Review Article

Strategic tailored design of electrocatalysts for environmental remediation based on density functional theory (DFT) and microkinetic modeling

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Abstract

Environmental electrocatalysis has a wide range of applications at the water-energy nexus and will play a key role in mitigating climate change. Performance and selectivity of electrochemical processes are driven by specific electrocatalyst interactions with electroactive species and by-products. Research advances and competitive translation to higher technology readiness levels depend on the identification of suitable electrocatalytic materials. Theoretical modeling can guide electrocatalyst discovery, engineering, and design, which can overturn typical trial-and-error approaches for material discovery in favor of a hypothesis-driven and strategic tailored synthesis approach to electrocatalysts development. In this current opinion, we present an overview of some of the virtues of density functional theory and microkinetic modeling as tools for reinforcing our understanding of complex charge transfer processes in environmental electrochemistry.

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Introduction

Electrocatalysis has been an essential gear driving the evolution of the industrialized world [1] [2••]. Electrochemical processes are accelerating the transition to sustainable development in the 21st century [3,4]. Environmental electrochemistry processes encompass a variety of electrified technologies, including water splitting for a hydrogen economy [5,6], green electrosynthesis of value-added products [7,8], resource recovery [9,10], energy production [11,12], electro-generation of H_2O_2 [13,14], climate change mitigation through CO_2 electro-reduction [15,16], and electrochemically driven water treatment [17,18]. Despite the unique aspects of each electrochemical technology, there is a clear connection between them: the need for advanced electrocatalyst design and electrode manufacturing [19•].

Active catalytic sites control selective transformations at the electrode surface, determining the Faradaic efficiency (FE) of electrochemical reactions [20,21]. Interfacial charge transfer processes are indisputably related to material selection and structure (e.g., shape, morphology, and crystalline structure). Control of these aspects is essential for effective electrocatalyst design. The conventional way to design the catalyst is to use previous experimental data from bulk materials, nanoparticles, and even single-atom configurations to develop new hypotheses that can be tested [22−24]. Many research groups develop materials by educated and inspired guesses that work well. However, the practice of gathering knowledge systematically has led the field into an increasing tendency to develop electrocatalysts based on high-throughput screening and trial-and-error approach [25•]. These trial-and-error approaches (also known as "cook-and-look") is based mostly on the synthesis and systematic characterization of electrocatalysts, but it often lacks thorough benchmarking. Failing to identify metrics and key performance indicators blurs the research roadmap and results in a growing list of forgotten "novel materials." The re-iterative approach produces huge amounts of uncompetitive materials, wasting resources, and time. Furthermore, unsuccessful results often go unreported, which leads to considerable duplication of effort. Thus, the key question is how researchers can leverage existing knowledge to guide the rational design of catalytic materials.

Density functional theory (DFT) and microkinetic modeling tools provide a theoretical framework for elucidating mechanistic aspects of chemical reactions, which has been demonstrated extensively in the literature [26••] [27•] [28•] [29]. The use of DFT has become routine in some instances, and as a result, some research articles report superficial modeling data to support preconceived conclusions based on experimental results. However, theoretical modeling offers much more than a means to complete the simple checkbox of "required results" to be reported in a research article. By providing an understanding of thermodynamic and kinetic driving forces, DFT and microkinetic modeling can serve as a compass when sailing the vast ocean of "facile" synthesized materials, guiding researchers toward the desired destination: highly active and selective electrocatalysts [30,31]. When used improperly, however, that compass can lead explorers astray. An important challenge on the employment of DFT as a predicting tool is related to some limitations when describing molecules with double and triple bonds and sometimes even with single bonds. This means that meaningful species in many electrochemical processes of interest may be in some instances poorly described. Examples of these challenges for O_2 and H_2O_2 [32••] [33•] [34], C-species (e.g., CO, CO_2, and many organic compounds) [35•] [36] [37••], and N-species (e.g., N_2, NO, NO_3^-, etc.) have been reported for the prediction of calculated equilibrium potentials [38•]. These issues become more evident when the first (adsorption) or the last (desorption) electrochemical steps are potential limiting, resulting in errors and deviations from the experimental onset potentials. It is of high relevance to be aware of these issues and not ignore them since modeling approaches should overcome such barriers to be more accurate on modeling and predicting behaviors. Discrepancies between experimental results and theoretical predictions are common, even under highly controlled conditions and reporting them in the literature is an important practice [•39] [40]. Nevertheless, recent advances are enlightening a promising future path for modeling as an electrocatalysts discovery tool. Figure 1 summarizes some of the potential rewards that can be gained by merging theoretical modeling with experimental electrocatalysis, as well as some of the pitfalls. This current opinion provides a view of the current landscape of theoretical modeling tools used to identify and define required material compositions and structures for optimum performance in environmental electrochemistry for sustainable societal development.

Identifying optimal catalyst composition with computational modeling

Electrocatalysis is driven by direct charge transfer processes that occur at the electrode interface through inner sphere, outer sphere, and/or complex processes with coupled electron transfer and chemical reactions (e.g., proton-coupled electron transfers) [41−43]. Considering that elementary electrochemical reactions involve the transfer of one electron per step, it is obvious that most processes require multi-step pathways with many divergence points. Supercomputing has powered advances in computational and theoretical chemistry, making it now possible to routinely describe the electronic properties of multi-electron systems with hundreds of atoms [44]. Recent modeling advances also have made it possible to model redox reactions occurring as heterogeneous processes at electrode/electrolyte interfaces. In electrochemical systems, DFT investigates intramolecular interactions to elucidate the elementary mechanisms of reactions, which can be used to identify key aspects that drive selective transformations [45•] [46•]. Despite being conventionally used to merely rationalize observed experimental results, successful DFT models can go further by guiding electrocatalyst design. Indeed, accurate interfacial models can identify optimum elemental compositions of multi-component electrocatalysts (e.g., bimetallic electrocatalysts, metal mixed oxides, and nanocomposites), thus guiding experimental efforts and relieving the need to exhaustively synthesize all possible compositional variations. In the following section, we highlight examples of how DFT is used to accelerate the discovery of optimal electrocatalysts with respect to composition.

The oxygen evolution reaction (OER) is the limiting half-reaction of water splitting. Overcoming this energetic barrier would be a keystone advancement in the transition toward a renewable energy economy based on hydrogen [47]. Thereby, it is not surprising that a high level of effort has been devoted to overcoming barriers for the theoretically simple water oxidation reaction (1) that involves four electrons.

$$2H_2O \rightarrow O_2 + 4\,H^+ + 4e^- \qquad (1)$$

Thermodynamic understanding through DFT of this reaction has already proven to be a valuable predictive tool [48]. Figure 2a shows how the formation of an alloy of cobalt with nickel modifies the OER energy diagram of pristine cobalt. The DFT model derived for a working electrode potential of 1.23 V vs RHE establishes that the oxidation of adsorbed OH* to adsorbed O* is the potential-determining step (PDS) for both compositions. We note that the PDS is distinct from the rate-determining step (RDS), as the RDS refers to the step with the highest kinetic barrier, whereas the PDS corresponds to the step that is thermodynamically least favorable [49••] [50]. The RDS and PDS do not always correspond to the same step, and care must be taken when using either concept to devise descriptor-based catalyst design strategies. For example, it is possible in

Figure 1
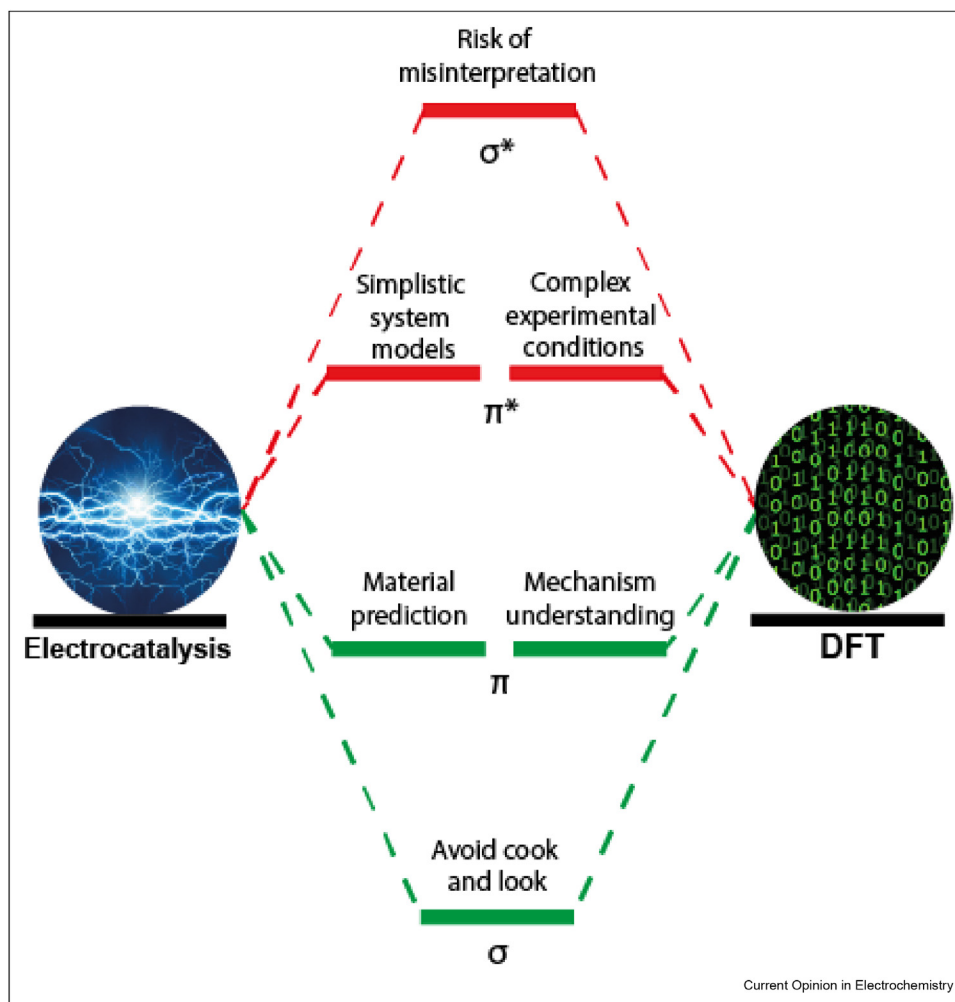
Schematic illustration of the advantages (bonding orbitals) and challenges (antibonding orbitals) of the "hybridization" of experimental electrocatalysis and density functional theory (DFT) to guide electrocatalyst discovery and design for enhanced performance in environmental applications.

some cases to increase the kinetic barrier of the RDS by lowering the limiting potential of the PDS, which can lead to incorrect catalyst design strategies [49••]. However, the energy differential between the free energy of both intermediates (i.e., OH* and O*) provides a key insight into the electrocatalytic improvement induced by different electrode compositions. For instance, the lower ΔG of 0.79 eV determined for the alloy CoNi/Co−N$_4$-CNTs when compared to pristine Co/Co−N$_4$-CNTs (ΔG = 0.87 eV) may suggest an enhanced performance for the former despite such high DFT overpotentials may hint that those materials may not be competitive for the OER [51••]. Furthermore, it is important to remark that given the accuracy of DFT, such a small difference of less than 0.10 V may not be enough to claim that one electrocatalyst may be better

than the other one. Indeed, such a small differences may show that electrocatalysts behave in a similar fashion. In some instances, deductions from modeling should not be considered absolute at this point, and caution is advised.

In a similar fashion, DFT can predict catalytic improvement of nanocomposite structures, such as silver decorated layered alkali metal oxide NaCoO$_2$. Figure 2b illustrates how the reaction energy of NaCoO$_2$ for the OH* oxidation to O* of 1.37 eV is dramatically diminished to 0.57 eV by the formation of a silver interface. The DFT modeling accurately describes the positive effect of metal oxide surface nano-decoration with a noble metal. Moreover, the effects of stoichiometric composition can be pre-assessed. Figure 2b

Figure 2
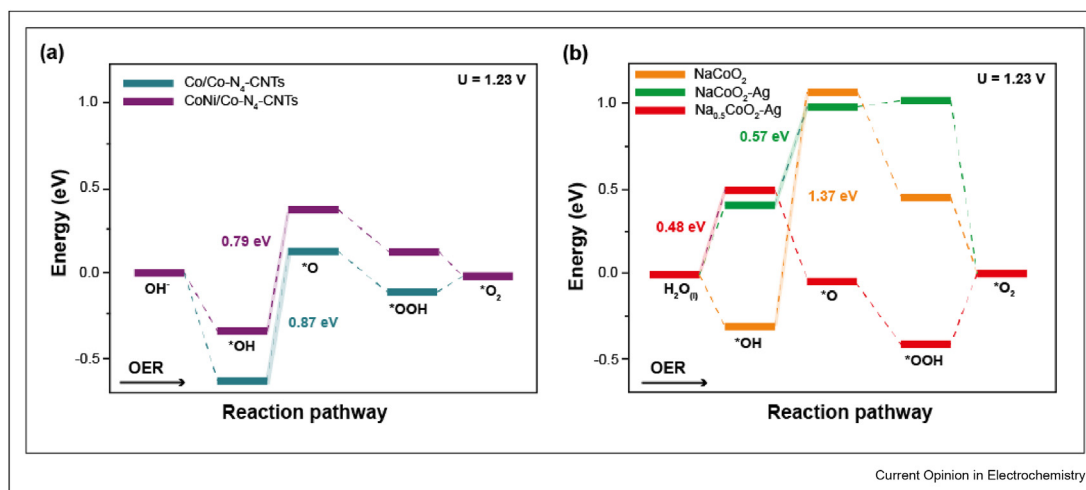
Free energy pathway of oxygen evolution reaction (OER) for (a) pristine $Co-N_4$-CNTs, $Co/Co-N_4$-CNTs respect alloy $CoNi/Co-N_4$-CNTs at the equilibrium potential U = 1.23 V vs RHE and (b) for metal oxide electrodes, $NaCoO_2$, $NaCoO_2-Ag$, and $Na_{0.5}CoO_2-Ag$ at 1.23 V vs RHE which indicate effects of nano-decoration as well as impact of stoichiometry. Figures adapted from Ref. [51••] [52••].

suggests that desodiated $Na_{0.5}CoO_2-Ag$ could stabilize adsorbed O* on the surface decreasing the free energy. Note that in the case of the $Na_{0.5}CoO_2-Ag$ electrocatalyst, the adsorption of OH* becomes the RDS with an even lower energy requirement of 0.48 eV [52••].

This example demonstrates how computational models can be employed to suggest the different elemental composition and even optimum stoichiometry with higher activity. It is important to note that reaction energies computed with DFT evaluate the thermodynamic favorability of reactions but do not necessarily predict reaction kinetics. Reaction kinetics can be computed with DFT only if reaction barriers are determined by identifying rigorous transition state structures. Reaction energies often scale with reaction barriers, but not always. Transition state scaling relations are derived from the versatile Brønsted—Evans—Polanyi (BEP) relations. The BEP relations describe correlations between transition state barriers and reaction energies, which arise from similarities in the geometric structure of the transition state and product state. They are closely related to adsorbate scaling relations, wherein the adsorption energy of similar adsorbates (e.g., O* and OH*) form a linear relationship [53] [54•] [55••] [56]. In electrocatalysis, the BEP relations are conceptually connected to Butler—Volmer equation parameters for potential-dependent reactions [57•] [58••] [59]. Thus, caution should be used when drawing conclusions from reaction energies alone. Also, it is important to keep in mind that the synthesis of material compositions suggested by DFT may be complicated or not feasible through existing methods. DFT, on the other hand, can be used to compute material formation energies and thus identify compositions that are likely to be stable

and synthesizable. Together, these DFT computations can point out paths forward and minimize unnecessary synthetic detours.

Mechanistic insights of modeling to identify active crystalline facets

Crystallographic planes and facets affect electrocatalytic processes by defining the preferential adsorption mode of electroactive species and defining preferential reaction pathways [60—62]. High nitrate concentrations in water are reported as one of the top ten water quality violations worldwide [63]. Electrochemical reduction of nitrate (ERN) can provide selective transformation toward (i) innocuous nitrogen gas for drinking water applications by reaction (2) or (ii) ammonia as a resource recovery approach through reaction (3) [64,65]. Selective transformations of nitrate into nitrogen have a strong dependency with crystalline structure as demonstrated in seminal studies using single-crystal electrodes of Pt (100) [66,67].

$$2 \ NO_3^- + 12 \ H^+ + 10 \ e^- \rightarrow N_2 + 6H_2O \tag{2}$$

$$NO_3^- + 9 \ H^+ + 8 \ e^- \rightarrow NH_3 + 3H_2O \tag{3}$$
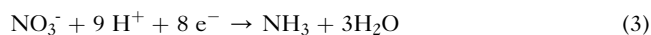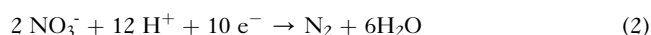
A recent study employed DFT in conjunction with the experimental synthesis of shape-controlled nanoparticles to elucidate how surface facets can be engineered to tune product selectivity during ERN [61••]. In that work, DFT energetics demonstrated why differing facets of Pd nanoparticles yield substantially different nitrate reduction rates and selectivity. DFT was used to evaluate the reaction energy associated with *NO_3 dissociation to *NO_2 + O*, which was found to

be more favorable on the Pd(111) facet compared to the Pd(100) facet. This result explains why octahedron clusters yield faster nitrate reduction kinetics compared to cubic clusters, as the octahedron clusters expose the Pd(111) facet and the cubic clusters expose the Pd(100) facet as summarized in Figure 3. Additionally, the DFT analysis revealed that *NO$_2$ binds weaker to Pd(111) compared to Pd(100), so nitrite can readily desorb from Pd(111). Thus, the octahedron particles yield high overall activity but with selectivity primarily to nitrite. Conversely, the cubic particles exhibit slower reaction kinetics but higher selectivity to ammonia over nitrite. These results then suggest an avenue for designing catalysts that are both active and selective: expose both the Pd(111) and Pd(100) facets so that the Pd(111) facets catalyze the nitrate-to-nitrite step and the Pd(100) facet catalyzes the nitrite-to-ammonia step. Indeed, the experimental results show that cuboctahedron particles exposing both facets achieve greater activity and higher selectivity to ammonia. DFT can also suggest compositional modifications to tune reactivity. For example, catalyst design for the treatment of NO$_2^-$ requires high activity and selectivity toward N$_2$ for drinking water treatment. A computational study by Henkelman and co-workers suggested that a Pd monolayer over Au might boost nitrogen production over ammonia production. Experiments conducted by Wong and co-workers confirmed that the Pd overlayer on Au

does indeed enhance activity and selectivity for nitrite reduction. Different Pd contents were evaluated, and the predicted activity trends followed those observed under controlled conditions [68●].

The different activity observed for isolated crystal facets is a relevant finding. Complex mechanisms that have pathway bifurcation may complicate the prediction of product selectivity in DFT-based models because reaction paths are often dependent the nature of specific crystal facets, as well as on adsorbate coverage. A general strategy for designing catalysts is elucidating a particular pathway on a specific facet of a specific metal and then extrapolating these results to other materials in the search for a catalyst that would perform optimally for that particular reaction [69●●]. While this method enables large-scale catalyst design effort, it is limited in situations where entirely different reaction paths are followed on different facets or at different coverages. This issue has been reported for NO reduction on Pt, where preferred reaction paths change as a function of facet and adsorbate coverage, as reported by Calle-Vallejo and Koper [70●●]. It is also a known issue in the CO$_2$ reduction literature [35] [69●●] [71●]. Thus, catalyst design studies that assume that the same reaction mechanism applies on different crystal facets must be taken with a grain of salt. However, they are useful nonetheless for initial screening studies that can

Figure 3
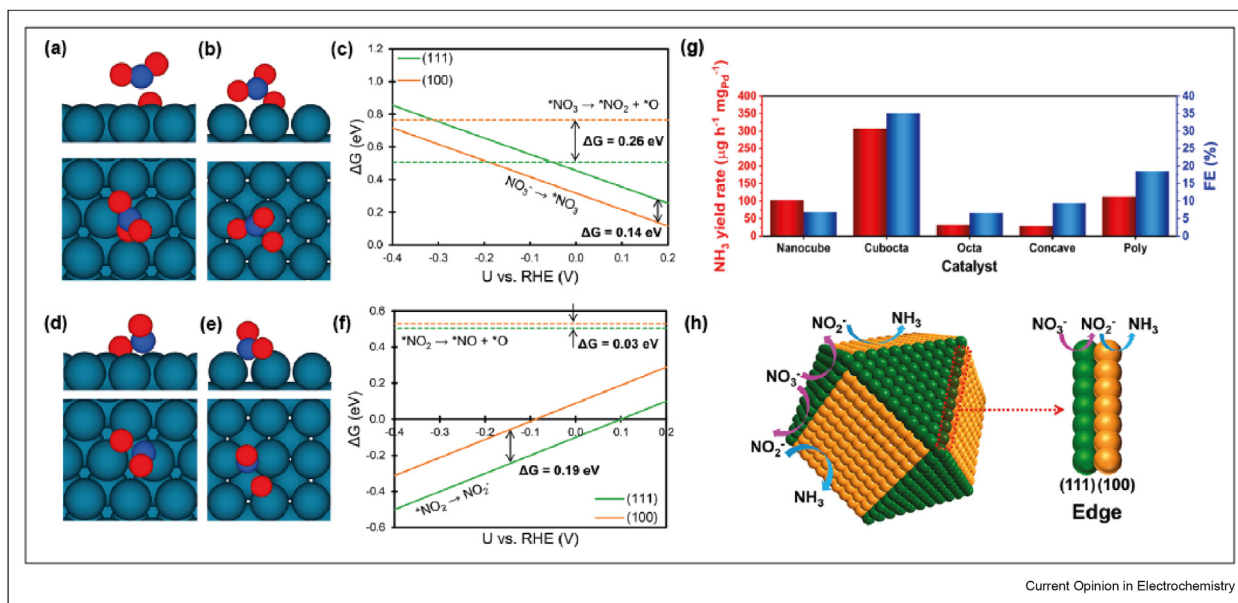
(a, b) Top and side views of the transition state of *NO$_3$ → *NO$_2$ on (a) Pd(111) and (b) Pd(100). (c) Energy of NO$_3$ – adsorption at pH = 0 and the activation barrier for *NO$_3$ → *NO$_2$ plotted against the applied potential. (d, e) Top and side views of the transition state of *NO$_2$ → *NO on (d) Pd(111) and (e) Pd(100). (f) Energy of NO$_2$ – desorption at pH = 0 and the activation barrier for *NO$_2$ → *NO plotted against the applied potential. The red, blue, and green spheres represent O, N, and Pd, respectively. (g) Ammonia yield rate and Faradaic efficiency (FE) at 3 h for different Pd nanoparticle catalyst shapes. (h) Schematic of the specific role of Pd cuboctahedrons facets on the reduction of nitrate. Figure adapted from Ref. [61●●].

be used to select particular systems for deeper analysis. Predictions from DFT can be greatly enhanced when DFT energetics are combined with rigorous kinetic Monte Carlo or microkinetic models. For example, Greeley and co-workers developed a kinetic Monte Carlo procedure for evaluating NO electrochemical reduction rates on Pt(100) [72]. Note that for NO reduction, several possible reaction paths must be explored to derive robust predictions from DFT.

Predicting kinetics and beyond: microkinetic modeling to predict larger-scale events

Theoretical modeling of electrocatalyst-mediated reactions not only provides a solid understanding of thermodynamic aspects related to mechanistic aspects and reaction pathways but also can quantify energies of activation for each elementary step [73,74]. DFT energetics can be combined with microkinetic models to predict overall reaction rates. Such a combination represents a bottom-up approach that completely captures atomistic intricacies and events on the electrocatalyst surface to allow for an accurate representation and prediction of macroscopic observable outcomes. Microkinetic modeling solves coupled differential equations that consider different relevant aspects not usually captured by simple thermodynamic calculations summarized in reaction energy diagrams, such as electroactive species concentration, surface coverage, surface interaction strength (i.e., Sabatier principle), catalytic site blocking terms, and other meaningful aspects that define macroscopic

experimental observations [26,31]. The capability of describing macroscopic response enables predictions related to not only kinetics but also product selectivity.

Electrocatalytic reduction of CO_2 is an environmental hot topic related to climate change action [75,76]. Capture and selective transformation of CO_2 to species of added value are of utmost importance to decrease greenhouse gases in the atmosphere by artificial carbon fixation processes [24,77,78]. The electrocatalytic reduction can selectively yield different products such as methanol, formic acid, or even form C−C bonds leafing to ethanol electrosynthesis. Recent studies suggest the catalysts classification depending on the adsorption energy of H*, COOH*, and CO* [79••]. For example, the Cu (111) tends to produce C_1 products, and the Cu (100) face tends to produce C_{2+} products during CO_2 reduction [80•]. A similar classification may be applied to nitrate reduction and the understanding of the selectivity and mechanism based on NO* and H* adsorption energies [81•]. Further efforts in computational modeling for CO_2 reduction are related to coordination numbers and reaction rates for selectivity predictions [16,82].

Figure 4a depicts the accurate fitting between microkinetic modeling and experimental results observed for the electrochemically driven reduction of CO_2 on Pd/C [83••]. These results demonstrate that when major drivers of electro-kinetics are considered, the microkinetic models capture the essence and describe the

Figure 4

Current Opinion in Electrochemistry
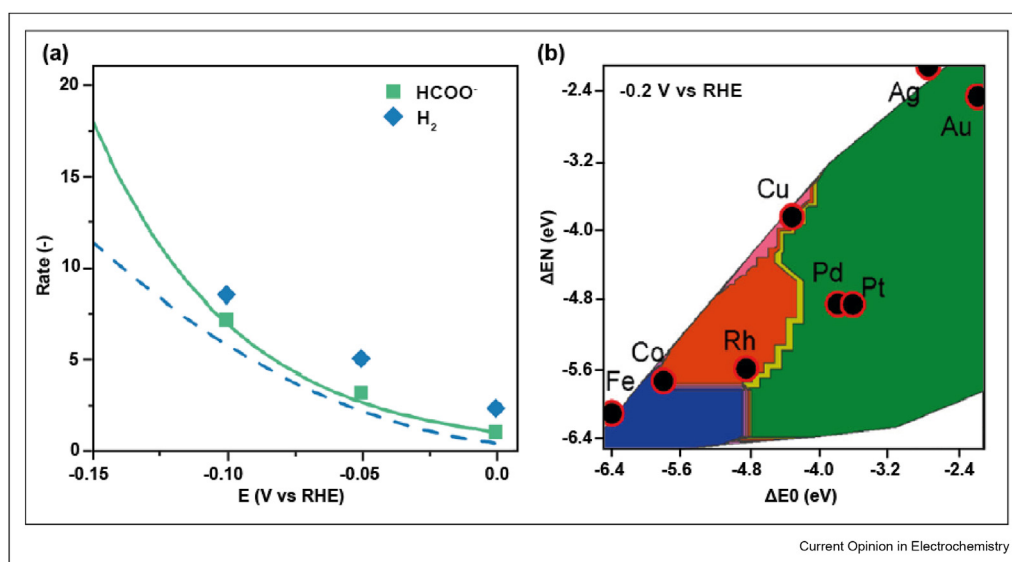
(a) Comparison between the theoretically calculated rate from microkinetic simulations (solid and dotted lines) and experimental observations for (■) formate production and (◆) hydrogen evolution rates at various electrode potentials during CO_2 electrochemical reduction in 1 M $KHCO_3$ at P_{total} = 1 bar and p_{CO2} = 1 bar. Rates are normalized versus the observed rates of formate formation (r_{HCOO^-}) at 0.0 V vs RHE. (b) Theoretical selectivity mapping of N-species products from electrochemical nitrate reduction as a function of oxygen and nitrogen adsorption energy at −0.2 V vs RHE for different transition metals. Color code: NO = green; NH_3 = red; N_2 = blue; N_2O = pink. Figures adapted from Ref. [83••] [85••].

rates of reaction. Similar results have been reported for single-atom Pb-alloyed Cu catalyst (Pb₁Cu) that selectively forms formate with a ∼96% FE [84•]. The microkinetic modeling was able to accurately predict macroscopic outcomes of charge transfer processes in terms of turnover frequency (TOF), expected kinetic rates (k), as well as current density response at a given working electrode potential [37,38].

Microkinetic modeling can provide estimated predictions on product selectivity that depend on operational and system conditions. Figure 4b illustrates theoretical preferential selectivity maps for nitrate reduction of different transition metals as a function of oxygen and nitrogen adsorption energy under potentiostatic operation. Note that predicted results are subjected to identical operation conditions and may differ from those observed for other operation modes such as galvanostatic condition, or even those obtained under different applied potentials on the working electrode [85••]. These informative qualitative predictions may fail to predict quantitative distributions at this stage of model development given that small changes in energies may result in dramatic variations of catalytic selectivity. However, involving sensitivity analysis can provide an overall guidance for preferential product identification and guide research toward exploring specific metallic combinations (e.g., single-atom catalysis, bimetallic alloys, and nanocomposites).

Conclusions and key insights

Scientific and technologic advances are positioning electrocatalysis as a keystone of sustainable development. Electrocatalytic processes of environmental relevance are different in nature and may follow different ultimate goals; nevertheless, all require specific electrocatalyst design to improve product selectivity as well as performance. Most advances in electrocatalyst design have been conducted through tedious trial-and-error approaches synthesizing myriads of novel materials from which huge amounts are deemed uncompetitive. Computational modeling holds the promise of becoming a discovering tool, despite being unfortunately *infra*-used nowadays. This current opinion summarizes the possible benefits of using DFT and microkinetic modeling as a compass to guide the strategic tailored design of electrocatalysts. The use of DFT has undoubtedly advanced our mechanistic understanding of charge transfer processes but can unlock additional benefits for research beyond its simple role as an explanatory tool. DFT can set stepstones for tailored electrocatalyst design by predicting optimum elemental compositions of alloys, metal oxides, and even nanocomposites. Furthermore, DFT can identify optimum crystalline structures and facets that promote preferential pathways with lower activation energy. The addition of microkinetic modeling can provide breadth to the prediction of electrocatalyst systems

at a macroscopic level in terms of kinetics and selectivity given different electrolysis operational conditions. Altogether, accurate theoretical modeling can become a material discovery tool for accelerated electrocatalyst optimization. Theoretical frameworks can avoid tedious blindfolded synthesis and test and transform chance discoveries into well-informed tailored engineering synthesis and faceted control for optimum environmental electrochemistry system performance.

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.

Acknowledgements

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•• of outstanding interest

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