for example, already found some success in elucidating catalytic mechanisms by comparing simulated polarization curves or reaction orders against experiments [29, 30]. More recent models have now advanced to further include a more realistic description of the electrical double layer

while explicitly including field-dependent DFT kinetics. Ringe *et al.*, for example, simulated CO₂ electro-reduction over Au by (self-consistently) integrating such a 1p-mkm with a 1D transport model that could account for diffusion, migration, and buffer reactions [2]. Figure 3a) reproduces the resulting polarization curve which shows potential-dependent transitions between three distinct kinetic regimes: from a rate-limiting *COOH reduction step at low overpotentials, to the field-driven adsorption of CO₂ at intermediate ones, and finally CO₂ mass transport at high overpotentials. Importantly, this work shows that the experimental Tafel slope is only captured here by explicitly including CO₂ dipole-field interactions when modeling the electrochemical kinetics. Another situation which requires the detailed accuracy of a 1p-mkm is the sensitive kinetic competition that often arises in questions of electrocatalytic selectivity. For example, one of us recently discussed such a competition within a “desorption–re-adsorption–reaction” mechanism [7] to explain the selectivity towards acetate during CO electro-reduction over Cu [28]. The mechanism focuses on a specific surface-bound reaction intermediate and competing routes forward: continued conversion at the surface *vs* desorption and a subsequent solution reaction to form an early partially-converted product. This competition can only be resolved *via* a diffusion-coupled 1p-mkm which, in the case of acetate, yielded an intricate dependence upon potential, pH, and catalyst roughness ρ . The simulated selectivity is plotted in Figure 3b) and shows near-quantitative agreement with experiment. Finally, even more recently, we generalized the “desorption–re-adsorption–reaction” mechanism as being relevant across different processes and systems while highlighting the need for 1p-mkm coupling with more complex models of catalyst morphology [8].

4. Outlook

In summary, we discuss two prevailing trends for modeling transport-coupled kinetics in heterogeneous electrocatalysis. The two approaches generally differ in the target scientific questions that they aim to answer and, hence, in whether the larger focus is put on the description of the catalytic surface kinetics or mass transport. While the value of each of these models is easily demonstrated through many notable studies in the existing literature, remaining practical and methodological challenges are cur-

rently the object of ongoing research. Such efforts include, for example, developments towards a more systematic fitting of BV parameters [31, 32] as well as the exploration of improved phenomenological kinetic models such as, *e.g.*, the Marcus-Hush-Chidsey model [33, 34]. Simultaneously, in the realm of 1p-mkm, extensive methodological work is presently being devoted to advancing simulations of the working electrochemical interface [35, 36, 37, 38] while providing constant-potential energies and barriers [39, 40, 41, 42, 43]. Most noteworthy are also efforts toward an automatic exploration of reaction networks using machine learning [44]. Promising research along this direction aims to lift the bias in assuming a catalytic mechanism which is usually based on chemical intuition.

One of the more natural directions forward of course involves the coupling of 1p-mkm with elaborate transport models, in an obvious attempt to exploit the “best of both worlds”. Although there is no real practical bottleneck to conducting such simulations, it represents an interdisciplinary challenge, closely intertwining the fields of theoretical catalysis and chemical engineering. This situation might just be on the verge of changing. Gonvidarajan *et al.* recently combined the aforementioned 1p-mkm developed by Ringe *et al.* (Figure 3a) with a 2D flow cell geometry that treats the catalyst as an active strip [45]. The resulting mechanistic insight was found similar to that obtained in the original study by Ringe [2], thus highlighting the potential to further explore the effect of different geometries and flow conditions. Also within our group, efforts are already underway to expand the 1D concept of surface roughness to an explicit 2D or 3D geometry within the “desorption–re-adsorption–reaction” mechanism. Similarly, the concepts to couple spatially resolved kinetic Monte Carlo mkms to transport have also been established years ago for thermal catalysis [46, 47] and only wait to be employed within the context of heterogeneous electrocatalysis. These and similar advances will undoubtedly strengthen our understanding of detailed reaction mechanisms under (practical) operating conditions, while simultaneously allowing to gauge the level of detail that is required to be accounted for. The continued development of improved transport and kinetic models, along with accelerated ways to couple the two, thus offers a lot of promise in bridging the gap between atomistic processes at the electrified interface and mesoscale transport processes.

5. Declaration of Interest

None.

6. Acknowledgements

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