

Interplay of surface and subsurface contributions in electrocatalysis

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Abstract

Heterogeneous electrocatalysts stabilize adsorbed reaction intermediates at their surfaces and promote electron transfer to facilitate reaction rates. Although immense efforts—both experimentally and computationally—look to identify and understand the active site, many bulk descriptors have found utility in reactions such as the O₂ reduction and evolution and CO₂ reduction reactions. In parallel, studies modifying catalyst supports and other bulk parameters indicate a more complex picture in understanding heterogeneous electrocatalyst reactivity. Here we highlight the interplay between the subsurface and surface in electrocatalysis, including charge transfer, strain, and possible reconstruction of the active surface. These impacts illustrate the importance of considering not only the active site but also its surroundings in designing and understanding electrocatalysts.

Introduction

In heterogeneous electrocatalysis, reactions occur by electron transfer at a complex interface between a reactant (liquid or gas within an ion-conducting media) and solid catalyst. The catalyst further tailors the reaction pathway—generally lowering activation barriers as a result—through chemical bonding. Thus, understanding the catalytic activity in such systems justifiably seeks an understanding of the catalyst surface and bonds that form on them.¹ However, decades of research have made great strides in understanding electrocatalytic processes through consideration of bulk (volume-averaged) descriptors,² such as electronic parameters like d-band center in metals³ and O 2p-band center in oxides,⁴ lattice parameter in metal alloys,⁵ and generally composition. These advances suggest a connection between bulk and surface properties enables the utility of bulk descriptors in catalyst design. In parallel, other findings have shown that material processing (manipulating defects like grain boundaries⁶ and strain⁷) can also impact catalytic activity, and studies of adlayers⁸⁻⁹ and epitaxial films¹⁰⁻¹¹ point to an underlying role of the subsurface in numerous reactions as well. Here we highlight the interplay of surface and subsurface contributions in electrocatalysis, focusing on examples from the O₂ reduction and evolution reaction (ORR, OER) and CO₂ reduction reaction (CO₂RR) literature.

We define “surface” as the terminal layer of a catalyst directly in contact with the electrolyte. Atoms on the surface form bonds with reactive intermediates, while the “subsurface” is the region beneath this layer that can interact with the terminal surface. We reserve the term “bulk” for volume-averaged properties. The dimensions of the subsurface depend on two things: 1) the type of coupling under discussion (i.e. electronic or configurational, such as epitaxially-induced strain) and 2) the type of

catalyst material (here metal or oxide, however similarities can be drawn to other solids with non-metal bonding). The surface and subsurface of several catalyst systems discussed herein are shown in **Figure 1**. We here consider examples that attempt to isolate subsurface couplings that are electronic¹² (shorter length scale) and configurational¹³⁻¹⁴ (longer length scale) in nature, but note that the resultant effects such as electron transfer and strain are inherently correlated. We consider materials ranging from metals (shorter electron screening and relaxation lengths) to oxides (longer electron screening and relaxation lengths). As such, the subsurface region, impacting catalysis at the surface though not directly exposed to the electrolyte, can range from 1-2 atomic layers in metals for electronic effects and up to 10s of nanometers in oxides for configurational effects like strain (**Figure 1**).¹⁵⁻¹⁶ While experimental characterization techniques are often volume-averaged (commonly referred to in the literature as “bulk”) and consider the catalyst *ex situ*, we highlight the utility of considering not only the active surface, but also the subsurface beneath it as an integral part to understanding and designing active and robust catalysts.

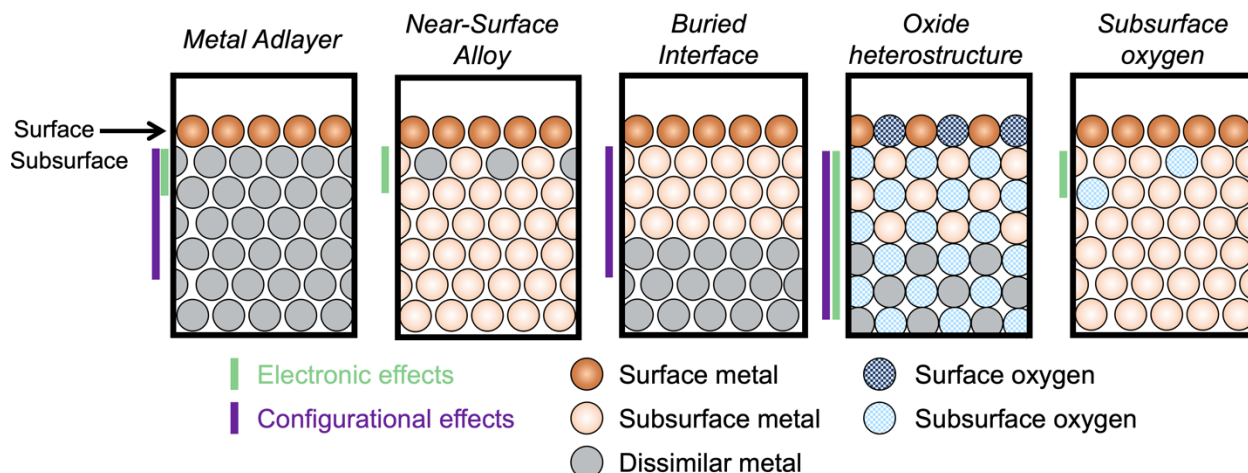


Figure 1. Schematic of surface and subsurface for different types of electrocatalysts. The relevant lengthscale of the subsurface is shown as a bar (schematically, for comparison purposes): green for electronic effects (shorter length scales) and purple for configurational effects like epitaxial strain (longer); for metals (shorter) and oxides (longer).

Electronic effects

Although reactants and intermediates bond to the catalyst surface, the terminal atomic layer is rarely isolated from the subsurface beneath it. The electronic structure of the surface is inherently linked to the atomic plane(s) beneath it. We first consider electronic effects in the case of metal adlayers (noting that some configurational effects, such as in-plane strain, are also at play in cases with lattice mismatch¹⁷). We then discuss cases where foreign atoms are present in the subsurface of metals, and extend to considering oxide heterostructures and supported materials.

In metals, high electron density results in a short screening length, with such electronic interactions typically limited to adjacent planes.¹⁸⁻¹⁹ For metal adlayers,²⁰ or electrodes where the surface is “modified” with a different element (historically referred to as modified electrodes), the catalytic

activity can differ dramatically via electronic interaction with the subsurface. We consider the case of Pd overlayers on Pt(111)—nearly lattice matched to better isolate electronic from configurational effects. Convoluting variables such as in-plane strain and strain-relaxation related defects may complicate the interpretation of data for cases where the adlayer and substrate lattice parameters differ significantly. The electrochemical behavior of a single Pd monolayer at the surface (atop a Pt subsurface), also called an adlayer (**Figure 1**), is clearly distinct from that of elemental Pt²¹ or Pd,²² but multiple Pd layers behave similarly.²³⁻²⁴ Electronic interactions between the surface (Pd) and subsurface (Pt) can be observed through shifts in the point of zero charge²⁴ and underpotential deposition of Cu and H.²³ Density functional theory (DFT) calculations show that electron transfer from Pt to the Pd monolayer leads to a downshift of the d-band center relative to the Fermi level, improving ORR activity by weakening O₂ bonding compared to Pd(111).²² Computational models provide resolution of electronic effects at the surface and subsurface challenging to achieve by experimental characterization, and play an important role in understanding physical origins of modified electrochemical behavior. However, such conclusions from DFT calculations rely on characterization of the surface and subsurface during (or at least following) electrochemical reactions, as the conditions for electrocatalysis and interaction with the electrolyte can sometimes change the composition and structure.²⁵

Additional examples of such surface-subsurface charge transfer or so called “ligand effects”¹⁷ are found in the case of subsurface layers¹⁵ or near-surface alloys (NSA).²⁶ For example, the activity of a Pt(111) surface can be modified through the introduction of a foreign metal in the adjacent layer of the subsurface (an NSA) with the remainder of the catalyst comprised of Pt(111) to limit geometric effects arising from lattice strain (**Figure 2a-c**). The Cu/Pt(111) NSA was observed to tailor the binding of OH* intermediates on a Pt-terminated surface experimentally and theoretically, resultant in improved ORR activity (**Figure 2a-c**).²⁶ The degree of electron donation or withdrawal is a function of distance from the surface layer, and Stephens *et al.* (2011) found that imbedding Cu in the fourth atomic layer had a negligible effect on activity. The order of magnitude activity improvement resultant from 0.45 monolayers of Cu in the subsurface illustrates the importance of such electronic coupling and necessity for electrochemists to consider the composition of the subsurface in addition to that of the surface and bulk.

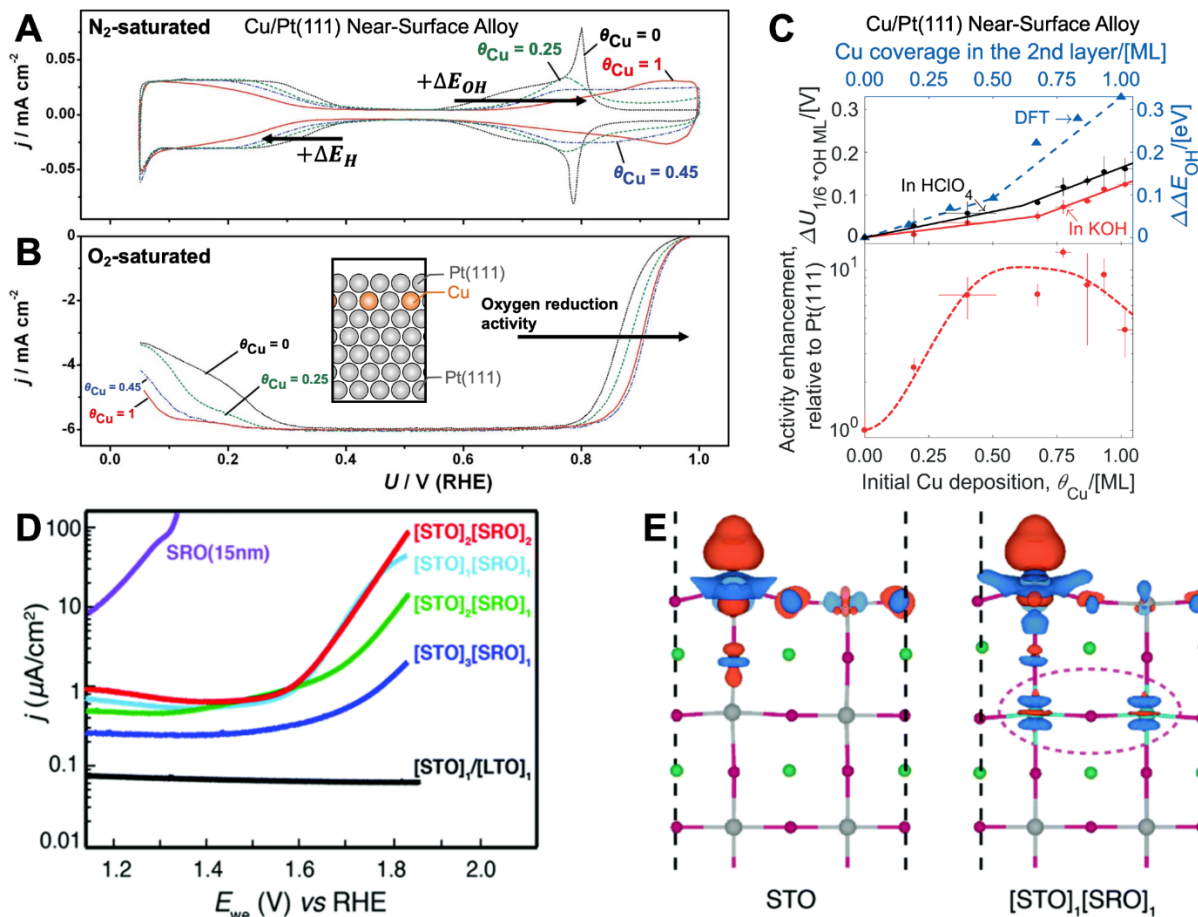


Figure 2. The subsurface can transfer charge to/from the surface, sometimes referred to as a ligand or support effect. In Pt, near-surface Cu tailors (A) the binding of OH* and (B) ORR activity in 0.1 M HClO₄ electrolyte. The upper plot of panel (C) shows the potential shift of 1/6 monolayer OH* adsorption experimentally and from DFT from ref. ²⁶ and the lower plot in panel (C) highlights the ORR activity enhancement in 0.1 M KOH for the Cu/Pt(111) NSA. (D) OER Tafel plots of (001)-[SrTiO₃]_n/[SrRuO₃]_m oxide heterostructure (where n and m subscripts denote the number of unit cells) in alkaline electrolyte. (E) Differential valence-electron charge density calculations for O* on a surface Ti atom show the charge redistribution upon addition of a single subsurface unit cell of SrRuO₃ (right) with regions of charge depletion (blue) and accumulation (orange). Panels A-B are adapted with permission from ref. ²⁶. Copyright 2011 American Chemical Society. Panel C reprinted with permission from ref. ²⁷. Copyright 2018 Angewandte Chemie. Panels D-E reprinted with permission from ref. ¹⁰. Copyright 2018 Energy & Environmental Science.

For more ionic materials such as oxide semiconductors, electronic coupling like charge transfer and band bending can extend to length scales up to several unit cells.²⁸ Such effects have been observed both for conformal catalyst layers that are impermeable to the electrolyte as well as for electrodeposited layers that are less-defined in length scale and interaction with the electrolyte. While bulk SrTiO₃ is a poor OER electrocatalyst due to its large bandgap, adding a subsurface unit cell of SrRuO₃ (**Figure 2d**) donates electrons toward surface Ti atoms (**Figure 2e**), increasing activity of the SrTiO₃ surface for OER.¹⁰ The

resulting (001)-SrTiO₃/SrRuO₃ oxide heterostructure demonstrates that activation an otherwise electrocatalytically-inactive material by the ligand effect is possible, a strategy that can be extended to core-shell systems as well.

While we have thus-far highlighted studies of model systems designed to investigate electronic interactions between the surface and subsurface, such effects are pertinent in more complex catalysts as well.²⁹ For example, the local electronic structure of a metallic surface can be modified by the presence of residual oxygen in the subsurface (**Figure 1**). This subsurface oxygen has been observed to modify activity and/or product selectivity for CO₂RR³⁰⁻³² and ORR³³. We also highlight that electronic interactions between the subsurface and surface layer need not arise from heterogeneity but can also be manifested as size-dependent effects resultant from electron delocalization. For example, electron redistribution with nm-scale changes in the size of Co oxide particles modified the extent of Co oxidation during OER, triggering changes in terminal oxygen chemistry and differences in OER activity.³⁴ Electronic interactions between the subsurface and surface can also be considered in the case of single atom catalysts, however this picture is more complex given exposure of the support to the electrolyte as well (here deviating from our definition of the subsurface). Together, the breadth of electronic interactions in both model and complex systems illustrate the importance of considering the subsurface layer in design of active and stable catalyst surfaces.

Configurational effects

The subsurface can also interact with the surface and modify the electrocatalysis occurring on it through configurational effects, such as strain and its relaxation. We first consider this in as-fabricated heterostructures in which strain results from epitaxy at a buried interface. We subsequently consider metal alloy catalysts that demonstrate segregation³⁵ to form a strained overlayer. Depending on the thickness of this layer, electronic effects can also be at play.¹³ Regardless of whether internal strain arises from fabricated interfaces or ones which form during cycling, strain alters the width and center of the d-band, leading to strengthening or weakening of chemisorption of reactants for compressive and tensile strain, respectively.³⁶

Studies of epitaxial systems provide well-defined systems where strain—extending to the surface—is introduced through lattice mismatch at an interface located within the subsurface. The lengthscale of such effects depends on the degree of lattice mismatch, with larger strains resulting in smaller relaxation lengths. For large strains, or thicknesses above the relaxation length in epitaxial systems, strain relaxes via the formation of defects, which can also impact catalytic activity and selectivity (though possibly convoluted with change in site density).³⁷ Considering epitaxial oxides, strain was first shown to impact ORR and OER activity in LaCoO₃¹⁶ for thicknesses up to the relaxation length—on the order of 10s of nm for low strain conditions. While small strains can be introduced from the subsurface over lengths typically larger than electronic effects of charge transfer, we note that strain in oxides can also change the degeneracy of transition metal d-states, as shown in the case of NdNiO₃³⁸, impacting in- vs out-of-plane bonding to oxygen. Strain from epitaxial mismatch can also be introduced in metals, for example Cu(001) grown on single-crystal Si substrates (**Figure 3**). Considering activity and selectivity for the CO₂RR, tensile strain and its resulting upshift of the Cu d-band center increased CO insertion and hydrogenation via changes in adsorbate binding.³⁹ Like subsurface-driven ligand effects,⁴⁰ strain effects can also be scaled to high surface area materials in core-shell particles.⁴¹

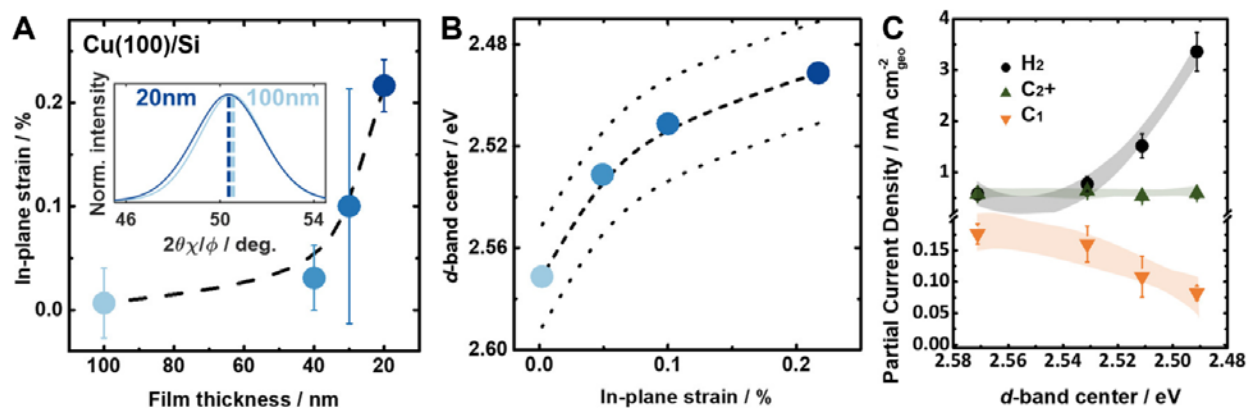


Figure 3. The subsurface can introduce strain at the catalyst surface, such as in epitaxial Cu(100) on Si. A) Thinner films have larger residual in-plane strain, leading to B) an upshift in the d-band center. C) The upshift in d-band center increases the ratio of C₂/C₁ products in CO₂RR. Adapted with permission from ref. ³⁹. Copyright 2021 American Chemical Society.

Strain can also result from buried interfaces that form during synthesis or electrochemical cycling of alloy catalysts. Examples include surface segregation from differences in surface energy and/or immiscibility,³⁵ electrolyte-induced leaching of less-noble elements, and changes in metal-metal distances resultant from variations in particle size⁴². Such leaching is well-observed in Pt-lanthanide alloy catalysts for ORR,⁴³ leading to a strained Pt-overlayer ~1 nm thick with a volcano-trend in activity described by Pt-Pt distance.⁵ Depending on the thickness of this layer, ligand effects can also contribute.¹³ Similar surface leaching of lanthanide and alkaline earth elements (A-sites in the ABO₃ perovskite family) is observed in some complex oxides employed as OER catalysts in alkaline media,⁴⁴ leading to surfaces rich in first row transition metal oxides.⁴⁵ Open questions remain as to the extent the resulting oxide surface is configurationally influenced by the subsurface, which likely depends not only on the thickness of the A-site depleted layer, but also the dynamic nature of the redox-active surface. Together, the breath of configurational interactions resultant in both thin films⁴³ and particles⁴⁶ highlight the importance of considering the subsurface layer in catalyst design.

Subsurface templating of the reactive surface

Many studies, including some highlighted here, report that the active surface during electrocatalysis differs from the volume-averaged bulk. This difference can be solely configurational, as in the case of pure metals,⁴⁷ or compositional as well. Such surface changes represents a complex balance between interactions with the subsurface and electrolyte and depend on electrode free charge, possibly occurring over long timescales. Even so, the subsurface structure and composition can be leveraged to design a ‘pre-catalyst’ that triggers transformation (or reconstruction) toward an active terminal surface. Here the subsurface provides a structural template from which some elements may leach out of, resulting in a unique active catalyst surface that could be influenced electronically and configurationally by the subsurface layer (depending on the length scale of such transformations). In some cases, such as Pt alloys for ORR, this is widely accepted and the active surface is well-characterized both for well-defined

systems⁴⁸⁻⁴⁹ and high surface area particles^{46, 50}. In other cases, such as oxides for OER, reports are mixed as to the extent that oxide surfaces might change under reaction conditions.^{44-45, 51} Here we highlight that even in the case where oxides might yield similar active surfaces during OER—for example transition metal oxide/oxyhydroxide phases⁴⁵—interplay with the subsurface can still impact activity. The established utility of volume-averaged (bulk) descriptors to accurately describe reactivity trends further highlights this fact.⁴

As an example, we take the case of Ni oxides for OER. Electrodeposited films are widely reported to form a NiOOH active phase during OER, the activity of which can be modified by the presence of an Au support.⁵²⁻⁵³ Recent reports suggest that other Ni containing oxides, such as perovskites, in some cases lose crystallinity in the top (few) atomic layer(s).⁵⁴ Epitaxial films enable the comparison of NiO_x surfaces with comparable Ni density but differences in subsurface composition and lattice constant, resultant in OER activity differences of about an order of magnitude (**Figure 4**). The activity of a unit cell of NiO_x increases when supported on LaNiO₃ versus a conductive Nb:SrTiO₃ substrate (illustrating electronic effects), but is surpassed still by the NiO₂-termination of epitaxial (100) LaNiO₃ film (expected to have contributions from both electronic and geometric effects).⁵⁵ For LaNiO₃ films with unresolved termination, tensile strain from epitaxial growth increases activity⁵⁶, and activity can be increased further still by A-site substitution considering strained NdNiO₃ (mixed electronic and geometric effects)³⁸. These comparisons illustrate that even if all catalysts are terminated with a NiO_x surface under OER conditions, the interplay with the subsurface via crystallographic templating, epitaxial strain, and the ligand effect still have notable influence on the resultant activity.

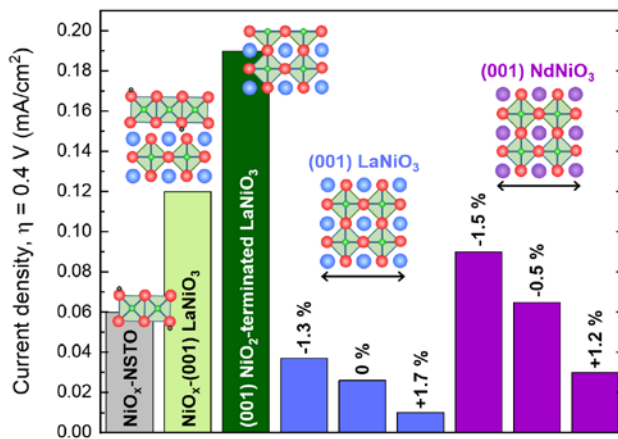


Figure 4. Influence of the subsurface on catalytic activity in 0.1 M KOH at 1.63 V vs RHE on (001) nickelate perovskite films persists despite possible reconstruction. Comparison of 1 u.c. NiO_x on Nb-doped SrTiO₃ (NSTO, gray) and LaNiO₃ (light green), and NiO₂-terminated LaNiO₃ (dark green) from ref. ⁵⁵. Tensile strain increases activity in LaNiO₃ from ref. ⁵⁶ (blue), and substitution at the A-site to give NdNiO₃ increases activity further in ref. ³⁸ (magenta).

Further cases of complex catalysts where the subsurface might template formation of an active surface and influence it's activity include materials such as phosphides, selenides, and sulfides that result in dissimilar surfaces under reaction conditions. For example, metal phosphides form an oxidized surface under ORR and OER conditions,⁵⁷⁻⁵⁸ the activity of which is likely influenced by the subsurface though yet

to be understood from well-controlled investigations. Similarly, many growing research communities such as nitrate reduction consider oxide catalysts⁵⁹ under conditions thermodynamically expected to result in their reduction. We encourage researchers to draw from understanding in e.g. the CO₂RR community regarding potential electronic effects of subsurface oxygen, in addition to more gross effects such as changing surface area.

Conclusion

We highlight here that the active surface must not be viewed in isolation from the subsurface that interacts with it electronically and impacts the geometry of surrounding atoms. Just as volume-averaged (or “bulk”) characterizations of catalysts are insufficient to fully understand activity and selectivity, so too is consideration of solely the surface layer or active sites. While in high surface area systems such interactions between the subsurface and active sites might be intractable to characterize fully due to heterogeneity, model systems—such as metal single crystals, and oxide epitaxial films—offer the opportunity to better understand this interplay. Characterization techniques that probe composition and structure as a function of depth can help researchers understand catalytic activity in a more comprehensive way. Computational approaches including DFT analyses and machine learning from large material databases have the potential to help disentangle multiple phenomena at play to improve understanding of subsurface effects. As heterogeneous electrocatalysis continues to advance, designing electrocatalysts that leverage subsurface interactions via core-shell architectures and mechanical strain can provide forward-looking opportunities to maximize activity, selectivity, and stability in electrocatalysts.

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Declaration of Interest

None.

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