

Trends in Electrocatalysis: The Microenvironment Moves to Center Stage

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Electrocatalysis, an essential tool for storing renewable energy and promoting sustainable synthesis, is attracting attention from diverse communities. For years, the primary focus of research centered on the catalytically active material, resembling research in thermal catalysis. However, interest is shifting toward the complexities of the electrochemical interface, emerging from the interplay between the electrode surface and the electrolyte. This interface is shaped by the dynamic interaction among solvents, ionomer components, ions, and electroactive materials and is further influenced by the polarization of these components through inherent and externally applied electric fields.^{1–4} These are exciting times, as became apparent during the symposium entitled “The role of fundamental interfacial processes in electrocatalysis”, that we hosted at the 2023 ACS Spring Meeting in Indianapolis. In this commentary, we distill the noteworthy perspectives and findings from the symposium’s dialogues and presentations, aiming to offer a view of the principal trends emerging in fundamental aspects of electrocatalysis (Figure 1).

The resurgence of interest in the reduction of CO₂ added to work on electrochemical H₂ and O₂ catalysis to spark a surge in electrocatalysis research in the early 2010s.^{5–11} This led to a reinvigorated understanding and appreciation of the dynamics of electrified metal/solution interfaces. Initially, investigations

centered on the engineering of catalyst structures, with a broad focus ranging from atomic to mesostructured length scales.^{12–17} At the same time, the integral role of electrolyte cations, known since Hori’s seminal work,¹⁸ was acknowledged by Koper and Bell, igniting more refined investigations into the role of the interfacial microenvironment.^{19,20} In recent years, the realization has been emerging that intended or unintended changes to the electrochemical microenvironment, as defined by electrolyte properties and electrode modifications, have a strong impact on the outcome of electrocatalytic reactions.²¹

The significance of electrolyte ions for CO₂ reduction has escalated in recent years, with reports suggesting that the reaction cannot take place without the presence of metal cations.²² This subject was a vibrant point of conversation during our symposium. Beyond the well-recognized role of stabilizing charged transition states, a vast range of electrolyte properties must be considered when engineering electrocatalytic systems. Amankukwu showed that CO₂ reduction on Cu in aprotic solvents requires the presence of a proton donor for the reaction to take place.²³ Interestingly, the root of this behavior is not directly tied to catalysis. When a proton donor is absent, CO₂ acts as an oxygen acceptor during the reaction, resulting in the creation of insoluble carbonate salts. These salts precipitate on the electrode, obstructing active sites and deactivating catalysis. Yet, introducing methanesulfonic acid as a proton donor facilitates the conversion of carbonate back to CO₂, allowing the continued transformation of CO₂ to CO. We note that in a related study, Kenis demonstrated that the type of cation present in aqueous electrolytes significantly influences the formation of carbonate deposits. Electrolytes containing K⁺ formed dense deposits of varying morphology on the electrode surface. In contrast, Cs⁺-containing electrolytes resulted in the formation of small carbonate crystals that were well dispersed over the electrode.²⁴ Interestingly, the microstructure of the carbonate deposits had a significant impact on the deactivation rate, with Cs⁺-containing electrolytes displaying improved electrode stability. It is important to note that beyond deactivating the electrode, formation of

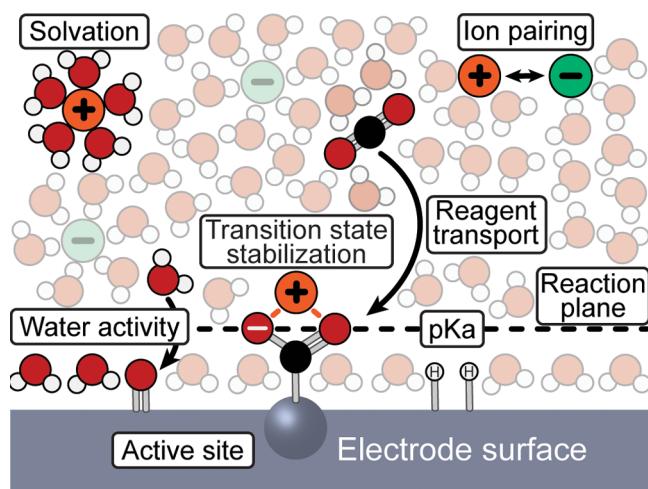
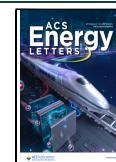


Figure 1. Schematic of the electrode/electrolyte interface, showing the importance of the microenvironment.

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carbonates during electrolysis can lead to a loss of CO_2 , incurring an energy penalty that lowers the energy efficiency of CO_2 reduction. Wang presented a strategy to address this, by recovering CO_2 from carbonate through clever management of ion transport in a solid electrolyte reactor.²⁵ Considering these insights, careful manipulation of electrolyte composition and the management of carbonate deposits will be pivotal to enabling efficient and stable CO_2 electrolyzer systems.

Similar interactions impart an important role to electrolyte anions in controlling CO_2 reduction in nonaqueous environments, where anions and cations are not fully solvated. While cations are critical to stabilizing the formation of negatively charged transition states that initiate CO_2 reduction, the formation of ion pairs with anions decreases the concentration of cations that can participate in this stabilizing role.²⁶ By correlating the rate of CO_2 reduction on copper in the presence of various solvents, electrolyte anions and cations, with the formation of ion pairs, Amanchukwu demonstrated a clear inverse correlation between the formation of ion aggregates and the rate of CO_2 reduction. This demonstrates the important role of free electrolyte cations and highlights that electrolytes should be designed to make these ions available. We note that such conditions are particularly important for the design of electrocatalytic systems employing membrane-based catalysts, where the solvation environment for ionic compounds is substantially different from solutions. Indeed, Mayer showed that the inadvertent transport of alkali cations from the anolyte through anion exchange membranes controls the outcome of CO_2 reduction in zero-gap type membrane electrode assembly (MEA) electrolyzers, causing a shift in the product distribution from C_1 to C_2 products.²⁷

The impact of electrolyte ions on reaction outcomes is multifaceted, influencing not only the stabilization of transition states but also the presence or absence of crucial substrates (e.g., protons) at the reaction plane. Biddinger demonstrated that the choice between hydrophobic (bis(trifluoromethane-sulfonyl)imide, TFSI^-) and hydrophilic anions (dicyanamide, C_2N_3^-) in CO_2 reduction reactions offers a means to regulate the hydrogen evolution reaction.²⁸ It was suggested that hydrophobic anions control the reaction outcome by limiting water transport to the electrode surface while enhancing CO_2 supply. Conversely, hydrophilic anions facilitate water access to the electrode, promoting hydrogen evolution. Interactions among ions and solvent molecules were further exploited by Hall, who showed that highly concentrated salt solutions lowered the activity of water, leading to suppression of hydrogen generation and increased selectivity for multi-carbon compounds from CO_2 reduction.²⁹ Understanding these complexities is essential for designing efficient and selective electrochemical processes.

Emergence of Microenvironment Modifiers. Just as the interaction of ions within the electrolyte and with the electrode surface controls the outcome of reactions, the chemical structure of the microenvironment, beyond the presence of ionic charges, is equally critical to the activity and selectivity of catalytic reactions. Agapie and co-workers demonstrated that the modification of Cu electrodes with polymerized N-substituted pyridinium led to substantial increases in the ratio of C_{2+} products relative to C_1 in CO_2 reduction.³⁰ Agapie assigned this effect to molecular interactions between the polymer and reaction intermediates or to the inhibition of proton transport by the polymeric environment similar to the interactions described by Biddinger. Ionomer layers, which are

commonly used to bind catalyst particles to membranes in MEA electrolyzers, create environments reminiscent of those investigated by Agapie and can therefore be expected to show a similar modification of reactant transport. This topic was elaborated upon by Weber, who emphasized the significance of how engineered ionomer layers can finely adjust the local CO_2 concentration, water content, and pH to optimize selectivity for C_{2+} products.³¹ A common theme of microenvironment modification is its impact on the transport of charged and uncharged compounds, as detailed by Weber and Agapie. While these effects play an important role, it is likely that microenvironment modifications impact more than transport. This line of thinking was addressed computationally by Che. Using multiscale simulations, Che found that the presence of an organic layer at an electrode/electrolyte interface can lead to significant alterations in the local electric field, dipole moments, and polarizability of the system, which may enhance the catalytic performance of CO_2 reduction to C_2 species as compared to a bare metal.³²

Impact of Mass Transport and Potential Variation on Electrocatalytic Reactions. Depending on the ease of transport, the local concentration of reagents at the reaction plane (where the catalytic reaction takes place) is substantially different from that in the bulk. This leads to changes in H^+ and OH^- concentration since many electrocatalytic reactions generate or consume protons or hydroxides. Knowing the local concentration of these species is thus of critical importance. Substantial efforts have recently been directed to solving this challenge.^{33,34} On a macroscopic scale, these alterations in the pH can be leveraged to provide reactants for tandem catalysis. For example, Schreier demonstrated that chloroethanol, produced via the oxidation of ethanol with chloride radicals, could be transformed into ethylene oxide. This transformation was achieved through base-catalyzed alkane cyclization, which was facilitated by merging the outlet streams from partially oxidized species at the anode with hydroxide generated at the cathode in a continuous flow cell.³⁵

Transport considerations at electrode surfaces become more complex when multiple reagents are involved. Modestino discussed these complexities in the context of the electrochemical dimerization of acrylonitrile to adiponitrile, which requires careful control of fluxes of acrylonitrile and water to avoid side-product formation.³⁶ Since mass transport is a time-dependent phenomenon, reaction outcomes can be controlled by changing the time provided for mass transport to take place. Modestino demonstrated that careful use of voltage pulses improved the electro-hydrodimerization of acrylonitrile by allowing the boundary layer of the electrochemical interface to be replenished with substrates before initiation of the reaction. This example highlights the importance of mass transport in defining the composition of the electrocatalytic microenvironment and asks for methodologies to measure these effects *in operando*. In this context, Jaramillo presented on the development of spectroscopic methodologies that couple hydrodynamic control with attenuated total reflection surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS), enabling investigations into the influence of mass transfer constrained microenvironments on the activity and selectivity of electrochemical reactions.³⁷ Overall, these studies underscore that the intricate interplay between mass transport and electrochemical kinetics is a pivotal factor in determining the outcome of electrochemical reactions. Beyond controlling mass transport processes, time-dependent potentials can also

be leveraged to independently promote electrode processes like adsorption, C–C bond scission, and hydrogenation steps within the broader multistep fragmentation of ethane to methane, as shown by Schreier.³⁸ This experiment demonstrated the feasibility and effectiveness of managing separate steps of a complex process through temporal control of the electrode voltage.

Where Does the Reaction Occur within the Electrocatalytic Microenvironment? The strategies employed to control the microenvironment raise a pivotal question: Where exactly is the reaction plane, the exact location where the catalytic reaction takes place, and how does it influence reactivity? Surendranath discussed this aspect in the context of carefully engineered electrodes modified with molecular catalysts capable of switching between functioning as electronically coupled to the surface and functioning as solution-bound molecules, contingent upon their location within the double layer (Figure 2).³⁹ Molecular active sites, as provided by

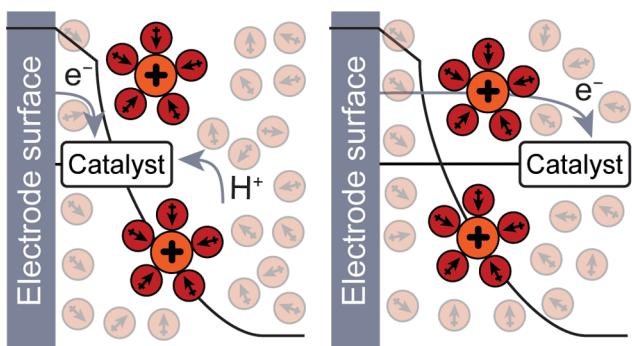


Figure 2. Schematic showing how the position of the catalyst within the double layer influences charge transfer dynamics. (left) Catalyst shielded by a double layer, behaving like an active site on a metal surface. (right) Catalyst outside of the double layer, behaving like a molecule in solution. Ions/solvents not to scale.

metalorganic complexes for example, can act as electrocatalysts either by taking up charges, and then passing them on to reactants, or by serving as a conduit for charges stored in the electrode. Surendranath has previously shown that molecular catalysts behave like metallic active sites if they are conjugated to surfaces.⁴⁰ The origin of this behavior is related to the position of the molecular complex within the electrochemical double layer. Using a flexible linker, combined with aqueous and nonaqueous solvents, a cobalt porphyrin catalyst was positioned either at the electrode surface (under water) or away from the electrode (under nonaqueous solvents). In the latter case, the catalyst took up charges like a molecular catalyst in solution with a fixed redox potential. In contrast, when the catalyst was folded onto the electrode surface, it no longer stored charges and instead acted like an active site that is part of the electrode. This distinction was explained by the position of the catalyst within the potential drop in the double layer. A catalyst at the surface of the electrode will be fully shielded by the double layer and, thus, be coupled to the electrostatic potential of the electrode surface. As such, it behaves like a catalytic site on the electrode and funnels charges between the electrode and electrolyte. This work highlights the critical importance of the active site location within the electrocatalytic microenvironment and is crucial to the realm of heterogenized molecules. Currently, the prevalence of electronic coupling among other molecular catalysts situated within the double

layer remains uncertain. However, this factor deserves careful consideration within the scientific community.

Molecular vs Heterogeneous Active Sites. A critical aspect of molecular active sites at electrode surfaces, as mentioned in the previous paragraph, is their ability to foster H and O atom transfer, as well as the impact of electrode potentials on these reactions. Mayer discussed these processes from a thermodynamic perspective, showing that hydrogen atom transfer (HAT), proton-coupled electron transfer (PCET), and the free energy of hydrogenation (ΔG°_H) are conceptually equivalent.⁴¹ A notable example of this concept was described by Berlinguette, who used the side of a palladium electrode opposite to the electrolyte to facilitate electrochemical hydrogenation reactions.⁴² Palladium electrochemically intercalates hydrogen and passes it on to a hydrogenation reaction opposite of the electrolyte. In this case, the thermodynamics of hydrogen atom transfer are fully defined by the properties of the Pd surface. Similarly, Raciti has recently observed facet-specific interaction of Cu with hydrogen leading to the formation of a 2D surface hydride that influences the onset kinetics of hydrogen evolution.^{43,44} The understanding of molecular and heterogeneous active sites for H and O atom transfer not only builds foundational knowledge in the field but also contributes to the development of practical applications for various electrochemical reactions, as was shown by Manthiram for electrochemical epoxidation reactions, wherein olefins take up electrogenerated oxygen from active sites.⁴⁵

Insight from Well-Defined Materials and Advanced Characterization. The electroactive material is a vital part of the solid/solution interface, and it can be used in parallel with microenvironment control to shape the performance of an electrochemical system. A common approach to enhancing the properties of a solid is to combine multiple elements to form alloys. These alloys amplify catalytic reactivity by altering the electronic structure of the active element or through bifunctional effects where both the active element and the alloying component work together to stabilize key reaction intermediates.^{6,46} The geometric arrangement of elements within the alloy plays a key role in determining the extent of these modifications.⁴⁷ Skrabalak showed that high entropy alloys, which are attracting considerable interest in electrocatalysis, may possess structures different from what is commonly assumed. Skrabalak used Monte Carlo–molecular dynamics (MC–MD) simulations in combination with experimentally measured Scanning Transmission Electron Microscopy energy-dispersive X-ray Spectroscopy (STEM–EDS) images to show that high entropy alloys exhibit intraparticle heterogeneity, an aspect that was overlooked until recently.⁴⁸ Some of the elements of the alloy were segregated into small domains that were dispersed randomly throughout the nanoparticle, thereby giving the illusion that the elements were homogeneously mixed. This issue arises from the inherent flaws of representing a 3-dimensional structure with a 2-dimensional projection, similar to how a photograph compresses the depth and complexity of a three-dimensional space into a flat image. Although this was found in the context of high entropy alloys that exhibit four or more elemental combinations, it has broader implications, extending even to systems of simpler elemental compositions such as binary or ternary alloys.

The dynamic nature of materials during electrocatalytic reactions further complicates the understanding of the active

site. For instance, during CO_2 reduction, the local pH increases significantly, leading to an accumulation of hydroxyls at the interface. This can alter the structure of certain materials, especially oxophilic ones like Cu. Gewirth demonstrated that in the initial phases of electrochemical CO_2 reduction, Cu^{2+} ions are released into the electrolyte.⁴⁹ These ions subsequently react with local OH^- ions, leading to the formation of precipitates such as $\text{Cu}_2(\text{OH})_2\text{CO}_3$. These precipitates linger on the electrode surface for extended periods, potentially influencing the reaction outcome before being fully reduced.^{49,50}

Single-atom catalysts have recently come to the forefront as a promising approach to developing catalysts with precisely defined active sites. During our symposium, Huang demonstrated that these materials can enable efficient reduction of CO_2 to CO .⁵¹ However, while single-atom catalysts are relatively well-defined upon preparation, there exists significant uncertainty whether these materials maintain their structure during catalytic reactions. To gain insight, Liu simulated the stability and the dynamic rearrangement of electrocatalysts under operating conditions using constant-potential hybrid-solvation dynamic models at the atomic scale.⁵² As a case study Liu applied this model to graphene-based single-atom catalysts during CO_2 reduction, revealing that the strong adsorption energy of hydrogen on Cu promotes the agglomeration of single Cu atoms into clusters under negative applied potentials. This cluster structure was identified as the catalytically active site that promotes CO_2 reduction to ethanol. In related work, Stach showed that substantial advances in liquid-phase Transmission Electron Microscopy enable chemical and structural analysis of electrodes at the nanoscale.⁵³ It can be expected that these advances will contribute to a more detailed understanding of the dynamic changes catalytic materials undergo during electrocatalysis.

Impact of Material Structure on Ion Adsorption. As emphasized earlier in this Energy Focus, the interaction of anions and cations with the electrode surface is pivotal in shaping the outcome of electrocatalytic reactions. Central to this discussion is the potential of zero charge (PZC), which refers to the specific electrode potential at which the net charge at an electrode/electrolyte interface approaches zero.⁵⁴ The PZC is contingent on the electronic structure of a material, implying that the material significantly impacts the observed electrochemical behavior. While the d-states and geometric effects are often regarded as primary determinants of the catalytic activity in complex materials, the role of the PZC is frequently overlooked.^{55–57} Ren presented on using scanning electrochemical cell microscopy (SECCM) and electron backscatter diffraction (EBSD) to unveil the relationship between the PZC, local crystal grain orientation, and hydrogen evolution activity.⁵⁸ Such information not only emphasizes the intricate interplay of surface properties and electrocatalytic activities but also showcases the layered complexity inherent in electrochemical systems.

Summary and Key Takeaways. Recent years have seen a renewed realization of the importance of the microenvironment in governing the outcome of electrocatalytic reactions, as was apparent from the talks presented during the symposium we hosted at the 2023 ACS Spring Meeting. The appeal of this area of research emerges from the complex interactions between the active site, electrolyte components, substrates, products, and catalytic intermediates. We expect future research in this field to lead to breakthroughs in controlling

electrocatalytic reactivity not just for the electroreduction of CO_2 but also for other electrocatalytic processes that will be critical to the energy transition, e.g., NH_3 synthesis, water electrolysis, and electrocatalytic transformations relevant to a sustainable circular economy, such as plastics recycling. In conclusion, the intricacies of the electrochemical micro-environment and its impact on electrocatalytic reactions offer exciting prospects for engineering technologies to support the energy transition.

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Notes

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