Linking Electric Double Layer Formation to Electrocatalytic Activity

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Abstract: Electric double layers form at all electrode-electrolyte interfaces and often play defining roles in governing electrochemical reaction rates and selectivity. While double layer formation has remained an active area of research for more than a century, most frameworks used to predict electric double layer properties, such as local ion concentrations, potential gradients, and reactant chemical potentials, remain rooted in classical Gouy-Chapman-Stern theory, which neglects ion-ion interactions and assumes non-reactive interfaces. Yet, recent findings from the surface forces and electrocatalysis communities have highlighted how the emergence of ion-ion interactions fundamentally alters electric double layer formation mechanisms and interface properties. Notably, recent studies with ionic liquids show that ionic correlations and clustering can substantially alter reaction rates and selectivity, especially in concentrated electrolytes. Further, emerging studies suggest that electric double layer structures and dynamics significantly change at potentials where electrocatalytic reactions occur. Here, we provide our perspective on how ion-ion interactions can impact electric double layer properties and contribute to modulating electrocatalytic systems, especially under conditions where high ion concentrations and large applied potentials cause deviations from classical electrolyte theory. We also summarize growing questions and opportunities to further explore how electrochemical reactions can drastically alter electric double layer properties. We conclude with a perspective on how these findings open the door to using electrocatalytic reactions to study electric double layer formation and achieve electrochemical conversion by engineering electrode-electrolyte interfaces.

1. INTRODUCTION

Electrochemical interfaces formed between charged solids and liquids are ubiquitous in nature and are key to many emerging technologies in the growing area of sustainable energy, including electrocatalysis and energy storage. [1-6] Increasing interest in electrochemical processes drives substantial enthusiasm for exploring electric double layers through the perspective of catalysis science. In our view, this strongly complements and aligns with inquiries into the molecular level details of solid-liquid interfaces that have been pursued within the colloid and interface science fields.

In electrochemical systems, the liquid portion of solid-liquid interfaces is composed of an electrolyte with dissolved ionic species, which experience electrostatic forces in the vicinity of the charged surface. These electrostatic interactions attract oppositely charged "counterions" and repel like charged "co-ions" to screen the applied potential. This results in the formation of a near-surface portion of the solution where the electrolyte is de-mixed into a counterion-rich and co-ion-depleted region called the "electric double layer" (Figure 1).

The properties of this electric double layer region are defined by a balance of electrostatic and entropic driving forces. [7, 8] Electrostatic interactions favor more compact electric double layers with higher local counterion density. On the other hand, entropy favors thicker, more disordered electric double layers with smaller relative interfacial potential gradients. The degree of disorder and distance over which surface potentials are screened by imbalances in local ion densities are often key determinants of the performance of electrochemical devices.

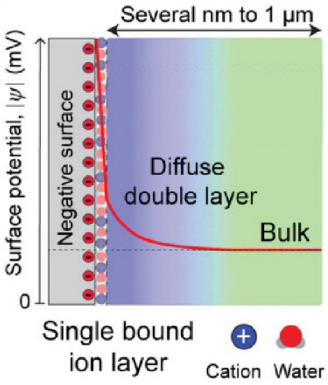

Figure 1. A schematic showing an example of classical models of electric double layer. Such models divide double layers into bound and diffuse layers. The bound layer is composed of solvent and counterions and is assumed to be a counterion diameter in thickness. The characteristic size of the diffuse layer is given by the Debye screening length, λ_D, which typically exceeds 10 nm under conditions where classical theory applies. The diffuse layer is enriched in counterions and depleted in co-ions, and this charge imbalance screens the surface potential, which drops to 0 V in the bulk electrolyte. Reproduced with permission from ref (44). Copyright 2023 Wiley.

For example, the distance over which surface potentials are screened defines the magnitude of local potential gradients, or electric fields, at interfaces, which is often a governing descriptor for reaction rates and selectivity. [9-14] Further, changes in interfacial ion densities and potential gradients can have a drastic impact on water hydrogen-bonding network properties, [15-17] influence relative changes to solvation energetics, [18, 19] change the binding energies of intermediates, [20, 21] modify the concentration of reactive species (e.g., protons and hydroxide anions), [22, 23] and even drive surfaces to reconstruct or dissolve. [24, 25] Together, these effects modulate the interfacial reaction microenvironment, [26] and such effects are increasingly understood to play defining roles in sculpting reaction pathways. [27, 28]

The study and analysis of electric double layer formation arguably serves as a foundational direction for the field of colloidal science. From Helmholtz's pioneering studies in the 1850s[29] to contemporary investigations into diverse topics including colloid assembly, [30-32] soft materials, [33, 34] and biology, [35-39] ionic assembly and electric double layer formation have been consistent threads connecting communities of researchers in colloid and interface science.

In this perspective, we provide background on the development of classical electric double layer theory from the viewpoint of colloid and interface science to provide context that complements catalysis science. We then discuss recent advances and open questions pertaining to how electric double layers differ under conditions of high interfacial charge densities and large ion densities, which are often inherent characteristics of electrochemical interfaces and electrocatalytic processes.

Following this conceptual overview, we describe different experimental approaches for investigating electric double layers and contextualize why the intersection of colloid science and catalysis is a promising avenue for advancing understanding of double layer formation at reactive interfaces. We then discuss how emerging understanding of electric double layer formation under conditions of high polarization and ion densities could provide new avenues for modulating electrocatalytic activity. We conclude with a perspective on how to leverage electrocatalytic reactions to understand electric double layer formation.

2. THEORETICAL UNDERSTANDING OF ELECTRIC DOUBLE LAYERS

Most contemporary understanding of electric double layer formation remains rooted in the hallmarks of classical electric double layer theory, which was primarily developed between the 1850s and 1950s. [40] Recent developments in electric double layer theory have begun to incorporate features of nonclassical conditions, such as high ion concentrations and high polarizations. [41-43]

2.1. Classical Electric Double Layer Theory

The Helmholtz model, [29] published in 1853, proposed that charged solid-liquid interfaces could be modeled by parallel planes of charge. One plane represents a charged surface and the other represents a single ion layer that fully screens the surface charge. In this model, the separation distance between the charged planes and the total charge density of the planes defines the interfacial capacitance, which is proportional to the electrochemical energy stored at the polarized interface. The Helmholtz model led to the concept of a "double layer" of charged species, but it significantly overpredicts the magnitude of interfacial capacitances and neglects the essential role of entropy in governing molecular level details of electric field screening. [44]

By the early 1900s the double layer concept proposed by Helmholtz was being refined in parallel with expanding interest in statistical thermodynamics. It was found that the entropic cost of "de-mixing" a bulk electrolyte into a single layer of charge-compensating ions would incur an entropic penalty that would vastly outweigh the energetic stabilization offered by electrostatic screening. Gouy[45] and Chapman[46] independently put these conclusions on quantitative footing using Poisson-Boltzmann theory, a mean-field approximation, which assumes that all ions are independent point charges.

The Poisson-Boltzmann theory models how relative changes in ion density are linked to variations in electrostatic potential adjacent to charged surfaces. The key characteristic of this model is that electric double layers are comprised of a diffuse layer of ions, rather than a single layer of bound ions. This diffuse layer is predicted to screen the surface charge over distances that can extend tens to hundreds of nanometers from the electrode surface, depending on the ion concentration in the bulk solution.

Importantly, the core Gouy-Chapman assumption that treats ions as independent point charges neglects any influence from ion-ion interactions, ion size, and ion shape. As a result, the Gouy-Chapman theory predicts unphysically large ion densities immediately adjacent to solid surfaces, which also leads to erroneously large predictions of interfacial capacitance and local potential gradients. [40, 41]

In 1924, Stern bridged the approaches of Helmholtz with that of Gouy and Chapman by imagining the "double layer" as a region composed of a near-surface "bound" ion layer in series with a longer range "diffuse" double layer that extends into the bulk electrolyte. [47] The bound layer is composed entirely of counterions and solvent, while the diffuse layer contains a modified distribution of ion density (Figure 1). An extension by Grahame linked the bound and diffuse double layers via a defined "Helmholtz plane." [48] These papers comprise the core of the Gouy-Chapman-Stern model of electric double layer formation, which remains a common formalism for analyzing electric double layers in both colloid and catalysis science.

There are two important scaling lengths for evaluating electric double layers in classical systems. The first scaling length is the Bjerrum length (l_B), which is a parameter that defines the distance where the electrostatic interaction energy between two elementary charges equals the energy of thermal fluctuations, or k_BT:

$$l_B = \frac{e^2}{4\pi\varepsilon\varepsilon_0 \mathrm{k_B} T} \qquad (1)$$

where e (C) is the elementary charge, ε is the relative permittivity, ε_0 (F/m) is the permittivity of free space, $\mathrm{k_B}$ (J/K) is the Boltzmann constant, T (K) is the temperature. In classical dilute electrolyte solutions, bulk ion concentrations are sufficiently low that the average separation distance between ions always greatly exceeds the Bjerrum length.

The second parameter is the Debye screening length, [7, 8] which is derived from the Poisson-Boltzmann framework that describes the characteristic length scale of electrostatic screening. For a classical electric double layer, which is typically below 1 mM in aqueous solution, surface potentials are screened by 66% (or 1/e) at one Debye length away from the surface: [8]

$$\lambda_D = \sqrt{\frac{\varepsilon\varepsilon_0 \mathrm{k_B} T}{2(ne^2)\rho}} \qquad (2)$$

where ε is the relative permittivity, ε_0 (F/m) is the permittivity of free space, k_B (J/K) is the Boltzmann constant, T (K) is the temperature, e (C) is the elementary charge, n is the ion valence, and ρ (ions/m^3) is the ion density per unit volume.

The Debye screening length is a parameter that emerges from the balance of entropy and electrostatics that governs double layer formation. Increasing bulk ion concentration in the absence of ion-ion interactions results in smaller screening lengths as abundant ions can be recruited to screen surface potentials with a minimal influence on the system entropy. In contrast, raising temperature increases the magnitude of entropic driving forces which oppose the formation of compact double layers and results in a larger Debye screening length.

Many predictions of classical double layer theory are commonly applied to electrocatalytic interfaces, including the assumption that double layers always become more compact as ion concentrations increase and co-ions are excluded from the near-surface region. Despite the convenience of the assumptions made for classical electrolyte theory, increasing study of double layer formation in concentrated electrolytes and under high electrode polarization reveals that the emergence of ion-ion interactions, or ionic correlations, requires revisiting many of these classical pictures of interfacial properties.

2.2. Non-Classical Electric Double Layers Arising from Ion Correlations

In electrochemical systems, high applied potentials and high ion concentrations mean that ion-ion interactions cannot be neglected. As a specific example, classical models of electric double layer formation prohibit co-ions from being in the bound layer, as such an outcome would incur both electrostatic and entropic penalties. Yet, co-ion effects are rife in electrochemistry and electrocatalysis.[49-52]

In general, many efforts to analyze double layer formation under more complex conditions involve approaches that correct the mean-field Poisson-Boltzmann expression to account for ion-ion interactions or the discrete molecular nature of solvent.[53] Computational and theoretical work indicates that double layer formation can exhibit signatures of self-assembly.[54, 55] Further, simulation studies find that like-charge co-ions can be present immediately adjacent to charged surfaces under conditions where ionic correlations drive formation of self-assembled ion networks.[40, 53] We view these departures from ideality as critical elements of understanding how double layer formation can modify electrocatalytic activity and acknowledge the importance of these complementary studies.

Since the 1950s, substantial efforts and successes have been achieved in extending electric double layer theory beyond the assumptions that are inherent in Gouy-Chapman-Stern theory. A full review of this extensive literature is beyond the scope of our perspective, and we direct the reader to references from Wu,[40] Fedorov and Kornyshev,[41] and Zhan et al.,[56] for detailed discussions of how development in theoretical and computational methods have advanced the field beyond Gouy-Chapman-Stern models. The core findings from many of these studies align with conclusions from the experimental evaluation of ionic liquids and concentrated electrolytes discussed in the next section.

In the remainder of this perspective, we focus on how experimental study of ionic liquids and concentrated electrolytes has advanced the understanding of electric double layer formation and, more recently, started to connect these departures from classical theory to electrocatalytic activity. By focusing on experimental methods and approaches, we aim to constrain the scope of this extensive area to the primary expertise of our laboratory. Nevertheless, we are enthusiastic about continued computational and theoretical development, and see major opportunities for such approaches to contribute groundbreaking insights into questions and opportunities identified in the remainder of this article.

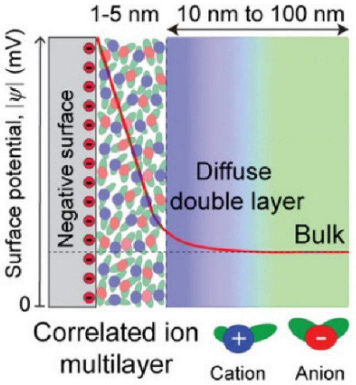

Figure 2. A scheme of a non-classical electric double layer. Electric double layers differ from classical models under conditions of sufficiently high bulk ion concentrations or surface polarizations that induce ion-ion correlations and co-ion effects. At bulk electrolyte concentrations exceeding 1 M, ion-ion correlation arises, and the double layer is composed of nanostructured ion clusters, which causes co-ions to become localized in near-surface bound ion multilayers that extend 1-5 nm away from surfaces. Reproduced with permission from ref (44). Copyright 2023 Wiley.

2.3. Electric Double Layer Formation at Electrochemical Interfaces

In many electrochemical systems, high applied potentials and high local ion concentrations bring electrochemical interfaces into the non-classical regime. For example, many electrocatalytic devices operate at applied potentials exceeding 1 V of polarization,[13, 49, 57-59] several times larger than thermal fluctuations, or 1 k_BT of energy (25 meV at room temperature). These high potentials readily drive the accumulation of near-surface bound ion layers with sufficiently large ion density that ion-ion interactions emerge and influence interfacial properties.[54]

Ionic liquids are widely studied model systems for exploring electric double layer formation (Figure 2).[51, 53, 60-64] As neat liquid salts often exceeding 4 M in ion concentration, ionic liquids provide opportunities to study double layer formation in highly correlated electrolytes.[41, 43] Ionic liquids also have many technologically advantageous properties,[60, 65] such as tunable molecular structures, high electrochemical stability, and negligible volatility. As such, ionic liquids have been broadly applied as electrolyte additives within the electrocatalysis community to control electrochemical reaction rates and selectivity.[13, 49, 66-68]

Early attempts to account for ion-ion interactions in concentrated electrolytes divided the total population of ions into "free" and "paired" groups. In solution, free ions contribute to screening with a background of neutral ion pairs. [41] However, more recent findings from the surface forces and soft condensed matter communities support the idea that ion-dense regions are better described as correlated networks composed of larger clusters of ions and solvent rather than distinct classes of solvent-separated "free" and "paired" groups. [43]

This important refinement suggests that correlated ion networks can modify interfacial microenvironments and hence influence electrocatalytic processes. For example, water and other molecules dissolved in ionic liquids have distinct properties from those of typical solvents. [69] Further, even many classes of ionic liquids can absorb substantial amounts of water, which often accumulates at interfaces[15] and influences electrochemical reactivity. [41] Ultimately, we envision that studying how ionic clustering can be used to tune solute concentrations and reactivity will yield new knobs for catalytic control.

Importantly, the formation of ionic networks at elevated concentrations also has a pronounced impact on electrostatic screening, which concurrently impacts the magnitude of electric fields at interfaces. [13, 42] As previously discussed, classical dilute electrolyte theory predicts that electrolytes with ion concentrations exceeding about 1 M should fully screen charged surfaces within molecular distances of less than 1 nm, reminiscent of the Helmholtz model of electric double layers. Such a picture would suggest that all concentrated electrolytes should universally result in highly localized potential gradients, leaving interfacial capacitance and electrochemical reactivity to become largely independent of the electrolyte composition.

Yet, surface forces experiments show that aqueous and ionic liquid electrolytes exhibit non-monotonic screening lengths with concentration. [42, 43, 70] Notably, screening lengths in highly concentrated solutions can even exceed 15 nm, which is larger than the Debye length for 1 mM aqueous NaCl. [42, 43] This is consistent with experiments that show double layer capacitances of neat ionic liquids in the range of 10 μC/cm^2, which is comparable to the double layer capacitance of dilute electrolytes. [41]

Further work proposed that most ions in concentrated electrolytes are correlated into a locally charge-neutral network, leaving a smaller population of available charges to behave as screening species. [71, 72] For example, fewer than 1 in 10,000 of the ions in typical ionic liquids would be required to be effectively dissociated to explain the observed diffuse double layer screening length of 5-10 nm that is increasingly observed across typical ionic liquids. [72]

This non-monotonic relationship between ion concentration and electrostatic screening length indicates that the formation of ionic clusters at higher concentrations begins to inhibit the ability of electrolytes to efficiently screen charged surfaces and causes interfacial potential gradients to extend further into the electrolyte. Indeed, recent studies from our lab show that CO_2 electrochemical reduction rates peak at intermediate concentrations in ionic liquid-derived electrolytes, [13] where strong interfacial potential gradients stabilize a key CO_2 reduction intermediate and resulted in improved device performance.

In correlated electrolytes, like-charged co-ions can also become confined in the bound ion layer, [43, 71] which is an outcome that is prohibited by classical electrolyte theory. In dilute electrolyte theory, co-ions should be completely excluded from the near-surface bound ion layer. Hence, classical dilute electrolyte theory would suggest that co-ions should have little influence on electrocatalytic reaction rates or selectivity.

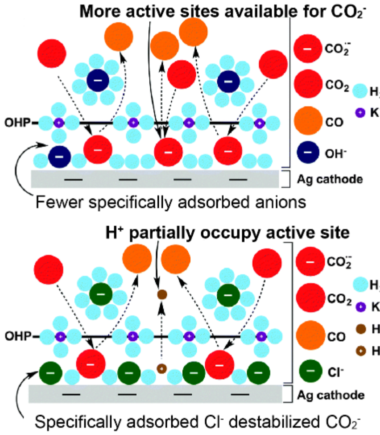

Figure 3. Co-ions present near the surface of a cathode. The adsorption of co-ions at electrode surfaces is a well reported non-classical effect. For example, hydroxide and halide anions near a negative cathode were reported to modulate electrochemical CO_2 reduction. Reproduced with permission from ref (51). Copyright 2016 Royal Society of Chemistry.

Yet, the electrocatalysis literature contains numerous examples of co-ion effects. [50-52, 73, 74] For example, the size of solvated anions was found to significantly influence their near-surface concentration and consequently rates of electrochemical CO_2 reduction (Figure 3), [51] indicating the necessity of considering anionic co-ions in cathodic reactions. Growing interest in electrocatalytic reduction of anionic species, such as nitrate, [75-77] further highlights the importance of studying the behavior of anions in electric double layers on cathodes. A more detailed discussion of co-ions effects is presented in Section 4.2.

In many cases, the specific details of how, when, and why co-ion effects can play a role in determining electrochemical reaction pathways remain open to investigation. We are optimistic that additional synergy between investigations in the areas of correlated electric double layer formation and electrocatalytic reactivity will provide fertile ground for transforming understanding of both electric double layer formation and electrocatalytic reactivity.

3. EXPERIMENTAL APPROACHES TO MEASURE ELECTRIC DOUBLE LAYER PROPERTIES

Electric double layer effects are increasingly investigated within the electrocatalysis field, [78, 79] spanning diverse reactions including water splitting, [80, 81] CO_2 conversion, [13, 49] and nitrate reduction. [14, 82] In many cases, systematic investigation of how modulations to electrolyte composition influence electrocatalytic reactivity has been insightful for linking double layer formation to electrochemical reactivity.

To date, study of electric double layer effects in catalysis has seen significant progress at modest electrolyte ion concentrations of around 0.1 M, where complementary electronic structure calculations are useful in linking adsorbate and intermediate binding energies to changes in reaction rates and selectivity. This approach has been used to bridge differences in alkali cation hydration energies to CO_2 reduction rates and selectivity.[83, 84]

However, systematic study of correlated electrolytes where collective ionic assembly can govern reaction rates and selectivity has remained much less explored. In these complex nanostructured electrolytes, the most effective works are those that integrate study of electrochemical reactivity, interfacial structure, and electrochemical properties in a synergistic manner. Below, we survey different experimental approaches to study interfacial and electrochemical properties in correlated electrolytes to show how tools and approaches from colloid and interface science can advance understanding of how electric double layer formation influences electrocatalytic activity.

3.1. Surface Forces Measurements on Ionic Liquids and Concentrated Electrolytes

Surface forces measurements provide a unique way to determine the spatial extent and nanoscale ordering of electric double layers. In a surface forces measurement, such as those performed with a surface forces apparatus[85] or atomic force microscope,[86] a probe surface is brought towards a sample surface. Once the two surfaces begin to interact via colloidal surface forces or hydrodynamic forces, the probe surface will begin to accelerate or decelerate (Figure 4A). The range and magnitude of any attractive or repulsive forces are measured by a calibrated spring. Additional details of experimental apparatus and analysis can be found in Kristiansen et al.[85] and Butt et al.[86] references.

Surface forces measurements as a function of separation distance provides powerful information about the physical structure of electric double layers. The resulting "force-distance profiles" can directly yield electrostatic decay lengths of the bulk electrolyte. Further, force detection sensitivity ranges from pN to nN, and distance sensitivity can approach 2-5 Å (Figure 4A),[43] which is about the size of a water molecule. Such force and distance resolution readily allows for the measurement of the thickness and even nanostructure of bound and diffuse ion layers, enabling one to develop quantitative understanding of how the electric double layer varies as a function of ion concentration, solvent properties, and applied electrochemical bias.[43, 85]

Surface forces interrogation of double layer formation at the interface between mica, ionic liquid, and gold in 2013 revealed that electric double layers formed by neat ionic liquids can extend much farther away from a charged gold electrode surface than expected.[71] Most models at the time predicted that double layers in neat ionic liquids should comprise either one or two bound ion layers,[41, 53, 63] reminiscent of the initial Helmholtz model of electric double layers. Instead, the diffuse layer electrostatic decay length reported for a common imidazolium ionic liquid was around 10 nm (Figure 4A).[71]

This work also reported oscillatory short-range forces extending 2-4 nm away from the charged surfaces,[71] which is consistent with surface forces measurements between two negative mica surfaces.[54, 87] Since the dimensions of imidazolium bis(trifluoromethylsulfonyl)-imide ions are around 0.5-1 nm, the results from these measurements indicate bound ion layers in ionic liquids extend multiple ion diameters away from charged surfaces and consist of both counterions and co-ions. Similar conclusions have been reached by other investigators using atomic force microscopy measurements.[43, 88, 89]

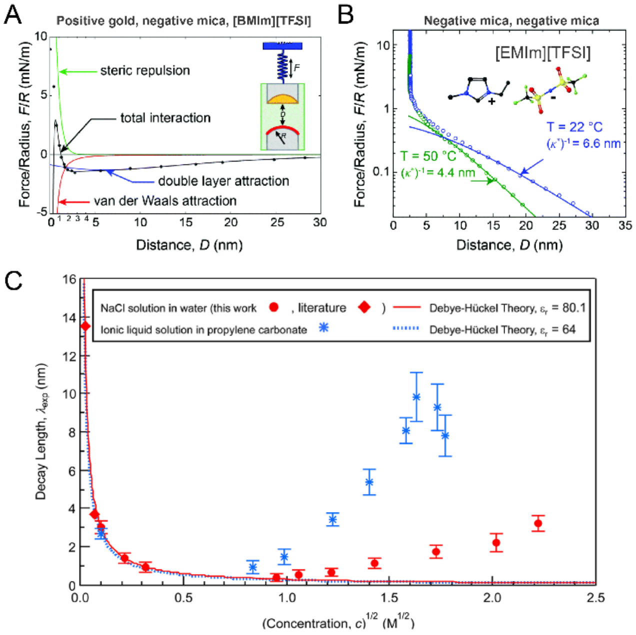

Figure 4. Surface forces studies of electric double layer in solutions with high ionic strengths. (A) Force-distance profile obtained using a surface forces apparatus with *in situ* electrochemical control. Forces were measured between a negative single crystalline mica surface and a positive (anodically polarized) atomically smooth gold electrode across the common aprotic ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [BMIm][TFSI]. The x-axis shows the surface separation in nm, the y-axis shows the force normalized by the radius of curvature, black points are measured data, and the solid lines are fitted interaction potentials. (B) The decay length of long-range repulsion between symmetric negative mica surfaces in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIm][TFSI]) decreases with increasing temperature. (C) Non-monotonic dependence of screening lengths with concentrations of electrolytes. Surface force measurements show that highly concentrated solutions of NaCl and Ionic liquids both have long screening lengths comparable to dilute solutions. Figure 4A reproduced with permission from ref (43). Copyright 2017 Royal Society of Chemistry. Figure 4B reproduced with permission from ref (72). Copyright 2015 National Academy of Sciences. Figure 4C reproduced from ref (42). Copyright 2016 American Chemical Society.

Subsequent work in the surface forces community revealed the electric double layer thicknesses in ionic liquids decrease as temperature increases (Figure 4B).[72] This temperature dependence differs from the predictions of classical theory and suggests that increased thermal energy disrupts ionic correlations to collapse double layers.

These findings have substantial implications for electrocatalysis by suggesting that experimental screening lengths vary non-monotonically with electrolyte ion concentration (Figure 4C). Consistent with classical theory, double layer screening first becomes more efficient, as evidenced by more compact double layers, as electrolyte ion concentration is increased from the dilute limit to around 10 mM. From around 10 mM to 1 M, electric double layer properties can have a more complicated concentration dependence, but growing consensus suggests that double layers are the thinnest and electric fields are the strongest at around 1 M in ionic strength. Beyond 2 M, the double layer increases with increasing concentration. This is particularly salient in aqueous electrolytes of alkali metal salts, in which measured screening lengths can exceed 5 nm, whereas classical electrolyte theory predicts screening lengths smaller than the size of a single water molecule. [42, 70]

We see many opportunities for continued surface forces investigation of compositionally complex electrolytes, especially as surface forces techniques are expanded to integrate *in situ* optical spectroscopy. These techniques will be especially valuable to investigate how double layer structures form under high polarizations, such as those exceeding ±1 V. At such strong electrode bias, we hypothesize that interfacial environments will contain the signatures of correlations, even with more modest bulk electrolyte concentrations below 0.1 M. These insights could be augmented by pairing surface forces tools with optical spectroscopy to fill in missing information about local chemical compositions and any intermediate species that may be present.

3.2. Electrochemical Impedance Spectroscopy of Interfaces

Electrochemical impedance spectroscopy (EIS) is a nondestructive analytical technique used to probe electrochemical systems for important charge transfer, mass transport, and kinetic information. EIS operates by applying a sinusoidal current or voltage perturbation over a range of frequencies to an electrochemical system and observing the corresponding response in voltage or current, respectively, to measure impedance. The resulting data is composed of both real and imaginary components due to observed phase shift between the perturbation and the response. Impedance is represented by the combined effect of resistance and reactance, which are the real and imaginary components, respectively. [90-92]

The relationship between the applied perturbation and the phase shifted components can be seen in Equation 3:

$$V = IZ = I(R + iX) \qquad (3)$$

where V (V) is the potential, I (A) is the current, Z (Ohm) is the impedance, R (Ohm) is the resistance, and X (Ohm) is the reactance. Reactance accounts for the combined response of inductance and capacitance. However, inductors are usually absent in most electrochemical systems, thus reactance often represents the capacitive response of the system. [90-92]

EIS is a common approach for evaluating double layer properties in the field of energy storage, where double layer capacitance is an important metric for benchmarking the energy density of electric double layer capacitors. [93, 94] EIS provides powerful information for catalysis studies as well, as capacitance measurements can shed light on interfacial properties that influence catalytic reactivity such as double layer capacitance, solution resistance, and charge transfer resistance. [90] Most studies into the relationship between capacitance and double layer structure are limited to conditions of zero or low applied potential to avoid complicating effects associated with catalytic activity or electrode surface restructuring under applied bias. [95-98]

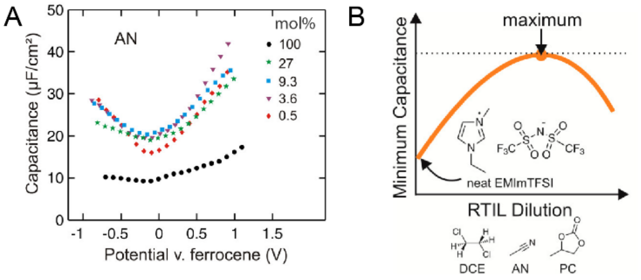

Figure 5. Electrochemical impedance spectroscopy (EIS) enables measurement of electric double layer capacitances as a function of applied polarization and ion concentration. (A) In acetonitrile (AN) solutions of [EMIm][TFSI], the double layer capacitance increases with electrode polarization. (B) Meanwhile, the minimum double layer capacitance, understood as the capacitance at the potential of zero charge, exhibits a non-monotonic dependence on ion concentration, which peaks at intermediate concentrations of around 1 M. Reproduced from ref (98). Copyright 2015 American Chemical Society.

A 2015 study used EIS to show that neat ionic liquids exhibit only modest interfacial capacitance of around 10 μF/cm² (Figure 5A), which is lower than the typical capacitance of 50-100 μF/cm² observed in aqueous electrolytes. [98] Notably, the study demonstrated a non-monotonic relationship between double layer capacitance and concentration where the capacitance at the potential of zero charge reached a maximum around 1 M (Figure 5B). As electrolyte concentration extends beyond 1 M, correlations induce the formation of ionic clusters, which reduces the number of free ions available to store charge. [98, 99]

The non-monotonic relationship between capacitance and ionic liquid concentration mirrors the relationships between CO_2 electroreduction rate and ionic liquid concentration we recently reported. [13] This connection between catalytic activity and double layer capacitance highlights how EIS can provide information that can be used to link electrochemical double layer responses and catalytic performance. Indeed, the use of EIS appears to be rapidly expanding in electrocatalysis studies. [12, 100, 101]

Yet, systematic exploration of how electric double layer capacitance changes during active electrocatalysis, where surfaces reconstruct, intermediates are generated, and proton gradients are induced, remains in the early stages. We see substantial opportunities for expanding the use of EIS under operating conditions, especially when EIS studies are used in conjunction with other techniques, including surface forces measurements and optical spectroscopy.

3.3. Optical Interrogation of Electric Double Layers

Interfacial vibrational spectroscopy provides important chemical information that complements measurements of electrochemical and structural properties of electrocatalytic interfaces. [102, 103] Widely used examples of interfacial vibrational spectroscopy include surface-enhanced Raman scattering (SERS) or infrared absorption (SEIRAS) and sum frequency generation (SFG) spectroscopy.

SERS and SEIRAS selectively enhance the signal of molecules near nanostructured noble metal electrodes through surface plasmon resonance,[104] while SFG achieves interface specificity by the retention of SFG signal at solid-liquid interfaces where the centrosymmetry is broken.[105] Several other emerging methods such as tip-enhanced Raman spectroscopy[106] or other means of leveraging nanoconfinement to enhance optical signals also show promise for continued study of electrochemical interfaces and are covered further in other reviews.[107-109]

One of the most important properties that can be probed by vibrational spectroscopy is the interfacial electric field. This is often achieved by confining probe molecules with permanent dipoles to interfacial environments such as a self-assembled monolayer (SAM) of aromatic molecules with a nitrile group (-CN).[102, 110] When an external electric field (i.e., interfacial electric field) is exerted on the probe molecule, vibrational states of the molecule would be either stabilized or destabilized depending on the alignment of its dipole and the electric field. The resulting changes in vibrational energies are observed as spectral wavelength shifts – known as Stark shifts – of the corresponding vibrational peaks.

The Stark shift is usually linear with the strength of the electric fields:

$$\Delta\nu = -\Delta\mu \cdot F \qquad (4)$$

where $\Delta\nu$ (cm^{-1}) is the Stark shift, F (MV/cm^{-1}) is the strength of electric field, and $\Delta\mu$ ($cm^{-1}/(MV/cm)$) is the Stark tuning rate that is characteristic for each probe molecule. Measuring the Stark shift of probe molecules at an interface enables the experimental quantification of interfacial electric fields.

For example, Dawlaty and coworkers used SFG and a SAM of 4-mercaptobenzonitrile to measure the interfacial electric field between an Au electrode and KCl electrolytes.[111] At the same applied potential (0.3 V vs Ag/AgCl), larger Stark shifts were observed when the concentration of KCl increased from 0 to 0.1 M, indicating the presence of a stronger interfacial electric field at higher KCl concentrations. Additionally, they observed that when scanning the applied potential in the cathodic direction, the interfacial electric field stopped growing once a faradaic process such as the reduction of water was initiated (Figure 6A), which was modeled as a "leaky capacitor". This result further indicates the non-classical behavior of electric double layer under high polarization and when charge transfer processes evolve at the electrochemical interface.

Similarly, the Stark shift of CO adsorbed on roughened Cu electrodes has been used as an *in situ* generated probe to study interfacial electric fields during electrochemical CO_2 reduction.[112, 113] It is noteworthy that in addition to interfacial electric fields, other intermolecular interactions such as the solvation of probe molecules or hydrogen bonding also contribute to Stark shifts.[114-116] Therefore, careful identification of the source of Stark shifts is necessary to accurately assess the interfacial properties.

In addition to Stark shift of adsorbates, our lab has shown that when double layers are composed of asymmetric ions such as ionic liquids, changes in relative SERS peaks can also be used to probe interfacial electric fields and orientational order in double layers. For example, *in situ* electrochemical SERS reveals that electrostatic forces drive the collective reorientation of the cation 1-ethyl-3-methylimidazolium ($[EMIm]^+$) near a negatively charged electrode as polarization is continually increased (Figure 6B).[13, 49]

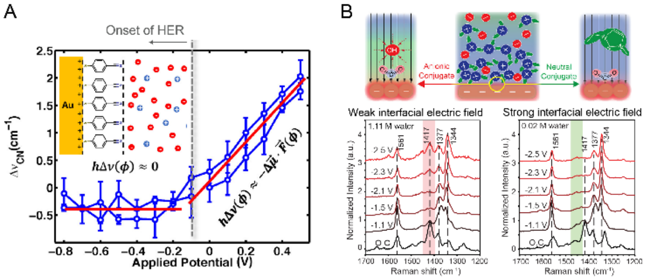

Figure 6. Interfacial vibrational spectroscopy can provide information on electric double layers. (A) Stark shifts of 4-mercaptobenzonitrile were measured to quantify local electric field at the electrochemical interfaces between an Au electrode and a KCl solution. Increasing the cathodic polarization increases the interfacial electric field until charge transfer processes (e.g., HER) start. (B) Relative changes in peak intensities of asymmetric ions, such as imidazolium cations, during in situ electrochemical surface-enhanced Raman scattering (SERS) measurements can be used to monitor changes of double layer in response to applied potential. The change in relative peak intensities is linked to collective reorientation of cations, which can be a qualitative descriptor of the strength of local electric fields. Figure 6A reproduced from ref (111). Copyright 2017 American Chemical Society. Figure 6B reproduced from ref (49). Copyright 2023 American Chemical Society.

As SERS only enhances the vibrational modes perpendicular to a metal surface, relative peak intensities of $[EMIm]^+$ change with the collective reorientation. Using this phenomenon, our lab studied the interfacial electric field between an Ag electrode and $[EMIm][BF_4]$-acetonitrile electrolyte during electrochemical CO_2 reduction. We found that the presence of co-ions, either brought by correlation with $[EMIm]^+$ at high concentrations or generated from electrochemical reactions,[13, 49] significantly weaken interfacial electric fields, leading to lower reaction activity.

Moving forward, we see major roles for continued investigation of how electric double layer formation influences electrocatalytic activity using interfacial optical spectroscopy. In addition to continued use of Stark probes and spectral shifts of anisotropic ions, we envision that the use of interfacial spectroscopy can provide important insights into how and when co-ions accumulate at interfaces. Further development of new methods that push spatiotemporal sensitivity into regimes where surface-bound intermediates can be identified and studied will open the door to new insights into how dynamic changes to surface structures and interfacial properties will modulate reaction activities.

3.4. Scattering Approaches and Operando Photoelectron Spectroscopy

Photoelectron spectroscopy methods provide ways to characterize double layer formation since the kinetic energy of emitted electrons is influenced by interactions with local electrochemical potentials. The kinetic energy of photoelectrons and the resulting spectral peak widths also provide chemical information, such as the atomic identity, charge states, and chemical environments of redox active species. Hence, photoelectron spectroscopy provides information to form a holistic understanding of how double layer properties influence electrocatalytic reactions.

The high energy resolution and detection sensitivity of synchrotron-based photoelectron spectroscopy facilities are powerful for probing electrocatalytic interfaces. For example, due to the limited mean free path of "tender" X-ray photoelectrons (ca. 10 nm), ambient pressure X-ray photoelectron spectroscopy (APXPS) has been used to probe the potential drop at the interface between an Au electrode and KOH electrolytes using water and pyrazine as probe molecules. [117] XPS peaks of oxygen in water (O 1s) and nitrogen in pyrazine (N 1s) in the double layer exhibit peak broadening when experiencing an electric field due to polarization of electrode surfaces. By combining experimental potential-dependent peak broadening and numerical simulations, a profile of potential drop within the electric double layer can be established (Figure 7).

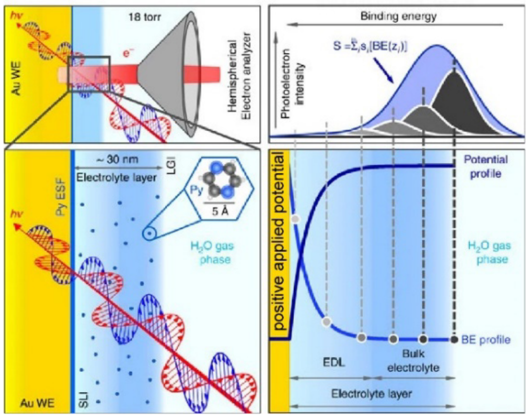

Figure 7. *In situ* electrochemical X-ray photoelectron spectroscopy (XPS) is an emerging technique that can provide information on both the chemical makeup of electric double layers and the propagation of potential gradients away from charged interfaces. XPS signals from elements in probe molecules broaden as a function of local potential gradient. The extent of spectral broadening from probe molecules at different locations depicts the profile of electric double layer. Reproduced with permission from ref (117). Copyright 2016 Springer Nature.

Other groups have used ultrabright synchrotron light for THz spectroscopy[118] or total electron yield mode X-ray absorption spectroscopy[119] to illuminate interfacial water networks and water structure as a function of applied potential in aqueous NaCl electrolytes on gold electrodes. Extending these and similar approaches to a wider range of electrolytes and reactions would provide exciting new ways to study the interplay between double layer formation and reaction metrics such as selectivity or reaction rate.

Synchrotron experiments require careful design, as necessary precautions are needed to eliminate background interference. Further, restrictions on samples that can be analyzed can pose a limitation, as vigorous reactions or volatile solvents may not be suitable for measurements using ultrahigh vacuum or high-energy X-rays. Nonetheless, insights gained from synchrotron experiments performed on more stable electrolytes show great promise for informing further development of models of double layer formation and reaction mechanisms that can be adapted to a wider range of electrolytes.

3.5. Complementary Analysis of Electrochemical Interfaces

Several other approaches employed in the colloid and interface science community can provide additional information on electric double layers and surface energies of electrochemical interfaces. We briefly summarize selected techniques, including contact angle measurements, [120] electrocapillarity, [48, 121] electrochemical quartz crystal microbalance, and zeta potential characterization. [122] These approaches can provide additional layers of insight when integrated with *in situ* approaches discussed above.

Contact angle measurements rely on observation of the angle formed at a triphase interface. [123] When a small liquid droplet is contacted with a solid surface, the contact angle is defined by the relative interfacial energies of the three phases. An angle of 0° indicates a fully wetted surface, while a nonwetting surface will have a contact angle greater than 90°. One of the most common uses of contact angle is to determine surface hydrophobicity when a water droplet is brought into contact with a solid surface. [120]

Under electrochemical bias, changes to electrode surface energies lead to changes in the contact angle between a liquid drop and a surface, an effect called electrocapillarity, which dictates surface wetting behavior. [48] Polarization of an electrode increases both the solid-liquid and solid-vapor interfacial energies, while leaving the vapor-liquid interfacial free energy comparatively unchanged. As a result, droplets typically spread further on a polarized electrode. This electro-wetting is dependent on applied potential, often leading to a situation where the electrode is fully wetted at high polarizations.

Changes in double layer properties are a major contributor to electrocapillarity. For instance, increasing surface hydrophobicity to partially exclude water molecules while enhancing the concentration of less polar reactants, such as CO_2, is one promising way to suppress the reduction of water and enhance the selectivity of reactions. [124, 125]

Electrochemical quartz crystal microbalance (EQCM) is another powerful tool to study changes at electrochemical interfaces. Applying a potential to a thin quartz crystal through metal electrodes induces vibrational motion of the crystal at its resonant frequency through piezoelectric effect. [126] Changes in the properties, such as electrode mass or the viscosity of nearby electrolytes alter the resonant frequency and other essential parameters of the crystal, making EQCM a sensitive technique to unravel interfacial chemical processes.

EQCM has been widely used to monitor processes such as electrode corrosion, [127] chemical adsorption or deposition, [128-130] and mass transport within nanostructured or porous materials. [130, 131] Recent studies demonstrate that EQCM is also capable of depicting double layer structures. [132, 133]

For example, an EQCM study on aqueous solutions of 1-butyl-3-methylimidazolium chloride ([BMIm][Cl]) and NaCl show a decrease of crystal resonant frequency when the solution ion concentration is increased due to the formation of denser double layer. [132] Combining with mathematical deduction, the study also revealed the saturation of interfacial electrolyte viscosity at intermediate concentrations (1 M), which suggests a non-monotonic dependence of Debye screening length on electrolyte concentrations, agreeing with conclusions from surface forces measurements.

Zeta potential measurements offer additional approaches to characterize double layers. [122] Zeta potential is defined as the potential at the boundary between bound ions surrounding a charged surface and the bulk electrolyte. These measurements are effective at determining if a given pairing of electrode and electrolyte is most likely to be positive or negative in charge, which can be used to deduce the propensity of different ions to chemisorb to surfaces. By evaluating how zeta potential changes as a function of composition and applied potential, information about double layer formation can be inferred. The zeta potential of an electrode can be evaluated through measuring streaming potential. [134-136]

4. INTERSECTION OF ELECTRIC DOUBLE LAYER PROPERTIES AND ELECTROCATALYTIC ACTIVITY

Electric double layer formation plays an integral role in sculpting interfacial microenvironments where electrochemical reactions occur. Properties such as ion and reactant concentrations and chemical potentials differ drastically from those of the bulk electrolyte. Double layer properties are often linked to interfacial processes that determine electrocatalytic activity, including surface reconstruction, intermediate binding energies, and local microphase separation. [7, 8] Hence, the propensity of electrolytes to alter the rate, selectivity, or efficiency of electrocatalytic reactions by modulating double layer properties are the subject of substantial ongoing research.

Below we discuss selected examples highlighting how electrolyte composition and electric double layer formation influence cathodic reactions. We do not intend to cover the entirety of the vast literature on electrolyte effects in electrocatalysis but rather focus case studies that highlight how interconnections between double layer formation and electrocatalysis promise to advance transformative understanding of electrochemical interfaces.

By focusing on electrocatalytic reduction, we aim to maintain consistency on counterions being positive and co-ions being negative. Importantly, many of the fundamental links between double layer formation and electrochemical reactivity should extend to anodic interfaces and electrocatalytic oxidation reactions.

4.1. Cation Effects at Cathodic Interfaces

Among electrolyte contributions to electrocatalytic activity, cation effects have been extensively studied for cathodic reactions, including water reduction for hydrogen production, [137, 138] CO_2 electroreduction, [12, 20, 139] nitrate electroreduction, [14] and more complex electrosynthesis reactions. [138] At cathodic interfaces, cations are strongly attracted to electrode surfaces via electrostatic interactions, particularly under large electrode polarizations, often exceeding -1 V. While protons (or hydronium cations) are also positive in charge, discussion of cation effects typically refers to the influence of salt species that are dissolved in a solvent to form an electrolyte, including alkali, alkaline earth, organic, and transition metal cations.

The hydrogen evolution reaction (HER) is considered one of the simplest reduction reactions. In aqueous electrolytes, this consists of the reduction of water into hydrogen. As a model reaction, HER has been considered largely independent of specific ion effects, but recent works have shown substantial effects of electrolyte composition on reaction rates. [11, 140] Continued progress towards revealing mechanisms by which electrolytes influence HER promises to inform design of electrolytes and interfaces for more complex electrocatalytic transformations.

Many explanations of cation effects in HER hinge on how cations alter the stability of reaction intermediates in the rate-limiting step on electrode surfaces[137, 141-143] or change local water hydrogen bonding networks. [144-146] For example, Koper and coworkers investigated the cation dependence of HER in neutral-to-alkaline conditions, where protons are sourced from water. They proposed that cations can promote HER by enhancing interfacial potential gradients to stabilize transition states involved in the water dissociation step. [10, 141] Under these conditions, the HER rate is sensitive to near-surface concentration of cations (Figure 8A) and increases with increasing ionic strength.

Notably, at high ionic strengths where ionic correlations are expected to emerge, [43] HER can become inhibited by cations rather than promoted. While such an inhibiting effect is attributed to blockage of water transport by a compact layer of cations, [141] we envision that recent findings on ionic correlations between cations and anions[42, 43] may contribute novel understanding on the overall mechanism.

Other examples of how cations can influence HER abound and further complicate understanding of how electrolytes influence reaction pathways and kinetics. [67, 140, 147] For example, Resasco and coworkers investigated the influence of cation size on electrodes with different inherent activities in acidic and alkaline aqueous media. This work found that cation effects are most pronounced in alkaline electrolytes and show convoluted trends on different metal groups. [137]

On noble metal electrodes such as Au and Ag, interfacial cations facilitate HER by lowering the activation barrier for water dissociation, which is the rate-determining step. They also found that larger cations such as Cs^+ were more effective in promoting HER on Au and Ag than smaller cations like Li^+ due to smaller hydration shells and thus higher interfacial concentrations. However, on reactive electrodes like Pt and Pd, where the desorption of $[OH]^-$ is the kinetically relevant, larger cations can limit rates by stabilizing adsorbed $[OH]^-$. Notably, cation effects appeared to play a minimal role under acidic conditions, where most protons required to drive HER are sourced from hydronium that do not strongly interact with metal cations. [137]

For more complex electrocatalytic reactions, such as CO_2 reduction and nitrate reduction, selectivity to different pathways becomes increasingly important, and electrolytes can play as important a role as electrodes in determining selectivity. Using CO_2 electroreduction as an example, the choice of cation has been shown to affect selectivity among H_2, C_1, and C_{2+} products on Cu electrodes through generation of local electric fields that stabilize key polar intermediates (Figure 8B) through electrostatic interactions. [2, 11]

Larger cations (e.g., Cs^+) were proposed to accumulate at higher concentration at the interface than smaller cations (e.g., Li^+), thus providing a stronger electric field that enhances the selectivity of C_{2+} products. Cations were also

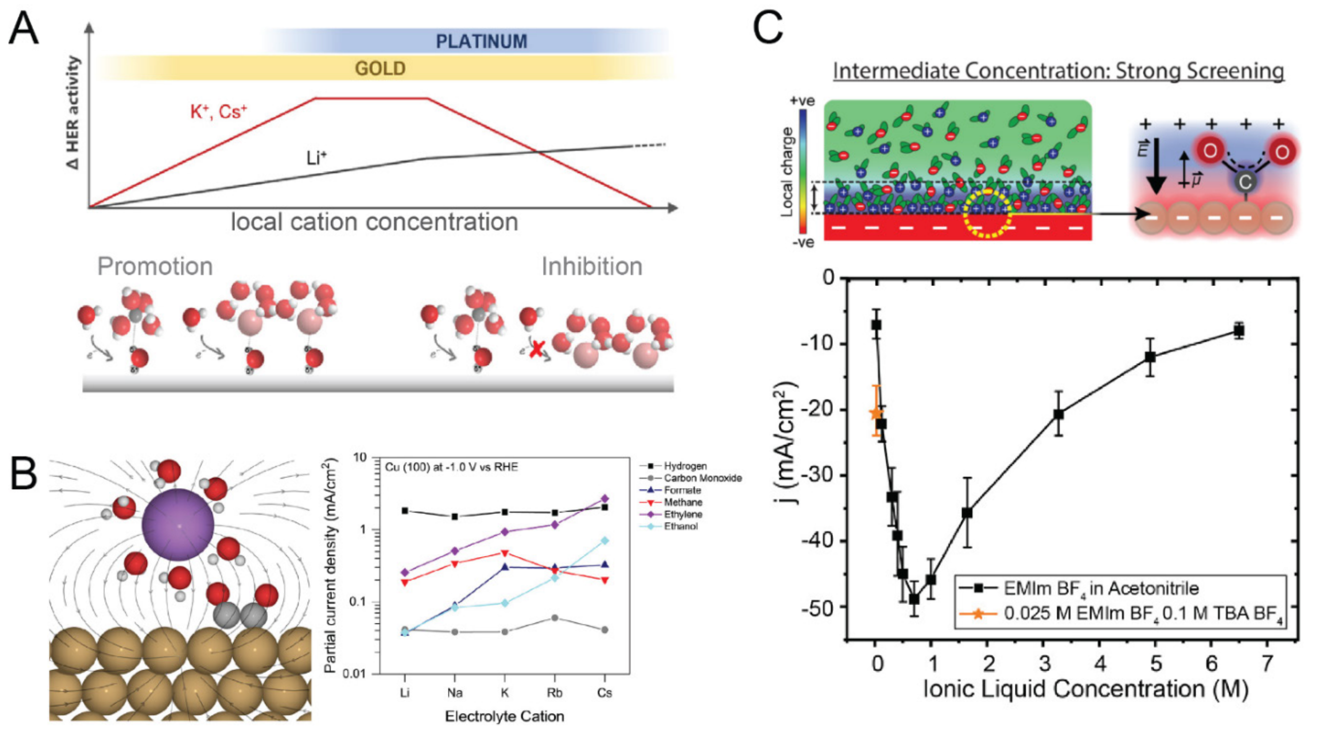

Figure 8. Interfacial properties influencing the activity of electrochemical CO_2 reduction. (A) Concentration of cations in the double layer governs the rate of HER. The rate of HER initially increases with the concentration of cations as cations can facilitate water dissociation. This promoting effect was more pronounced for larger cations. However, further increasing the concentration of cations may inhibit the rate of HER due to the blockage of the surface for H_2O transport. (B) Solvated cations at electrode-electrolyte interfaces contribute to local electric fields. Weakly solvated cations are expected to have smaller effective radii, thus enabling higher interfacial concentrations, and providing stronger electric field that can better stabilize the transition state of electrochemical CO_2 reduction and enhance the selectivity of C_{2+} products. (C) In [EMIm][BF_4]-acetonitrile electrolytes, concentration of cations at interface is maximized when the bulk concentration of [EMIm][BF_4] is in the intermediate regime (0.5 to 1 M), leading to the shortest screening length and strongest interfacial electric field. Figure 8A reproduced from ref (141). Copyright 2021 American Chemical Society. Figure 8B reproduced from ref (11). Copyright 2017 American Chemical Society. Figure 8C reproduced from ref (13). Copyright 2022 American Chemical Society.

proposed to influence the selectivity of CO_2 reduction through enhancement of local CO_2 concentrations, modulation of the interfacial electric field,[12] or suppression of water dissociation.[14, 148-150]

Similar cation effects have been reported for nitrate reduction, where larger numbers of proton and electron transfer steps are required. For example, nitrate reduction to ammonia requires transfer of 9 protons and 8 electrons, which often yields a mixture of side products.[148] Reported cation effects point towards the interaction strength between a metal cation and nitrate anion[14] or the promotion of hydrogen adsorption[149] as the reason behind enhanced reaction rates and selectivity in the presence of certain cations. Where there is emerging interest in synthesizing organic molecules such as urea,[151] adiponitrile,[150] and peroxides,[152] cation effects identified from studying simpler reactions have proven promising avenues for improving overall selectivity and reaction rates.

We note that most studies of cation effects to date have focused on how single cations can modify the binding energies of individual intermediate species within a near-surface bound ion layer, which is reminiscent of the Gouy-Chapman-Stern framework discussed above. Yet, emerging evidence suggests that larger applied potentials and higher concentrations often employed in electrocatalytic processes can have a substantial impact on electrocatalytic rates and selectivity in ways that cannot be predicted using classical theories where ion-ion interactions are neglected.[13, 22] The most notable effect is the inclusion of anions in the electric double layer and the observation of co-ion effects.

4.2. Anion Effects and Interfacial $[OH]^-$

In classical electric double layer theory, accumulation of anionic species at cathodic interfaces is disfavored by both electrostatic repulsion and entropic effects. However, co-ions can have major effects on interfacial micro-environments and reactivity. For example, our study on CO_2 reduction in [EMIm][BF_4]-acetonitrile electrolytes shows that at concentrations of [EMIm][BF_4] exceeding 1 M, strong correlations between $[EMIm]^+$ and $[BF_4]^-$ confines anionic $[BF_4]^-$ to the interfacial region, which leads to a thicker double layer and weaker interfacial electric field.[13] The highest CO_2 reduction rate was observed when the concentration of [EMIm][BF_4] was in an intermediate regime of 0.5 to 1 M (Figure 8C), before ionic correlations begin to dominate.[13]

Co-ion effects are even more pronounced when interfacial anionic species are electrochemically generated. For example, the electrochemical generation of interfacial $[OH]^-$ via consumption of protons from water during electrocatalysis is broadly acknowledged as a key determinant of reaction rates, selectivity, and process efficiency for many reactions.[49, 57] Such effects are often referred to as an altered "interfacial pH,"[26, 51] and many trends can be explained by consideration of specific chemical coordination interactions.

For example, CO_2 electroreduction generates $[OH]^-$ and subsequently (bi)carbonates as possible byproducts in aqueous electrolyte,[153] especially when HER is a competing reaction. The mechanistic details of how $[OH]^-$ impacts CO_2 electroreduction selectivity are subject to ongoing study.

One current understanding of interfacial pH effects on CO_2 reduction is its influence on local availability of protons to facilitate CO_2 reduction to more reduced products.[9, 154-156] Further, interfacial pH can be modified by the hydrolysis of water in cation hydration shells. This changes local CO_2 concentration by tipping the equilibrium between (bi)carbonate and CO_2[26, 79, 157-159] or otherwise suppresses the competing hydrogen evolution reaction.[159]

While we agree with the utility of viewing the impact of interfacial $[OH]^-$ generation through the lens of pH effects, we are increasingly exploring the degree to which ionic correlations provide complementary insights into how generation of interfacial co-ions can modify CO_2 electroreduction activity.

Our recent work on CO_2 reduction in ionic liquid-derived electrolytes shows spectroscopic evidence of substantially lowered interfacial potential gradients that occur at the potential where interfacial $[OH]^-$ generation begins via dissociation of water to drive CO_2 reduction.[49] In contrast, we find larger interfacial potential gradients are maintained when cationic proton donors are used to drive CO_2 reduction, as the associated conjugate base is neutral rather than anionic. Our findings show how the generation of charged byproducts at interfaces can either attenuate or enhance local potential gradients and points towards additional approaches to modifying interfacial properties.

Co-ion effects are also an important consideration in water electrochemistry, particularly for reduction reactions where anions are found to adsorb to electrode surfaces.[160, 161] For instance, Jaramillo and coworkers show the oxygen reduction reaction (ORR) displays anion dependent kinetics on Pt (111),[162] Pd,[163] and Ag[163] surfaces. Although the surfaces have different intrinsic catalytic activity for ORR, they all displayed lower ORR reaction rates in electrolytes containing halide anions than in electrolytes containing oxygenated anions such as $[ClO_4]^-$, $[NO_3]^-$, $[SO_4]^{2-}$, and $[PO_4]^{3-}$.[162, 163]

This study postulated that lower ORR rates in halide-containing electrolytes arises from strong chemisorption of halide anions to surfaces.[163] In contrast, oxygenated anions bind weakly to surfaces, promoting higher ORR rates, where the weakest binding anion, $[ClO_4]^-$, yields the highest ORR rates on all surfaces.[160-163] These trends could be due to a combination of competitive adsorption between the anions and ORR intermediates, and the influence of bound anions on the electronic structure of neighboring active sites.[162, 163]

Much like oxygen reduction, hydrogen reduction is greatly influenced by co-ion effects. Often, the hydrogen binding energy is a major focus for HER studies, but recent evidence shows that $[OH]^-$ binding energy is also correlated with HER reaction rates by modulating reaction pathways[100] or hydrogen bonding networks.[17]

Current research suggests that $[OH]^-$ binding energy displays a "volcano type" relationship between adsorption strength and HER rates on various catalysts, showing that both hydrogen binding energy and $[OH]^-$ binding energy should be tuned in concert.[100] Some reactive surfaces bind $[OH]^-$ very strongly, which can become detrimental to HER reaction rates as cations near the electrode surface can further stabilize adsorbed $[OH]^-$ and prevent its departure from the electrode.[137]

For example, certain metals such as Pt(110) and Ru bind $[OH]^-$ particularly strongly, in which case, water dissociation is no longer the rate-limiting step but $[OH]^-$ removal. Other metals such as Au and Ag do not bind $[OH]^-$ strongly, meaning that $[OH]^-$ adsorption correlates with the energy of water dissociation.[100, 137]

Additional research addresses the relationship between $[OH]^-$ binding energy and pH, illuminating a possible reason for the differences in activity between acidic and alkaline water electrolysis. Chen and coworkers found that there is an inflection point in catalytic reactivity when moving from acidic to alkaline pH instead of decreasing monotonically.[80] This inflection point occurs at lower pH on surfaces that bind $[OH]^-$ more strongly and signifies a narrowing of the kinetic gap between acidic and alkaline HER pathways. Such findings are encouraging for further exploration of how co-ions influence HER.

An emerging area that shows promise for progressing understanding of co-ion effects in electrocatalysis is that of nitrate electroreduction, as nitrate is anionic and must be present at cathodes to be reduced to products like ammonia. Nitrate reduction provides a compelling example where a negatively charged anion must approach a cathode surface for reduction to occur. In these cases, the composition of the electric double layer is key, and we view ionic correlations as important for understanding electrochemical nitrate reduction rates and selectivity.[14, 22]

For further context into how electric double layer formation under non-classical conditions can lead to novel interfacial processes, the reader is directed to studies on potential-induced structural transitions of electrodes including surface reconstruction and dissolution,[78] formation of ion concentration gradients,[158, 164, 165] and formation of strong interfacial electric fields.[13, 159] These phenomena synergistically modify microenvironments around active sites, and we see many avenues for investigations on how correlated double layer formation influences electrocatalytic activity.

4.3. Microphase Separation and Carbonate Precipitation

As electrochemical reactions proceed, the accumulation of solute species at interfaces can influence interfacial nucleation energetics and induce microphase separation processes. In the area of CO_2 electroreduction, microphase separation plays a prominent role, as formation of insulating carbonate films blocks electrode surfaces and limit device lifetimes.[166-168]

Recently, strategies to modulate electric double layer properties have been explored to disrupt carbonate film formation. A recent study showed that cation identity can modify carbonate crystal nucleation energetics and precipitate morphology.[169] For example, Cs^+ based electrolytes showed longer device lifetimes compared to electrolytes containing smaller cations like K^+ or Na^+.

An additional method for mitigating carbonate precipitation would be to source protons from organic cations as opposed to water. While promising, this approach adds an additional degree of complexity in that the conjugate bases of organic cations can often also coordinate CO_2 to form complexes, such as the formation of imidazolium-CO_2 adducts. [49] These complexes can then be thermally or electrochemically recycled to release CO_2 and recover the imidazolium cation. [170-172]

Another prominent example of microphase separation is the nucleation, growth, and detachment of bubbles due to generation of gaseous products. For example, researchers are increasingly investigating how the energetics and dynamics of hydrogen bubble formation and detachment from surfaces can influence water electrolysis. [173-176] While double layer effects are in early stages of investigation, work on electrocapillarity suggests that electrolyte composition can play a major role in determining surface energies, [48, 177, 178] which in turn determines the rate of bubble nucleation and residence time of hydrogen bubbles prior to desorption.

Concentrated, correlated electrolytes could provide intriguing opportunities for leveraging both co-ions and counterions to modulate interface properties and microphase separation. For example, study of water-in-salt electrolytes, where water is dissolved into salt to form a single-phase liquid that is predominantly salt, has revealed that the emergence of microphase separation in bulk electrolytes is primarily governed by the properties of anions. [179-182] Hence, we envision that these effects will become more pronounced at electrochemical interfaces and will provide promising avenues for controlling microphase separation phenomena in electrocatalytic processes.

5. OUTLOOK: LEVERAGING ELECTROCATALYTIC REACTIONS TO UNDERSTAND ELECTRIC DOUBLE LAYER FORMATION

We conclude with an overview of how tools and frameworks developed in the electrocatalysis community are opening new opportunities for advancing the frontiers of understanding electric double layer formation in correlated, nanostructured electrolytes.

We envision that reactions with mechanisms that have been extensively characterized by the electrocatalysis community can be used to probe double layers in new electrochemical systems. For example, electrochemical reduction of CO_2 to CO on Ag has ideal characteristics for serving as a probe of interfacial potential gradients, as this reaction involves a low polarity reactant and highly polar intermediate. Hence, the rate of CO_2 electroreduction to CO as a function of electrolyte composition could be used as a sensitive probe of how interfacial potential gradients are altered by electrolyte composition under the large bias that is characteristic of realistic electrocatalytic conditions.

This strategy is enabled by substantial advancements within the electrocatalysis community, which has established tools and protocols for quantifying the CO content of gas streams with exceptional precision, yielded *in situ* and *operando* optical spectroscopy tools for determining interfacial properties, and mapped out plausible reaction pathways via electronic structure calculations. [5]

Further, electric fields have a stronger influence on molecules with large dipole moments, such as CO, than nonpolar molecules, such as hydrogen. Therefore, comparing how reaction kinetics and selectivity for formation of CO and H_2 changes in response to varied electrolyte compositions may provide additional nuance on the role of interfacial electric fields. Such an approach would provide complementary advantages to the surface forces, electrochemical impedance, photoelectron spectroscopy, and other methods discussed above.

Taken together, we envision that using electrocatalytic reactions to study how the double layer changes in dynamic systems can accelerate our understanding of double layers in a variety of fields. Using double layers to understand electrochemical reactions and electrochemical reactions to study the evolution of double layers provides a cyclic approach that can offer new insights into double layers at electrochemical interfaces that promises to extend beyond electrocatalysis and into other important fields, such as batteries and perhaps even biological interfaces.

6. CONCLUSION

Electric double layer properties can strongly influence electrocatalytic activity. Increasing study of how local reaction environments influence reaction kinetics and selectivity has led to the realization that descriptions electrocatalytic activity are often incomplete without specific consideration of electrolyte properties. We remain optimistic that continued work at the intersection of the vibrant fields of catalysis and colloid science shows great promise for revealing additional means of controlling electrocatalytic activity and advancing understanding of electric double layer formation under non-ideal conditions.

Advanced characterization techniques, such as surface forces measurements and interfacial spectroscopy, will shed new light on the role of double layers in electrocatalysis. These approaches will offer novel insights into the influence of ions, ionic correlations, and microphase separation on reaction rates and selectivity. Future work aimed at revealing how electrolytes impact reactivity using model reactions such as CO_2 reduction would uncover double layer design principles that could facilitate electrosynthesis reactions, further bridging our understanding of electric double layers and electrocatalysis. We envision that further scientific exploration at the intersection of electric double layer formation and electrocatalytic activity will offer many new opportunities to pursue a future where electrocatalytic transformations play an integral role in decarbonizing chemical processing and energy use.

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Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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