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Understanding the influence of the electrochemical double-layer on heterogeneous electrochemical reactions

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A detailed understanding of the electrical double layer is key to the optimization of heterogeneous electrochemical reactions. In this work, we provide a brief summary of key experimental and computational studies of three key aspects of the double layer: Firstly, potential-dependent structure of the solvent; secondly, reaction-induced concentration gradients; and finally, the potential-dependent behavior of electrolyte cations and their effect on double layer structure, reaction activity, and selectivity. Studies of the double layer in polymer ion exchange membrane devices are also assessed. Finally, we discuss the importance and implications of the previous literature, and provide recommendations for future topics of study and methodological improvements toward a more complete understanding of the effect of various aspects of the electrical double layer on heterogeneous electrochemical reactions.

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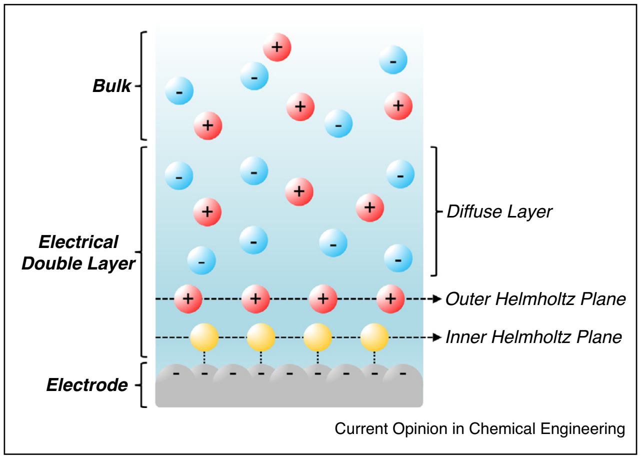
Introduction

Improved understanding of the electrical double layer has been responsible for many significant innovations in electrochemistry, particularly in the development of energy storage devices such as electrochemical pseudocapacitors and supercapacitors [1–3]. However, the effect of various aspects of the electrical double layer on the activity and selectivity of heterogeneous electrochemical reactions, which occur at the electrode–electrolyte interface, remains poorly understood. The structure of the electrochemical interface is typically divided into five distinct regions (Figure 1) [4–7]. First is the electrode itself, where either the current or electrical potential is controlled. Just beyond the electrode is the Helmholtz plane, first described by Helmholtz and later divided into the Inner Helmholtz plane (IHP) and the outer Helmholtz plane (OHP) by Bockris *et al.* [5]. Species that are specifically adsorbed on the electrode surface, including solvents molecules, reactants, products and reaction intermediates, and any other specifically adsorbed molecules or ions on the electrode belong to the IHP. Beyond the IHP, is the OHP, which includes the nearest layer of ions and corresponding solvation shell that are drawn to the electrode via electrostatic forces. Owing to the interaction with the surface, species in the OHP are often referred to as nonspecifically adsorbed ions. The OHP is primarily comprised of ions with an opposite charge of the electrode. For example, and negatively charged electrode will repel anions while attracting cations via electrostatic forces, so that for a negatively charged electrode, the OHP is comprised of electrolyte cations and their solvation shells, and the opposite is true for positively charged electrodes. The diffuse layer, first described by Guoy and Chapman, consists of loosely alternating layers of anions and cations which maintain charge neutrality throughout the double layer, accounting for the exponential decay of the potential away from the electrode [7]. Beyond the diffuse layer is known as the bulk, where the potential of the electrode no longer affects the electrolyte structure.

Despite the widespread acceptance of its importance, significant challenges still exist in studying the effect of changes in the double layer structure on electrochemical reactivity. The presence of the electrolyte complicates many common microscopic and spectroscopic techniques, making them unsuitable for probing electrochemical systems. As a result, computational approaches are attractive; however, explicit modeling of both ions and the solvent make first principles based simulations of the double layer computationally expensive. The effect of the electrolyte is typically approximated using continuum solvent models or other simplifying techniques. In this article, recent developments in both experimental and computational methods for analyzing both the structure and the effect of various double layer properties are briefly reviewed, including the potential-dependent behavior of solvents, current-induced interfacial concentration gradients and

Figure 1



Schematic of the electrical double layer.

their effect on electrokinetics, the effect of nonspecifically adsorbed cations in the OHP on reaction activity and selectivity, and investigations of the interface between the electrode and solid polymer electrolytes. We then provide insights into how these existing studies could inform future experimental design and evaluate key obstacles toward developing a thorough understanding of the effects of the electrical double layer on heterogeneous electrochemical reactions.

Solvent structuring within the double layer

Because the vast majority of electrochemical reactions of interest occur in aqueous environments, the structure of water at the electrode–electrolyte interface is of particular importance. A previous, detailed review of both computational and experimental investigations of water behavior at the electrochemical interface was given by Ito in 2008, including studies using *in situ* infrared spectroscopic and scanning tunneling microscopy [8••]. Of particular interest is the use of attenuated total reflectance surface enhanced infrared absorption spectroscopy (ATR-SEIRAS), in probing the potential dependent orientation of water [9–13]. ATR-SEIRAS is a highly surface-sensitive infrared spectroscopic technique which allows for selective investigation of the electrolyte within 5–10 nm of the electrode surface. Briefly, a spectroelectrochemical cell designed in an ATR configuration, with a thin metal film (~20–50 nm) deposited on the reflecting plane of an internal reflection element. The evanescent wave is amplified by plasmon resonance within the metal film, causing a localized enhancement of the resultant infrared evanescent wave within 5–10 nm of the electrode. Dunwell *et al.* conducted a comprehensive study of potential-dependent water orientation in electrolytes within a wide pH range using ATR-SEIRAS on Au [11]. It was found that at low pH, the H-bonding network of water was increasingly disrupted with increasing electrode potential by specific adsorption of water within the IHP or within the hydration shell of anions in the OHP. Bands associated with electrostatically attracted H_3O^+ were also observed at lower pH (1.4, 4.0, 6.8) at low electrode potentials. Conversely, an additional OH stretching band, which increased in intensity with increasing potential, was assigned to hydroxide in the IHP. This understanding of the pH-dependent behavior of interfacial water and related species could be a key factor in understanding activity differences in the hydrogen evolution (HER) hydrogen oxidation (HOR), oxygen evolution (OER) and oxygen reduction (ORR) reactions between acid and base [14–18]. For example, Ledezma-Yanez *et al.* investigated the potential-dependent orientation of water and propose that the increased ordering of water at high pH at the same RHE potential (lower potential on the SHE scale) causes an additional energy barrier for the HER, resulting in lower activity at high pH than at low pH [19•]. These findings underscore the fact that simply maintaining the same RHE potential is not sufficient to compensate for changes in electrolyte pH. Rather, special consideration should be paid to the structure of the solvent both due to changes in the solvation of different ions (H_3O^+ and corresponding anions versus OH^- and corresponding cations) when examining reactivity changes. Additionally, despite thorough studies of interfacial water behavior, there remains a distinct need for studies of the solvent structure under *operando* conditions beyond the HER/HOR. For example, studies of solvent reorganization during the CO_2 reduction reaction (CO_2RR) could provide key insights into the identity of the proton donor (i.e. H_2O, HCO_3^-, or H_3O^+).

Similar investigations of potential-dependent solvent behavior have also been conducted with room temperature ionic liquids (RTIL) using infrared and sum frequency generation (SFG) spectroscopies [20–23]. RTILs have been demonstrated as attractive family of solvents for electrochemical processes such as CO_2RR, due to their high CO_2 solubility and selectivity toward CO_2RR products over the HER [22]. Anaredy *et al.* probed the time-dependent structuring of RTILs, and found that the ordering of RTILs is significantly different than water in two key aspects: structural equilibration occurs on time scales far longer than typical aqueous electrolytes (30–120 min) and ordering of RTILs persists up to 2 μm from the substrate surface [23]. Additional SFG studies by Baldelli were aimed at probing the potential-dependent behavior of RTILs in the double layer [20,21]. Surprisingly, despite observations of the long range ordering of RTILs, the potential-dependent spectra obtained using CO as a probe molecule suggest that a single molecular layer is sufficient to screen the electric field from the electrode due to the high charge density of the electrolyte, so that the 'double-layer' consists of only a single molecular layer, and the diffuse layer is entirely absent.

The molecular orientation of this single layer is also described, with the imidazolium ring lying more parallel to the surface as the electrode becomes more negatively charged, and standing normal to the positively charged electrode. A detailed understanding of the molecular orientation of RTILs could be necessary toward developing a mechanistic understanding of various electrochemical processes such as the CO_2RR in ionic liquid electrolytes [22].

Reaction-induced concentration gradients in the double layer

Concentration gradients caused by electrochemical reactions have been shown to have a significant impact on reaction kinetics via mass transport limitations. However, these changes are often ignored due to difficulty in the quantification of concentration profiles within the double layer. Concentration gradients of protons (or changes in near-electrode pH) in particular, have a strong impact on electrochemical processes such as HER and HOR, in which 1 proton or hydroxide ion is produced for every electron transferred in the reaction [24]. Katsounaros *et al.* quantified changes in near-electrode pH during cyclic voltammetry between hydrogen evolution and hydrogen oxidation potentials in hydrogen-saturated, unbuffered solutions of pH 1, 4, 7, 10, and 14, as well as in a phosphate buffered solution at pH 7.2 by relating experimentally observed currents to proton concentration via the Nernst–Planck equation and well-defined convection (rotating disk electrode with a rotation rate of 1600 rpm) [25•]. It was found that with current densities up to 1 mA cm^{-2}, near-electrode pH only changes by <1 pH unit in strongly acidic or alkaline environments, while in neutral electrolytes (buffered or unbuffered) near-electrode pH can deviate from the bulk value by >3 pH units. These deviations from bulk pH cause large concentration overpotentials for HER/HOR at intermediate bulk pH values.

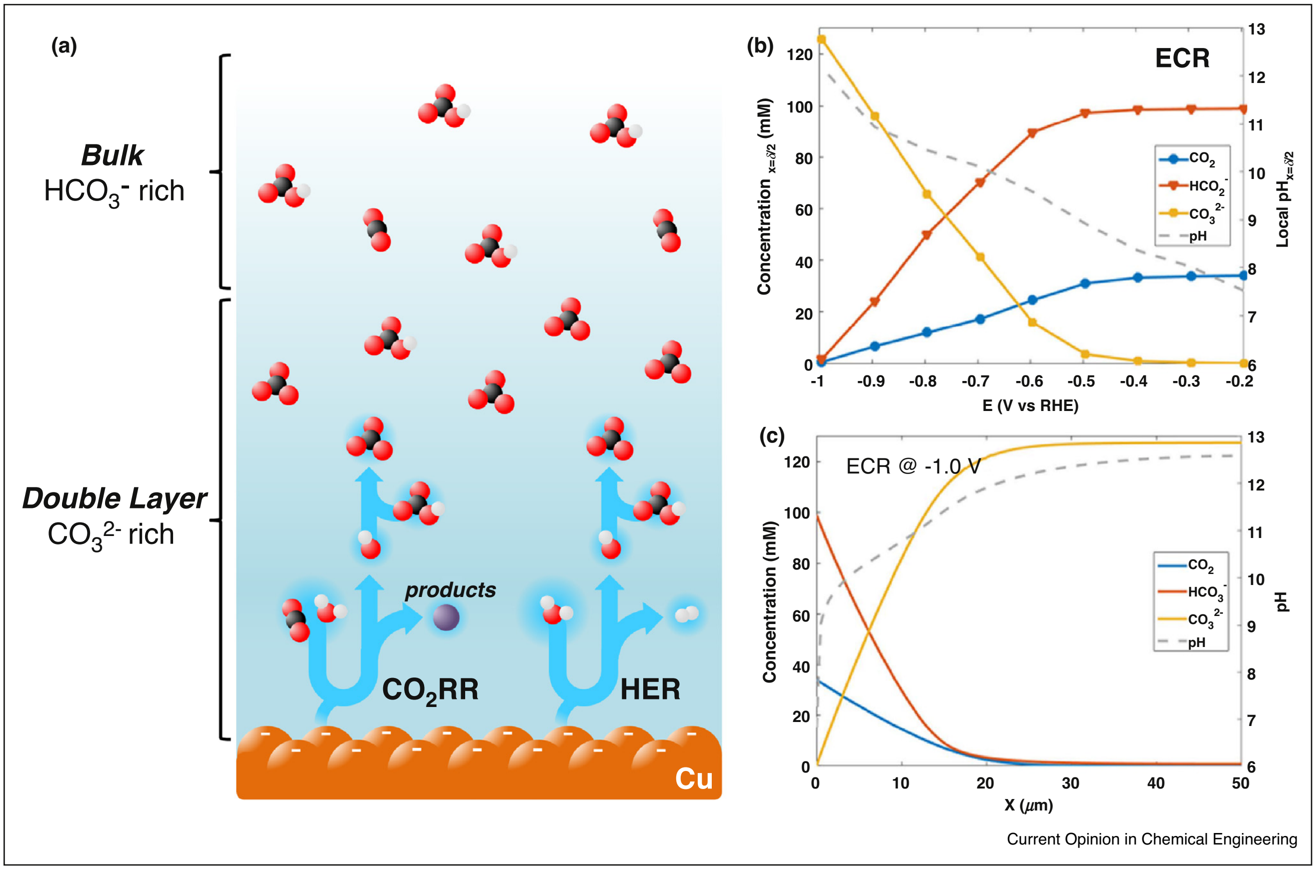
In addition to the HER/HOR, interfacial pH and gradients have been shown to have a strong impact on the activity and selectivity of the CO_2 (CO_2RR) and CO (CORR) reduction reactions. Hori *et al.*, studying the CO_2RR and CORR on Cu in various electrolytes, first observed an increase in CO production during the CO_2RR and an increase in selectivity toward C_2 products during the CORR in less buffered electrolytes [26,27]. They attributed activity and selectivity changes to increases in interfacial pH, which in turn suppressed the HER, increasing desired product selectivity (Figure 2a). Gupta *et al.* later conducted more rigorous simulations of interfacial concentration gradients during the CO_2RR on planar Cu electrodes and predicted that near-electrode pH could increase by >2 units under typical reaction conditions [28]. More recently, Raciti *et al.* coupled reactivity studies with detailed simulations of the interfacial concentrations along Cu nanowires oriented perpendicular to the bulk Cu electrode, and showed that C_2 product selectivity in the CO_2RR is maximized when the near electrode pH is 9–10, so the rate of the HER is suppressed without significant changes to near-electrode CO_2 concentrations [29••]. However, additional increases in overpotential can severely deplete reactant concentration near the electrode, with CO_2 concentration reaching $\sim$0 half-way down the nanowire at –1.0 V versus RHE (Figure 2b,c). In our recent work, we used ATR-SEIRAS to experimentally quantify near-electrode concentrations and pH by monitoring the ratio between carbonate and bicarbonate bands during the CO_2RR on Au, and observed an increase of 1.15 and 0.82 pH dec^{-1} of current density, corresponding to concentration overpotentials of 68 and 48 mV dec^{-1} in unstirred and stirred CO_2-saturated 0.5 M $NaHCO_3$, respectively [11,30]. Moreover, it was found that although CO_2 concentration reached nearly 0 at –0.8 V versus RHE when the electrolyte was unstirred. Meanwhile, no appreciable reduction in the CO_2 concentration near the electrode surface was detected at a potential as low as –0.9 V versus RHE when the electrolyte was stirred using a magnetic stir bar at 1800 rpm. This work provides a framework for experimental quantification of near-electrode concentrations, and the extension of this technique to other reactions of interest and electrode morphologies (particularly nanostructured electrodes) will be a key step in developing a more complete understanding of the electrical double layer.

In light of both computational and direct experimental observation of significant near-electrode concentration and pH gradients, special care should be taken to consider these gradients in the interpretation of existing electrokinetic data and in the design of new electrokinetic experiments. The demonstrated interfacial gradients can cause significant concentration overpotentials with increasing current density, so that kinetic studies must be conducted in a sufficiently low current range such that concentration gradients are minimized. Furthermore, quantification of near electrode concentrations under more controlled reaction conditions such as in the use of rotating disk electrodes and flow cell configurations are necessary for the optimization of more developed electrochemical systems such as electrolyzers, fuel cells, and flow cells for the nitrogen and CO_2 chemistries.

The potential-dependent distribution of ionic species in the double layer

Electrolyte cations have been demonstrated to have a significant impact on not only the rate, but also the selectivity of many important electrochemical processes [16,26,32,33]. Indeed, ORR, HOR, and methanol oxidation reaction on Pt electrodes each showed increased activity with increasing size of alkali cations from Li^+ to Cs^+ in alkaline electrolytes [16]. Strmcnik *et al.* explained the difference in activities based on the hydration of different alkali cations, where Li^+ and Na^+ were

Figure 2



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(a) Scheme of reaction-driven concentration gradients evolving during the CO_2 reduction reaction. **(b)** Concentration of chemical species at half-way down electrochemically reduced (ECR) Cu nanowires depending on the electrode potential. **(c)** Distribution of species through the boundary layer at –1 V for the ECR Cu nanowires. (b) and (c) were adapted from Ref. [29••].

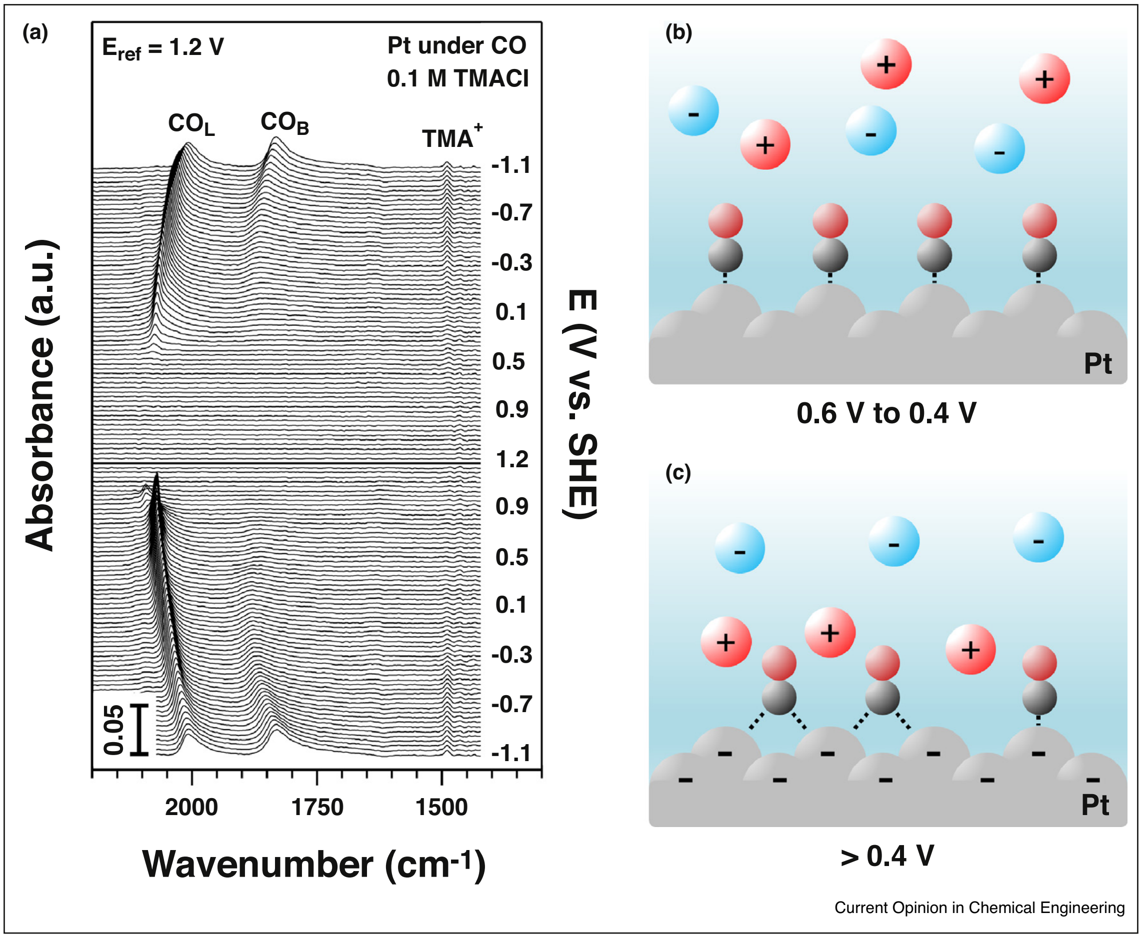
partially solvated not only by water, but by adsorbed hydroxide in the IHP. The partial solvation by IHP hydroxide was proposed to cause a site-blocking effect, prevent reactants from reaching active sites on the electrode. Conversely, K^+ and Cs^+ were proposed to be more fully solvated by water in the OHP, and are therefore less prone to blocking of electrochemical active sites. Similarly, both Mills *et al.* and Matanovic *et al.* proposed that specifically adsorbed alkali cations in the IHP are able to block hydrogen adsorption, thereby limiting the HER/HOR on Pt(111), whereas on Pt(110) and Pt(100), cations and hydrogen adsorb on different sites, thereby minimizing the impact of cations on these facets [34,35]. Later computational work by McCrum *et al.* however, suggested that although specific adsorption of K^+ is possible, it does not significantly impact hydrogen adsorption. Rather, The interaction between K^+ and adsorbed OH weakens the binding energy of OH, thereby impacting alkaline HER/HOR rates [36]. Subsequent combined experimental and computational work on Pt(553) also suggests that alkali cations weaken OH binding on step sites, as evidenced by a shift in the hydrogen underpotential deposition peaks in CV above pH 3 [37].

In addition to activity changes, Murata *et al.* first demonstrated the impact of alkali cations on the selectivity of the CO_2RR on Cu electrodes, with larger cations favoring C_2 over C_1 reduction products [32]. Selectivity changes were explained again by differences in the hydration energy of the cations leading to differences in the potential of the OHP for each cation. Subsequent computational work suggested that specifically adsorbed K^+ is able to stabilize reaction intermediates, promoting C–C coupling through the *CHO intermediate, leading to an increase in C_2 product selectivity [38]. Conversely, based on their own computational results, Singh *et al.* proposed that the pK_a of water in the hydration shell decreasing with increasing cation size, allowing larger cations (K^+, Rb^+, and Cs^+) to act as more effective pH buffers, leading to a relative increase in CO_2 concentration near the electrode, thereby explaining the observed changes in product activity and selectivity [39].

In order to investigate the effects of cations experimentally, Dunwell *et al.* used ATR-SEIRAS to probe the impact of cations on the adsorption of an adsorbed CO probe molecule on Pt and Au electrodes (Figure 3a) [40••]. It was found that both alkali and small organic cations were able to displace CO from a linear-bound configuration (CO_L) to a bridge-bonded configuration (CO_B) on Pt as cations in the OHP were drawn closer to the electrode with decreasing potential (Figure 3b,c). It should be noted that a lack of Stark tuning of the near electrode tetramethylammonium (TMA^+) cation suggests that no specific adsorption of TMA^+ occurs in the potential range studied. Interestingly, it was found that the degree of displacement increased with cation size, where Li^+ exhibited the lowest CO_B to CO_L ratio, followed by Na^+ and K^+. This trend suggests that, contrary to the aforementioned computational work, larger cations may interact more strongly with adsorbates in the IHP. Additionally, it was observed that on Au electrodes, cations are able to displace the weakly bound CO_L off of the electrode completely at potentials below –0.4 V versus SHE in 0.1 M $KClO_4$. Similarly, in ATR-SEIRAS investigations of the CO_2RR on Au, Na^+ has been shown to be able to displace CO_L from the Au surface below 0.0 V versus RHE in CO-saturated 0.5 M $NaHCO_3$ [40••]. The observation that the coverage of adsorbed CO under typical reaction conditions is ~0, is a key finding in understanding the mechanism of the CO_2RR on Au, as other experimental techniques, such as Tafel analysis, depend on the total surface coverage of the electrode during reaction [41].

The results of computational, reactivity, and spectroscopic studies all suggest that although ions in the electrolyte may not participate directly in the reaction, the interactions between ions, the electrode surface, and adsorbates can have a strong impact on both activity and selectivity of heterogeneous electrochemical reactions. Moreover, when comparing literature data, it is important to note differences in the electrolyte composition, as some reactivity

Figure 3



(a) ATR-SEIRA spectra (4 cm^{-1} resolution, 8 co-added scans) during anodic and cathodic scans at a scan rate of 5 mV s^{-1} from –1.1 V to 1.2 V versus SHE on chemically deposited Pt film electrode in 0.1 m TMACl under continuous CO purge. Reference spectrum collected at 1.2 V versus SHE. Scheme of cation behavior on Pt film electrode during the experiment as in (a) between **(b)** 0.4 and 0.6 V and **(c)** below 0.4 V versus SHE. (a) was adapted from Ref. [40••].

differences may be easily resolved by considering the effect of ions. Finally, future work should leverage the growing understanding of the effect of ions in order to further optimize reaction activity and selectivity, as demonstrated in the CO_2RR on Cu electrodes. Despite recent advancements, two key questions remain. First, what is the nature of cation adsorption? With the apparent contradiction between existing spectroscopic and theoretical work, additional studies are necessary to understand the degree to which specific adsorption of cations occur. Second, more robust spectroscopic studies of reactions under *operando* conditions are required to understand the mechanism of changing activity and selectivity, for example, the CO_2RR on Cu electrodes using different cations.

Venture into electrode–polymer electrolyte interfaces

With the rapid growth of polymer ion exchange membrane devices such as fuel cells, electrolyzers, and flow cells for improved transport for various electrochemical reactions, it is imperative that we understand how the interaction between polymer electrolytes and electrodes affect reactivity. Of particular interest is the potential-dependent behavior or anionic or cationic functional groups in proton and hydroxide exchange membranes, respectively. For example, Ong *et al.* studied the effect of various quaternary ammonium cations (common functional groups in hydroxide exchange membranes) on the rate of the ORR on Pt rotating disk electrodes in alkaline media [42]. It was observed that although smaller organic cations such as tetramethylammonium had no effect on activity, larger cations such as benzyltrimethylammonium and 1-benzyl-3-methylimidazolium caused a roughly threefold decrease in exchange current density due to site-blocking by aromatic ring-containing organic cations. Although Woodroof *et al.* demonstrated no effect on HOR activity in liquid versus polymer base electrolytes using a proprietary commercial membrane and ionomer (Tokuyama A-201 and AS-4, respectively) [43], it is not well-understood how hydroxide exchange membranes with other functional groups such as sulfonates, phosphoniums, quaternary ammoniums, or imidazoliums affect electrode surface mediated reactions.

To understand the nature of interactions between polymer electrolytes and electrodes, Kunimatsu *et al.* used ATR-SEIRAS to probe the potential-dependent behavior of Nafion membranes near the electrode surface [44,45• ,46]. Interestingly, it was found that the side chains in the Nafion membrane were sufficiently flexible to allow sulfonium groups to freely respond to changes in electrode potential, similar to the behavior of free anions in aqueous electrolytes [44]. Subsequent work clearly showed specific adsorption of the sulfonate group with increasing potential, and a corresponding decrease in interfacial water bands due to displacement by the Nafion functional group and corresponding ether side chain [45•]. Although current studies focus on Nafion and other proton exchange membrane interfaces [47,48], the methods outlined by these works can and should be extended to studies of alkaline systems with hydroxide exchange membranes. In particular, investigations of the relative binding strength to the electrode between various cationic functional groups and reaction intermediates could provide key insight into the optimization of the triple-phase boundary in fuel cells, electrolyzers, and other polymer ion exchange membrane devices.

Outlook

Recent developments and improvements in both computational methods for modeling the electrical double layer and *in situ* spectroscopic techniques allow for more detailed investigations of both the structure and impact of changes in the double layer than previously possible. In turn, these insights provide a more thorough mechanistic understanding of various important electrochemical processes. In particular, improved understanding of both interfacial concentration and pH gradients, as well as cation effects paves the way for the manipulation of these factors to improve both the activity and selectivity of important electrochemical processes such as the HER/HOR and the CO_2RR. However, many key questions still remain. With respect to solvent structuring and potential dependent orientation: How is the solvent structure at the electrochemical interface impacted by electrochemical reactions? How does solvent orientation affect the thermodynamics of the reaction? With respect to interfacial concentration gradients: To what degree do nanostructured electrodes, in particular nanoporous electrodes, exacerbate concentration gradients? How do different device configurations (i.e. polymer ion exchange membrane flow cells, rotating disk electrodes, unstirred planar electrodes) affect interfacial concentration gradients? Furthermore, future studies must consider resultant concentration overpotentials, particularly in mechanistic kinetic investigations. With respect to the potential-dependent distribution of ions in the double layer: are the interactions between ions and the electrode simply physical, or does charge transfer occur? What is the mechanism for activity and selectivity changes with different supporting electrolyte ions? Finally, with respect to non-traditional double layer studies of the polymer–electrode interface: How does the interaction between the electrode and polymer electrolyte change with potential? How do these changes affect activity and selectivity versus traditional electrolytes? We believe that ATR-SEIRAS will be an invaluable tool for answering these key mechanistic questions. Looking forward, improving the time resolution of *in situ/operando* spectroscopic techniques will be key to understanding dynamic interfacial changes, which could lead to further mechanistic understanding of and potential improvement of electrochemical reactions via techniques such as pulsed electrolysis.

Conflict of interest statement

Nothing declared.

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•• of outstanding interest

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