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Perspective

The Role of Surface Science in Electrocatalysis

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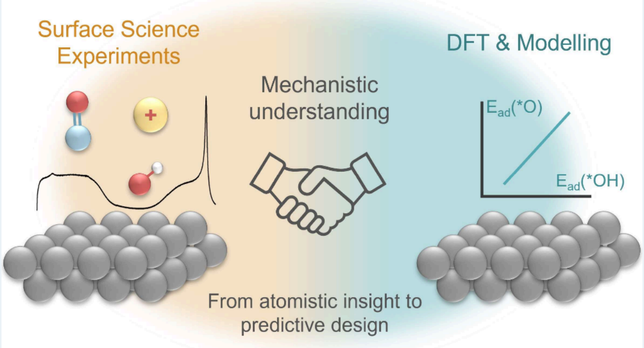
ABSTRACT: Surface science has long provided the foundation for mechanistic understanding in electrocatalysis. In this perspective, we revisit its relevance through the lens of *H/*OH adsorption in the H_{UPD} region of Pt and its role in CO electrooxidation, examples that illustrate principles that reach far beyond these systems. Electrochemical interfaces are complex and dynamic arenas where adsorbates, surface structure, and local electrolyte composition govern electrocatalytic performance. Untangling this complexity requires the atomic resolution of surface science, coupled with the reach of computational models. However, true predictive power comes only when theory and experiment act as partners, not substitutes. Rigorous mechanistic studies, often undervalued compared to the excitement of emerging materials, remain essential for achieving truly rational catalyst and electrolyte design.



KEYWORDS: *surface science, electrocatalysis, electrochemical interfaces, mechanism, computational electrochemistry*

1. INTRODUCTION

In the pursuit of sustainable energy technologies, the field of electrocatalysis has become increasingly defined by the search for "better" catalysts: materials that promise higher activity, selectivity, or stability for critical reactions. While this quest has yielded important advances, it has also fostered a tendency to prioritise performance metrics over fundamental understanding. For example, a simple title search in the Web of Science shows how the emphasis in electrocatalysis has shifted. The number of papers with "electrocatalytic" as keyword that also include "performance" has increased from about 1000 in 2010−2015 to roughly 9500 in 2020−2025. Similarly, the papers that include the keyword "activity" have increased from roughly 9000 in 2010−2015 to 18 000 in 2020−2025. In contrast, terms such as "surface science" or "mechanism" remain rare, each appearing in fewer than 500 papers between 2020 and 2025. Although these values are small in absolute terms, the relative growth of performance-oriented language compared to mechanistic descriptors highlights how easily fundamental insight can be overshadowed by claims of improved activity. Such tendency is understandable, but without a clear picture of the underlying mechanisms and interfacial phenomena, the criteria for what constitutes a "better" catalyst can become misleading.

One of the clearest examples of how deeper mechanistic understanding has reshaped this narrative lies in the study of hydrogen electrocatalysis on Pt. The hydrogen underpotential deposition (H_{UPD}) region on Pt has long served as a foundational system in electrochemistry.[1] However, for many years, its interpretation relied on data from polycrystalline electrodes,[2−4] leading to averaged-out views that masked the site-specific nature of key processes.

The advent of surface science changed this view. By isolating specific single-crystalline Pt facets and probing their interactions with hydrogen under controlled conditions, researchers were able to resolve the atomic-scale structure and thermodynamics of hydrogen adsorption on specific Pt sites.[5,6] Surface science thereby revealed the sensitivity of hydrogen binding energies (HBE) to atomic surface geometry, dynamic surface reconstructions, and even the presence of coadsorbates. Such insights would have been difficult, if not impossible, to extract from more complex or disordered systems. Surface science, as a deliberately reductionist approach focused on atomically well-defined interfaces, has provided clarity precisely by isolating and controlling the variables at play. In this sense, the primary aim of surface science is not, or not only, the rational design of "better" catalysts per se, but to validate the atomic-level picture that often guides the principles used in catalyst design strategies.

In parallel, first-principles density functional theory (DFT) calculations have emerged as powerful tools for modeling electrochemical interfaces. DFT calculations and related approaches, such as ab initio molecular dynamics (AIMD)

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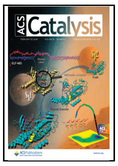

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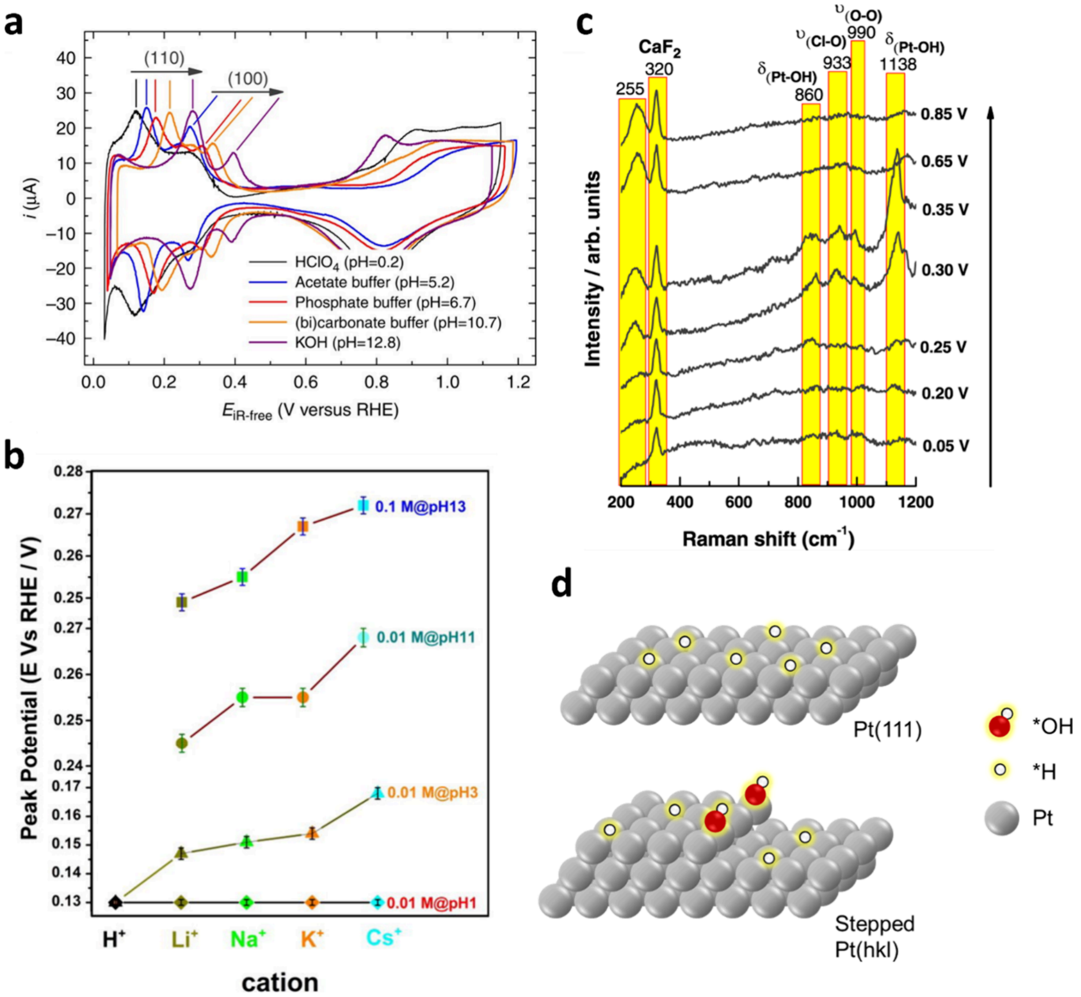

Figure 1. (a) Cyclic voltammogram of Pt polycrystalline in a full range of solution pH in nonadsorbing Ar-saturated electrolytes at a sweep rate of 50 mV s^{-1}. The CV curves have been corrected for solution resistance. Reproduced with permission from ref 12 Copyright © 2015 Nature publishing group. (b) Cation dependence of the (110)-step related voltammetric peak across a pH range of 1−13. The total alkali cation concentration (Li^+, Na^+, K^+, Cs^+) was 0.01 M at pH 1−11 and 0.1 M at pH 13. pH 1 was obtained using 0.1 M $HClO_4$ and pH 3 with 0.001 M $HClO_4$; in both cases, 0.01 M of the corresponding alkali cation salt ($MClO_4$) was added to this solutions to maintain the desired (alkali) cation concentration of 0.01 M. Peak potential determined in the positive-going scan. Reproduced with permission from ref 20 Copyright © 2018 John Wiley and Sons. (c) Potential dependent SHINERS spectra of Pt(311) in an Ar-saturated 0.1 M $HClO_4$ electrolyte. The different Raman bands are highlighted by the yellow squares. Reproduced with permission from ref 26 Copyright © 2022 Nature publishing group. (d) Simplified atomistic representation illustrating *H adsorption on Pt(111) terraces and *OH adsorption on Pt step sites in the H_{UPD} (0−0.4 V_{RHE}) previously discussed in the text.

simulations, have been instrumental in rationalizing trends in HBE, mapping out reaction energetics, and electronic and electrolyte structure of electrocatalytic interfaces. In many cases, DFT and surface science have advanced hand-in-hand (e.g., experimental findings on well-defined surfaces guiding theoretical modeling, and simulations offering predictive frameworks). Yet, the two approaches are inherently different: surface science builds knowledge from highly controlled experiments, while theory or computational chemistry constructs it from first-principles based on a model representation of experiment. In essence, while surface science simplifies "reality," computational chemistry simulates "reality," often in a way that is even more simplified than the surface science model. Interestingly, while the surface science approach using single-crystalline surfaces is not widely adopted by the electrocatalysis community (presumably related to the specific and significant experimental efforts involved), the computational study of simplified models of the complex electrocatalytic interface is currently widespread and part of the toolbox of many groups working in the field. As such, DFT calculations appear to have taken over the role of surface science experimentation. As electrocatalysis research increasingly gravitates toward more complex nanostructured systems, there is a growing risk that DFT simulations will be used as a substitute for experimental validation and surface science approaches, rather than as a partner to it.

It has been previously noted[7] that the limitations of computational chemistry, particularly in capturing interfacial complexity, solvation, and potential control, are still active areas of discussion in computational (electro-)catalysis. While DFT is efficient for capturing trends across materials, its predictive accuracy for specific systems depends on calibration against high-quality experimental data obtained using a surface science approach. Without such calibration and validation against surface science experiments, the "confirmation bias" mentioned by Pidko[7] is a prominent risk. In this sense, the dedicated integration of both theory, computation and surface science is essential for a full and accurate understanding of electrocatalytic phenomena.

In this perspective, we revisit the H_{UPD} region on Pt as a case study to show how surface science has shaped and will continue to shape modern electrocatalysis, specifically the accurate understanding of complex interfacial phenomena. We highlight how surface science has transformed our understanding of this system, and explore how theoretical models, particularly DFT, can complement (but not replace) experimental approaches. Rather than viewing DFT simulations as a one of the tools in the toolbox, we advocate for a more integrated, reductionist and critical approach to the combination of experiment and theory in electrocatalysis: one that uses both tools to refine, rather than reinforce, our models and theories about electrocatalytic activity. Stamenkovic et al. have recently highlighted the role of surface science in electrocatalysis from a more methodological point of view.[8] Our Perspective emphasizes the conceptual role of surface science.

2. NON-NERNSTIAN PH-DEPENDENT SHIFT OF H_{UPD} PEAKS ON PT

Before the advent of surface science techniques, our understanding of hydrogen adsorption (*H) on Pt was primarily based on studies with polycrystalline electrodes. In the voltammetric profile of Pt, the region between 0.4 V_{RHE} and the onset of the hydrogen evolution reaction (HER) has been historically attributed to the underpotential deposition of hydrogen (H_{UPD}). This region features several peaks that were initially interpreted as arising from two distinct types of *H, referred to as “weak” and “strong,” based on the potential range in which they appeared.[4] Peaks at less positive potentials (~0.12 V_{RHE} at pH 1) were assigned to weakly adsorbed hydrogen while peaks at more positive potentials (~0.27 V_{RHE} at pH 1) were attributed to strongly adsorbed hydrogen. This interpretation, while reproducible, treated the electrode surface as homogeneous and made no distinction between atomic sites.

Studies on well-defined single-crystal surfaces,[6] revealed that the apparent “weak” and “strong” *H actually corresponded to adsorption/desorption processes at specific crystallographic sites: namely, step sites resembling those found on Pt(110) and Pt(100), respectively.[9−11] What had been previously treated as potential-dependent variations in binding strength turned out to reflect site-specific adsorption/desorption governed by atomic surface geometry.

This site dependence also proved crucial in addressing the long-standing debate over the origin of the apparent non-Nernstian pH shift in the H_{UPD} peaks on Pt. On polycrystalline Pt, the features in the H_{UPD} region shift by approximately +0.15 V_{RHE} when the pH of the electrolyte changes from 0 to 13 (Figure 1a),[12] a deviation from the expected 0 mV/pH (on the RHE scale) predicted by the Nernst equation for a simple $1e^-/1H^+$ process. Initially, this behavior was attributed to pH-dependent changes in the hydrogen binding energy (HBE) at step sites.[9,13,14] However, surface science techniques combining single-crystal electrochemistry, theoretical modeling, and spectroscopy, revealed a more accurate explanation: the step-related peaks originate from the replacement of surface-adsorbed *H by hydroxide (*OH), which preferentially binds to low-coordination (110) and (100) step sites.

In the absence of cations (other than H^+), the potentials of both the (110)- and (100)-related peaks are Nernstian, showing no intrinsic pH dependence (Figure 1b). The apparent pH effect arises because *OH binding strength is cation-sensitive. DFT calculations revealed that cations compete with *OH for coordinating interfacial H_2O molecules, modifying *OH stability.[15−19] Since the interfacial cation concentration itself changes with pH on the RHE scale (as the potential of zero free charge shifts positively), the apparent non-Nernstian pH dependence is, in fact, a manifestation of cation effects.[15,20−22]

Theoretical and thermodynamic analyses further suggested that both *H and *OH contribute to the voltammetric features within the so-called H_{UPD} region on stepped Pt, showing that *OH binds more strongly to step-edge atoms than to terrace atoms, with binding energies strongly dependent on local coordination.[17,18,23−25] Complementary voltammetric studies on vicinal Pt(110) surfaces revealed complex low-potential features that were highly sensitive to CO cooling, suggesting that species other than *H, namely *OH, contribute to the response.[16] Supporting this, isotope exchange experiments on polycrystalline Pt demonstrated that *OH species were likely present even on polycrystalline Pt in the traditional H_{UPD} region, especially on rough or defect-rich surfaces.[19]

While this body of evidence strongly suggested that the H_{UPD} region involves not just *H, but also *OH and cations, direct spectroscopic confirmation remained elusive. Only recently, using SHINERS (Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy), was *OH adsorption on step sites detected spectroscopically at low potentials (Figure 1c).[26] Raman signatures for *OH at potentials as low as ~0.25 V_{RHE}, well below the previously assumed onset of ~0.55 V_{RHE} for *OH on Pt, appeared concurrently with voltammetric peaks associated with step sites and coincided with bipolar and negative features in CO displacement experiments, confirming the replacement of *H by *OH on step sites at low potentials. By conclusively linking spectroscopic, electrochemical, and structural observations, this work provided definitive evidence that *OH coexists with *H in the H_{UPD} region on Pt stepped surfaces. This confirmation marks the culmination of a decade-long effort and underscores the power of combining single-crystal electrochemistry, surface spectroscopy, and theory, to resolve complex interfacial phenomena.

The culmination of these findings presents a significantly revised picture of the H_{UPD} region: rather than a clean *H adsorption process, it is a competitive and site-dependent region where *H, *OH, and solvated cations dynamically interact, with the dominant species varying with surface structure, pH, and electrolyte composition. What once appeared to be anomalous peak shifts on polycrystalline Pt are now understood as the superposition of site-specific adsorption processes that only become distinguishable through structurally resolved studies.

3. ROLE OF SURFACE STRUCTURE AND *OH IN CO ELECTROOXIDATION AND BEYOND

Surface science and, in particular, the resolution of the adsorption/desorption processes that occur in the H_{UPD} region on Pt, has led to a fundamental re-evaluation of multiple electrocatalytic reactions. By revealing that the H_{UPD} region reflects a balance between *H and *OH on undercoordinated Pt step sites that is strongly influenced by surface geometry and electrolyte composition, surface science has reshaped our understanding of how intermediates form, compete, and evolve, under reaction conditions. This molecular-level insight is crucial because *OH plays a critical role in key pathways such as the bifunctional mechanism for the electrooxidation of carbon monoxide (CO) and small organic molecules. In this context, surface science provides not just a mechanistic correction, but a conceptual bridge that links model studies on ideal surfaces to

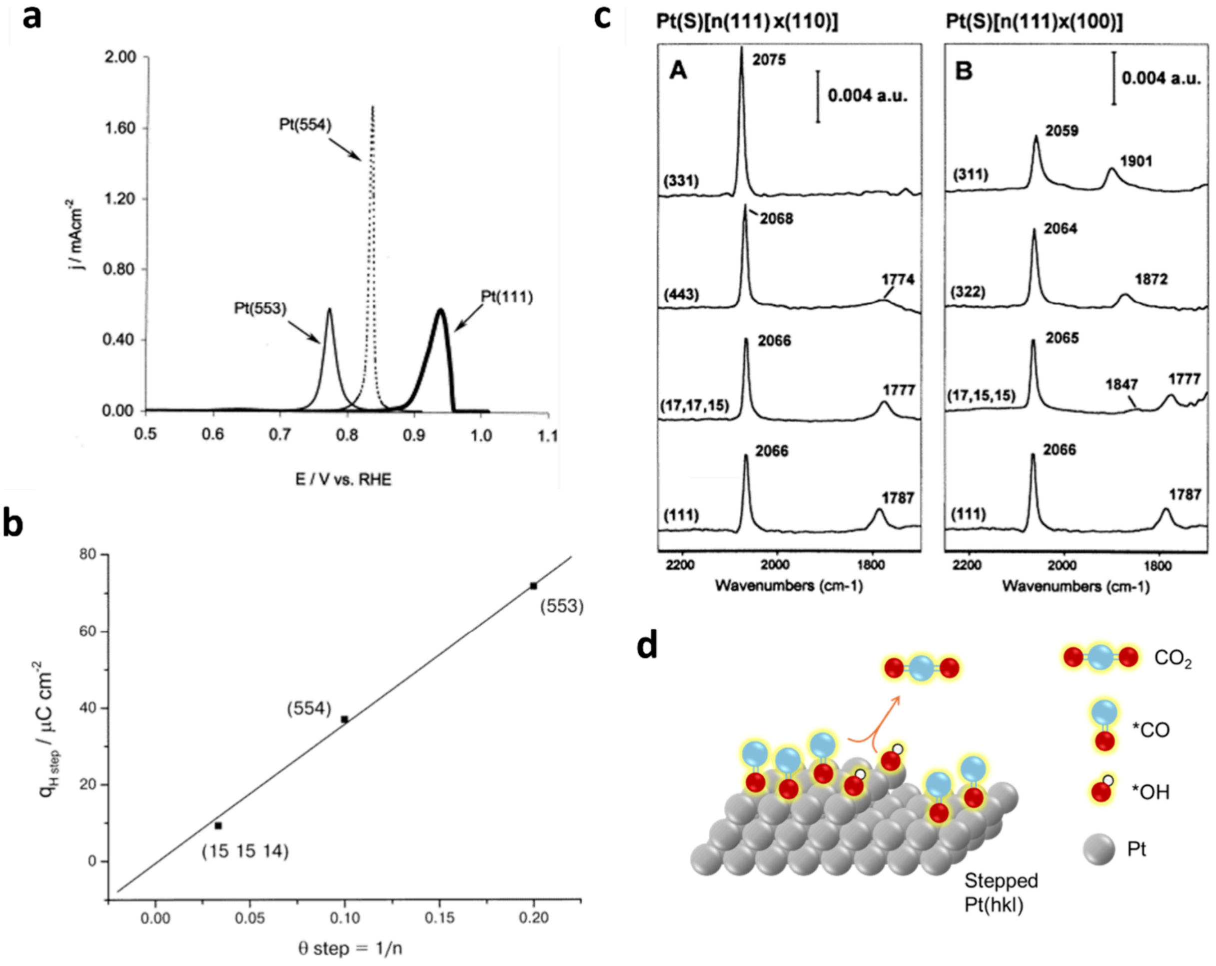

Figure 2. (a) Oxidation of saturated CO adlayers on Pt(553) (thin solid line), Pt(554) (dashed line) and Pt(111) (thick solid line) at a sweep rate of 50 mV s^{-1}, $T = 25$ °C. Reproduced with permission from ref 35 Copyright © 2000 Elsevier. (b) Dependence of the apparent rate constants (k) derived from chronoamperometric transients as a function of step fraction (θ step). Final potentials are 0.73 V (triangles), 0.755 V (diamonds), 0.78 V (squares), and 0.805 V (circles). Reproduced with permission from ref 34 Copyright © 2002 American Chemical Society. (c) Comparison of infrared absorbance spectra obtained for saturated CO adlayers at 0.1 V_{RHE} in CO-saturated 0.1 M $HClO_4$ for a series of stepped Pt surfaces in the (n(111) × (110)) (A) and (n(111) × (100)) (B) zones, as indicated. Reproduced with permission from ref 39 Copyright © 1999 American Chemical Society. (d) Simplified atomistic representation illustrating the LH mechanism of CO electrooxidation, in which *CO on terrace sites react with *OH on step sites to form CO_2.

more complex systems operating under real electrochemical conditions.

As an illustration of this impact, in this section we will focus on how surface science has reshaped our understanding of the CO electrooxidation mechanism. While this reaction had long served as a model system for probing electrocatalytic mechanisms,[27−29] its strong surface-dependence remained largely overlooked until surface science began to resolve its complexity (including but not limited to the role of *OH).

Beyond its mechanistic relevance, CO electrooxidation holds importance in applications such as air purification, sensing, automotive emission control, and the removal of trace CO in H_2 feeds for fuel cells.[30,31] The electrooxidation of CO on Pt follows a Langmuir−Hinshelwood (LH) mechanism, in which both adsorbed CO (*CO) and oxygen-containing species (namely *OH) react on the surface to form CO_2.[32] Although this mechanism was proposed in the 1980s,[33] surface science made it possible to isolate the structural and chemical origin of the activity.

Initial studies on Pt single-crystals established a direct link between surface structure and the catalytic performance of this reaction (Figure 2a). Using Pt[n(111)×(111)] surfaces, chronoamperometric studies revealed that apparent rate of CO electrooxidation increases linearly with the step fraction of the surface (Figure 2b).[34−36] This reinforced the idea that the enhancement in reactivity with surface roughness is not only due to geometric factors, such as increased surface area, but also due to specific catalytic roles played by the atomic steps.

Spectroscopic studies of *CO adlayers added a spatial dimension to the CO electrooxidation, revealing distinct adsorption patterns on terraces and steps (Figure 2c). On Pt(111), it was observed that *CO forms a compressed (2 × 2)-3CO structure in atop and 3-fold hollow sites, saturating the surface and restricting access for coreactants (*OH) to adsorb. In contrast, stepped surfaces disrupt this dense adlayer, exposing undercoordinated sites and allowing more open configurations.[37−39] As discussed in the previous section, such step sites favor *OH at lower potentials (in the H_{UPD} region), placing *CO and *OH in close proximity and enabling the LH pathway.[40,41] Since *CO binds strongly to steps, this geometry naturally colocalizes reactants and accelerates CO electrooxidation. Electrochemical and in situ spectroscopic studies

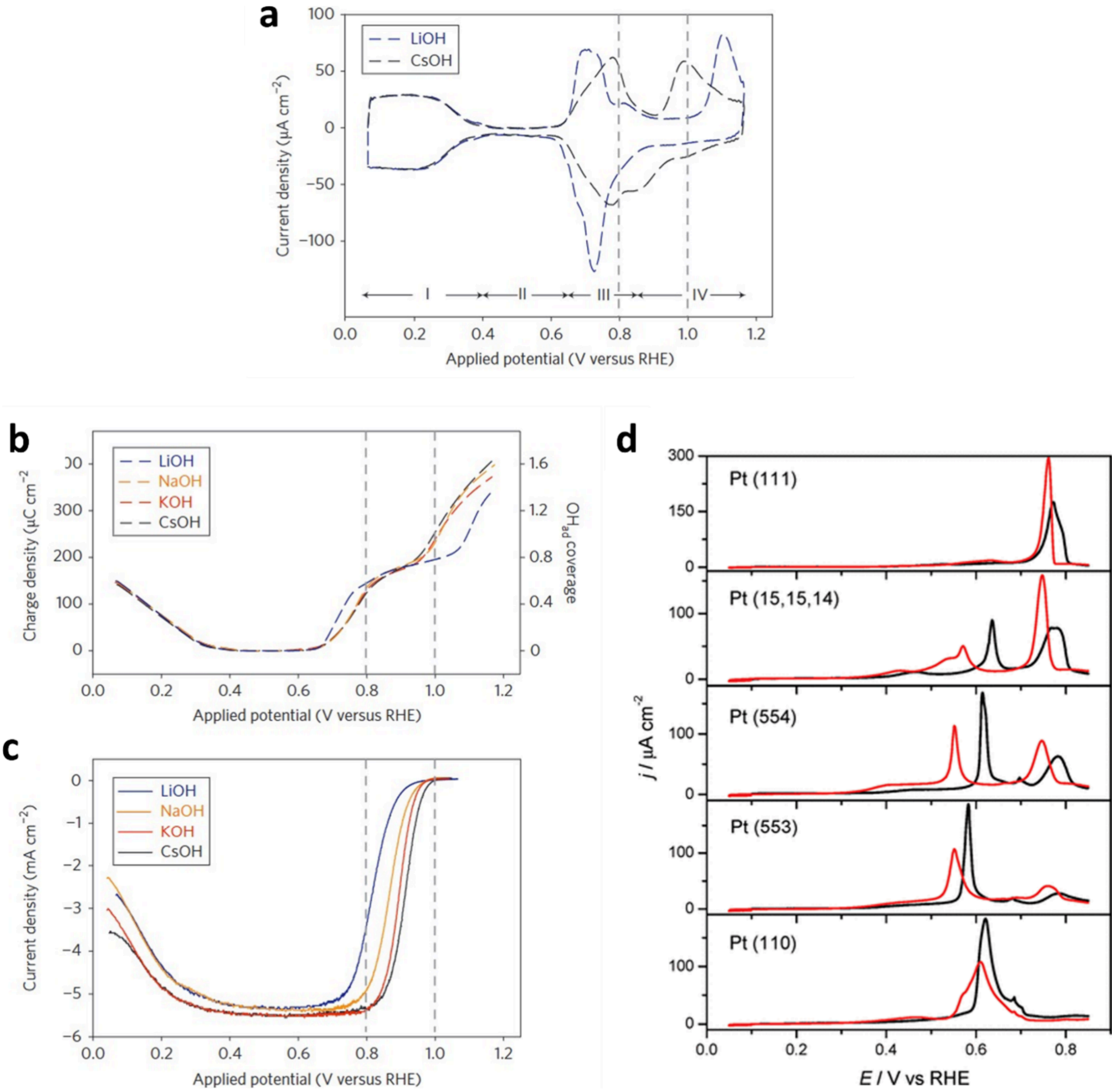

Figure 3. (a) The effects of Cs^+ and Li^+ on the shape of CVs, including H_{UPD} (region I), the double layer (region II), the reversible adsorption of *OH (region III) and irreversible oxide formation (region IV) at a scan rate of 50 mV s^{-1}. Reproduced with permission from ref 66 Copyright © 2009 Nature publishing group. (b) The effects of Li^+, Na^+, K^+ and Cs^+ on surface coverage (or charge density) of H_{UPD}, *OH and irreversible oxide. Reproduced with permission from ref 66 Copyright © 2009 Nature publishing group. (c) Polarization curves for the oxygen reduction reaction (ORR) in electrolytes that contain various cations. Scan rate 50 mV s^{-1}. Reproduced with permission from ref 66 Copyright © 2009 Nature publishing group. (d) Voltammetric profiles of CO stripping for Pt(hkl), as indicated in the figure, in 0.1 M NaOH (black) and 0.1 M LiOH (red) at a scan rate of 20 mV s^{-1}. Reproduced with permission from ref 71 Copyright © 2010 American Chemical Society.

confirmed that CO electrooxidation typically initiates at steps. In this configuration, the steps serve as the primary reactive centers where *CO and *OH meet to form CO_2, while the terraces act as a reservoir that continuously replenishes *CO at the steps via surface diffusion.[42−47] This spatial separation of roles (step as reactive site, terrace as supply route) marked a shift from prior homogeneous models to a site-resolved mechanistic picture.

Importantly, chronoamperometric studies show that even with this terrace-step cooperation, the reaction rate passes through a pronounced current maximum as time increases. Such a maximum is characteristic of surface-confined LH kinetics, but in this system it also carries mechanistic meaning. This rate maximum arises from a kinetic trade-off: at short times, insufficient *OH coverage at steps limits the reaction rate, while at longer times, oxidative stripping has reduced the *CO coverage, also limiting the rate.[42,48] The reaction rate reaches a maximum in time when the balance between available *CO and *OH is optimal. This transient-current maximum occurs in both acidic and alkaline media but shifts with electrolyte composition: alkaline lowers the onset due to greater *OH availability, while buffer species,[49] acid−base equilibrium,[50] and specific cation/anion effects,[51] modulate *CO coverage and *OH formation, tuning reaction kinetics.

Direct spectroscopic evidence also reconciled earlier discrepancies between UHV and electrochemical studies by confirming that *CO exhibits very high surface mobility on Pt(111) in both environments.[52,53] These studies demonstrated that limited

*OH or H_2O coadsorption can occur on terraces at sufficiently high potentials, explaining why Pt(111) exhibits CO oxidation activity despite the delayed onset of *OH formation.[52]

While CO electrooxidation on Pt has benefited from decades of careful surface science research, not all electrocatalytic systems rely on the same level of mechanistic clarity. The insight available now for the CO electrooxidation on Pt stands in marked contrast to other important electrocatalytic reactions such as the CO_2 reduction reaction (CO_2RR) on Cu. The limited number of surface science studies on CO_2RR (which we realize is more complicated due to the highly dynamic nature of the Cu surface) and a tendency to rely heavily (sometimes even too heavily) on DFT alone have left major aspects of the mechanism unresolved. The contrast among different electrocatalytic systems underscores a broader message of this Perspective: without surface science and atomistic grounding, even large research efforts can struggle to converge on a coherent and consistent mechanistic picture.

In sum, CO electrooxidation on Pt is now understood as a spatially- and chemically partitioned process driven by the interplay between *CO and *OH at terrace and step sites, respectively, with rates set by geometric accessibility and coverage balance. On stepped surfaces, CO electrooxidation begins at lower overpotentials because *OH forms readily at step sites while terraces supply *CO via fast surface diffusion. On Pt(111), where *OH occurs only at higher potentials, electrolyte conditions strongly influence the onset potential, with specific ion effects and oxygen-donor availability determining when the reaction can proceed. Defects in the surface also play a major role in the mechanism on Pt(111). This mechanistic framework not only redefines how we understand CO electrooxidation, but also our view in electrocatalysis on Pt. The identification of *OH at low potentials at step sites as a key step in the reaction mechanism extends to the oxidation of other organic molecules,[54] such as methanol,[55−57] and ethanol,[58,59] where similar bifunctional pathways are operative. This insight presents a clear path to designing more efficient systems, either by increasing step-site density or promoting *OH formation through alloying,[60] or alternatively by tailoring the electrolyte composition to tune adsorbate stability and reactivity.

4. INFLUENCE OF ELECTRIC DOUBLE LAYER STRUCTURE AND COMPOSITION ON *OH AND ON CO ELECTROOXIDATION

In the previous discussions on *OH in the H_{UPD} region and its role in enabling CO electrooxidation, we already noted that the electrolyte composition shapes fundamental processes at the Pt interface. What might appear as simple adsorbate−surface interactions are, in fact, strongly coupled to the surrounding electrolyte environment. Building on these insights, it becomes clear that the electric double layer (EDL), or more generally, the interfacial electrolyte, plays an active role in *OH adsorption, surface oxidation, and ultimately, electrocatalytic activity. Rather than acting as an inert background, the electrolyte modulates local electric fields, influencing the adsorption energetics and the stability of intermediates.[61−64] As a result, it is now well-established that virtually all electrocatalytic reactions are highly sensitive to the local composition and structure of the electrolyte at the interface.

A striking example of this comes from the apparent non-Nernstian pH dependence of the H_{UPD} peaks on Pt which has been attributed to cation-dependent *OH adsorption at step sites (discussed earlier in Section 2). Voltammetric studies reveal that alkali cations (Li^+, Na^+, K^+, Cs^+) systematically shift the potentials of *OH-related features in a trend that correlates with the cation size and hydration energy.[20,21,24,65,66] At undercoordinated step sites, cations interact with *OH and compete for interfacial water coordination.[15−19] This competition modulates the strength of *OH binding, shifting step-related voltammetric peaks depending on the cation's identity.[20,21,67,68] Strongly hydrated cations such as Li^+ stabilize *OH through noncovalent interactions, such as hydrogen bonding and electrostatic attraction, while weakly hydrated cations like Cs^+ can coadsorb with *OH. This coadsorption weakens the *OH binding to the surface by stabilizing *OH⋯cation complexes and shifts the *OH-related voltammetric features to more positive potentials (Figure 1b).[66,69]

This *OH⋯cation interactions not only explain the non-Nernstian pH dependence of the H_{UPD} region but also extend to *OH adsorption on terrace sites (Figure 3a). On Pt(111), weakly hydrated cations destabilize *OH by disrupting hydrogen-bonding network of interfacial water, making *OH easier to desorb and thereby facilitating oxide formation (Figure 3b). In contrast, strongly hydrated cations stabilize *OH, shifting the *OH-related peaks to less positive potentials and delaying the onset of Pt oxidation.[70−72]

Surface science studies on well-defined Pt single crystals have been instrumental in revealing these effects, and showed that *OH adsorption does not solely depend on the metal surface but it is strongly modulated by cation-water-*OH interactions. These insights have reframed our understanding of Pt oxidation: the onset of oxide formation, once thought to be a simple potential-driven process, is now seen as a cooperative phenomenon involving the surface structure and the electrolyte. Building on these insights, it becomes clear why interpreting electrolyte effects in electrocatalysis from theory alone is so challenging. On one hand, the interfacial region is highly dynamic and the limited time scale and system size available to AIMD (and even ML-derived versions thereof) can often not be expected to fully capture the constantly reorganizing water network. On the other hand, DFT calculations can unintentionally "place" ions or water molecules in positions that look reasonable but are not statistically representative. Without experimental grounding, such idealized models can drift toward biased mechanistic interpretations. This is precisely why pairing DFT with well-defined surface science measurements remains indispensable. Only the combination of the two can provide a consistent picture of how electrolyte composition shapes reactivity.

These same principles extend beyond blank voltammetry to electrocatalytic reactions where *OH is mechanistically essential (Figure 3c). CO electrooxidation provides a clear example. Since CO binds strongly to Pt, its oxidative removal requires the availability of *OH at adjacent sites (see Section 3). Small, strongly hydrated cations such as Li^+ (and even Be^{2+}) promote CO electrooxidation on Pt by facilitating *OH adsorption at lower potentials, especially on stepped surfaces where *OH forms most readily (Figure 3d).[71] In contrast, larger, weakly hydrated cations like Cs^+ are less effective, leading to weaker promotion of CO oxidation. The resulting activity trend correlates with the cation's ability to stabilize the *OH adlayer (Figure 3d), with in situ spectroscopy confirming that *OH and COOH intermediates are modulated by cation identity.[46,71,73] Importantly, CO electrooxidation is not unique in this aspect. Reactions such as hydrogen evolution and oxidation, carbon dioxide electroreduction, oxygen reduction, and the oxidation of alcohols also display high sensitivity to cation identity, underscoring how electrolyte composition can tune reaction rates and selectivity.[66,73−76] The exact mechanistic origin of some of these effects is still very much debated. There is little doubt in our minds that the resolution of these debates necessitates a surface science approach, combining well-defined single-crystalline surfaces with tailored first-principles calculations. The observation that these electrolyte effects (e.g., hydrogen evolution on Pt) are highly structure sensitive,[77] attests to the importance of accurately controlling catalyst surface structure. Remarkably, while many first-principles calculations have often used Pt(111) as a model surface for simulating the role of the electrolyte on the reactivity of polycrystalline Pt,[78−80] Pt(111) is the one single-crystal facet which deviates from the other facets, and from polycrystalline Pt.

Taken together, these results highlight a unifying principle: cations are not mere spectators that screen charge but are active participants that tune the thermodynamics and kinetics of key adsorbed intermediates and surface reactions. Surface science has been crucial in demonstrating this at the atomic level, while studies of model electrocatalytic reactions show how these electrolyte effects manifest in measurable activity trends. One broader implication is that electrolyte engineering provides a powerful design tool, in addition to tuning catalyst composition, in optimizing electrocatalytic performance.

5. CAN DFT REPLACE SURFACE SCIENCE?

While surface science provides the experimental basis to understand electrocatalytic reactions, density functional theory (DFT) offers a powerful theoretical framework to probe and predict atomic-scale mechanisms, active sites, and catalyst design principles.[81,82] Ab initio DFT calculations have revolutionized the field of surface science and surface catalysis. Modern density functionals now achieve chemical accuracy on the order of ∼20 kJ/mol. In combination with the ever-increasing computational power of modern computers, it is now possible to simulate from first-principles systems containing thousands of atoms. When combined with molecular dynamics, so-called ab initio molecular dynamics (AIMD), these methods can capture dynamics on the nanosecond time scale and estimate free energies of adsorbed species. Since the end of 1990s, DFT and AIMD calculations have become indispensable for modeling surface electrochemistry, enabling the simulation of potential-dependent adsorption, solvation, and reaction energetics under increasingly realistic conditions.

For many electrochemists, DFT is now a household method to evaluate the energetics of presumed active structures and intermediates during a catalytic cycle, and to thereby suggest or confirm electrocatalytic pathways and mechanistic details. With the opportunities offered by Artificial Intelligence and Machine Learning, the simulation of larger and more complex systems for longer periods of time is currently taking a quantum leap in performance. This is likely going to have a corresponding impact on the field of computational electrochemistry. Good reviews and perspectives on the promises and challenges of computational electrochemistry are available.[83−86]

Despite these advances, it is essential to acknowledge the intrinsic limitations of DFT. The accuracy of any DFT calculation depends not only on the chosen functional but also on the validity of the model used to represent the electrochemical interface. The system size and time scales accessible to DFT and AIMD are still short compared to the scales of electrocatalytic processes. For this reason, DFT is most powerful when it is used in a comparative way to elucidate semiquantitative trends and correlations. The seminal work of Nørskov et al.[87] is a prominent example: by comparing the energetics of key intermediates in the oxygen reduction reaction (ORR) across different metals, they elucidated both the observed activity trends and the fundamental limitations with respect to so-called scaling relations.[88−90] We consider the recognition of these scaling relations between adsorbate binding energies, and their impact and resulting limitations on catalyst design, as one of the most important conceptual, textbook-level advances in heterogeneous catalysis in the past decades, with computational chemistry playing a decisive role. Scaling relations have since become a cornerstone concept in catalysis teaching. Their development has also set in motion a whole new field of research in (heterogeneous) catalysis focused on "breaking scaling relations",[91] an activity that would unlikely have emerged without the insights provided by first-principles DFT calculations.

While first-principles DFT calculations have become an indispensable tool for the electrochemical surface scientist, their growing popularity has sometimes led to its use as a substitute rather than a complement to experiments. We are not in favor of using DFT to replace well-defined and tailored surface science experiments. Every DFT calculation involves defining a model of the active surface or active site and its environment. Such a model is often still highly idealized, and of a significantly lower complexity than even a well-tailored surface science experiment. Especially when the inspiration for the DFT calculation comes from "non-surface science" experiments, e.g. using poly- or nanocrystalline catalytic surfaces, such an idealized model carries the risk of enhanced bias toward a certain outcome.[7] A useful way to appreciate this sensitivity is to recall the Arrhenius relationship, which shows that a reaction rate (k) depends exponentially on its activation energy (E_a). For example, a typical uncertainty of ∼0.2−0.4 eV in a DFT activation energy might seem small, but at room temperature (298 K), this corresponds to roughly 8−15 times the thermal energy ($k_BT \approx 0.026$ eV). Because rates and equilibrium constants scale exponentially with E_a, such small error leads to a change of about several orders of magnitude ($\sim 10^3-10^7$) in the predicted reaction rate or equilibrium constant. In addition to this, in comparing experiment and simulation, there is always a risk of interpretation bias, and it may be difficult to eliminate bias completely, but we strongly believe that by letting surface science experimentation and DFT calculation go hand-in-hand, this risk is minimized.

In this sense, DFT and surface science are natural partners: surface science provides the atomic-scale benchmarks against which theory is calibrated, while DFT extends mechanistic understanding beyond what can be directly measured. The optimal cooperation between experiment and theory or simulation is therefore one that involves multiple iterations, and that also specifically targets conclusions about where the agreement between the two is still missing or uncertain. Such an iterative dialogue between computation and surface science experiment will be essential for developing truly predictive models of electrocatalysis.

■ CONCLUSIONS

This perspective intended to highlight how surface science remains indispensable for electrocatalysis. While we have focused on *H, *OH, and CO electrooxidation as illustrative examples, the role of surface science extends beyond these cases.

Rather than being a tool for chasing the next "best" catalyst, the true contribution of surface science is to provide the mechanistic clarity needed to understand why electrocatalytic interfaces behave the way they do. Without this foundation, claims of activity improvements risk being misinterpreted, oversimplified, or even irreproducible.

Electrochemical interfaces are inherently complex: adsorbates, solvent molecules, and electrolyte ions continuously interact dynamically in response to the applied potential, creating a microenvironment that controls reactivity. Untangling these effects requires experiments capable of resolving structure−reactivity relationships site by site, step by step, terrace by terrace. At the same time, computational methods such as DFT are indispensable for mapping trends and proposing and testing hypotheses. But theory and experiment should be viewed as complementary partners: surface science anchors models in reality, while computation extends insights beyond what can be directly measured. Looking ahead, the challenge is to balance the drive for application with the need for fundamental understanding. By embracing both fundamental rigor and ambition to apply, and by integrating experiment with computation, electrocatalysis can move toward predictive, rational control of interfacial reactivity and, ultimately, better catalysts.

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Notes

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