Role of near-surface environment in tuning electrochemical CO2 reduction reaction and H2 evolution reaction

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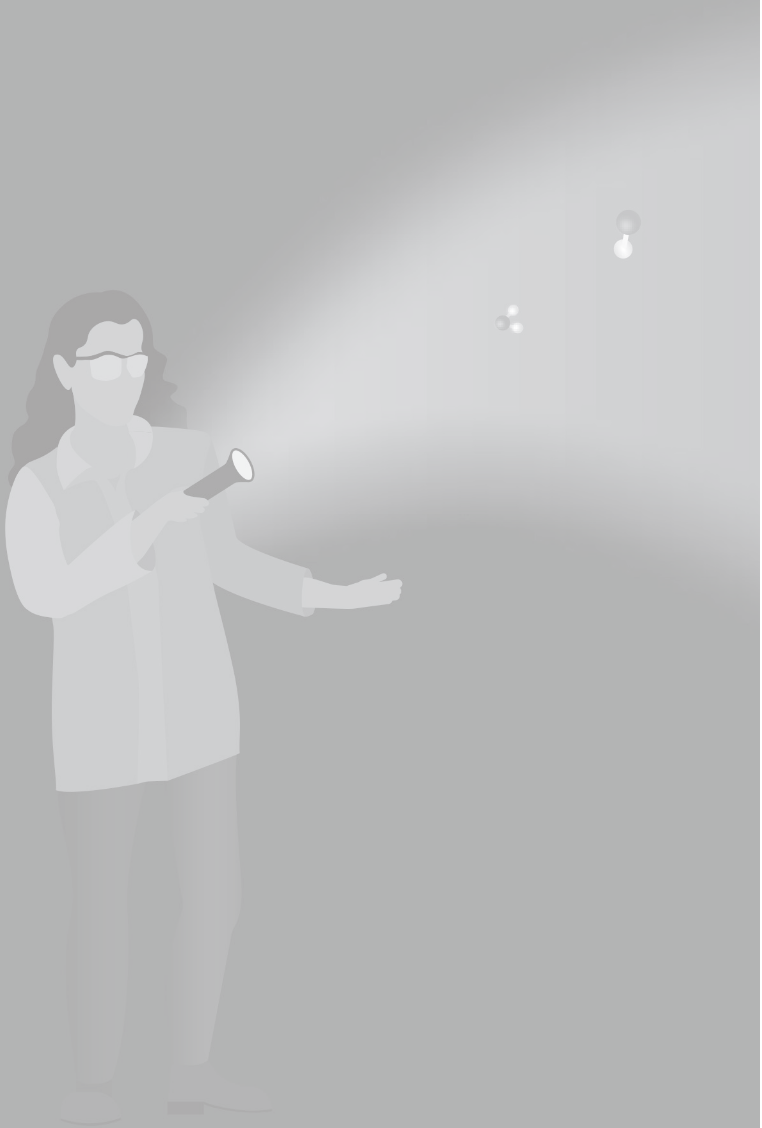

Chapter 1

Introduction

1.1. General Introduction

As the transition to renewable energy becomes inevitable, solving its intermittency problem is crucial if we wish to achieve carbon neutrality. Considering the timeframe specified by most international climate agreements (including Kyoto Protocol and Paris climate agreement), this issue is especially pressing.[1-2] This means that we need robust technologies that can store excess renewable electricity, thereby allowing us to deploy it on demand in energy lean periods.[3] For instance, electric energy can be stored in a battery[4] or it can be used to drive non-spontaneous chemical reactions that generate energy rich molecules such as fuels and energy carriers.[5-9] The latter process is similar to rolling a stone uphill and increasing its potential energy. This potential energy can then be converted into kinetic energy at a later point by simply letting the stone fall. Analogously, energy can be stored via the electrochemical reduction/hydrogenation of molecules and extracted via their oxidation (either by direct combustion or electrochemically) when required. In principle, the rate and efficiency of such an electrochemical conversion depends on the kinetic barrier of the reaction, which can be surmounted by employing appropriate electrocatalysts.

Broadly, electrocatalysts can be divided into two sub-categories, homogeneous and heterogeneous. As the name suggests, homogeneous electrocatalysts facilitate redox mediation in the solution phase by first undergoing an electron transfer reaction (at the electrode) followed by the relevant redox reaction with the substrate molecule in the solution phase. In general, these catalysts are designed to mimic naturally occurring redox enzymes (such as hydrogenases and nitrogenases) as these biological catalysts are able to achieve very high conversion rates, near the thermodynamic equilibrium potential of their respective reactions.[10-11] Hence, similar to the enzymes, most synthetic homogeneous catalysts also feature metal centers (such as Fe and Ni).[12-13] The latter are chemically tuned via suitable ligand design to achieve an optimal redox potential for the electron transfer reaction and the accompanying molecular rearrangement. However, the activity and the overall stability of these catalysts remains an issue, even in the cases where the structure of the synthetic analogues is nearly identical to that of the active sites of the enzyme.[7-8]

On the other hand, heterogenous electrocatalysis concerns itself with electrochemical reactions happening at the electrochemical interface via the direct movement of electrons/charge through different phases.[14] That is, the charge carrier is transferred between the solid electrode and the (liquid) electrolyte that contains the substrate molecules. Here, unlike homogeneous electrocatalysis, the electrode surface facilitates the molecular rearrangement that accompanies the charge transfer. Hence, the electrode surface is not just an inert supplier of electrons but participates actively in the reaction. Most well-known applications of electrocatalysis such as fuel cells, chlor-alkali electrolysers and water electrolysis are all forms of heterogeneous electrocatalysis, where multi-step electron transfer reactions take place at an electrode surface. The rate of such reactions is determined by the electrochemical potential gradient at the interface which is dependent on both the nature of the catalyst material and the identity of the electrolyte.[14] Hence, the key to the optimization of any heterogeneous electrocatalytic process lies in understanding and tuning the electrode-electrolyte interface.[5, 14-15]

Heterogeneous electrocatalysis will be the main topic of our discussion. With this chapter we will first introduce some concepts related to heterogeneous electrocatalysis, henceforth referred to as electrocatalysis. Afterwards we will present a more specific discussion on the role of the electrode-electrolyte interface in tuning two important electrocatalytic reactions, namely, CO_2 reduction reaction (CO2RR) and hydrogen evolution reaction (HER). These reactions will form the crux of the rest of the thesis.

1.2. Outer-sphere vs inner-sphere electron transfer

Electron transfer reactions at the electrode surface can be further classified as either outer-sphere or inner-sphere events. In outer-sphere reactions, the electron transfer between the electrode surface and the reactant molecule occurs via tunneling through a solvent layer. It is assumed that in these electron transfer events the geometry of the reactant molecules remains unperturbed. The change of the charge of the reactant causes a reorganization of its solvation shell only.[16] Marcus theory describes quite well the kinetics of an outer-sphere electron transfer reaction at a molecular level and according to this theory the rate of the reaction increases approximately exponentially with the increasing thermodynamic driving force (applied overpotential; $\eta = E - E_o$) for the reaction.[17-18] The theory predicts that the maximum rate for the reaction will be obtained when the thermodynamic driving force approaches the reorganization energy of the solvation shell.[17-18] Since, an outer sphere reaction assumes that there is no direct chemical interaction between the electrode and the electroactive species, the rate constant for such a reaction is expected to be independent of the electrode material. The theory for outer-sphere electron transfer reactions is well developed and can be derived in a more general way without consideration for any specific adsorption effects.

On the other hand, in an inner-sphere reaction, the electron transfer is accompanied by changes in the geometry of the reactant/intermediate molecules via direct chemical interaction between the electroactive species and the electrode surface.[16] Hence, in an inner sphere electron transfer reaction, the rate constants are sensitive to both the identity as well as the surface structure of the catalysts.[19-20] And even though the molecular considerations made in the Marcus theory are only applicable to an outer-sphere electron transfer, it is often applied to model inner-sphere electron transfer events, as the molecular factors that control the kinetics of the latter events remain poorly understood.[21]

Another important phenomenological model that describes the kinetics of the electron transfer at a macroscopic level is the Butler-Volmer expression.[16, 22-23] This empirical expression explains the observed exponential dependence of the reaction rate on the applied overpotential by assuming that the activation energy of the reaction is linearly dependent on the applied overpotential ($\Delta G^{\#} = \Delta G_0^{\#} - \alpha F\eta$). For a single electron transfer, the final Butler-Volmer expression gives the overall current density (j) for an electron transfer reaction in terms of the contributions from the forward and the backward reaction (eqn.1):

$$j = j_o\left(e^{\left(\frac{\alpha F\eta}{RT}\right)} - e^{\left(\frac{-(1-\alpha)F\eta}{RT}\right)}\right) \qquad (1)$$

where *F, R, T* represent the Faraday’s constant, the ideal gas constant and the temperature, respectively. j_o is the standard exchange current density, which represents the intrinsic activation barrier for a given reaction, such that a larger j_o means that the charge transfer step has a smaller activation barrier. α is an empirical proportionality constant (called the transfer coefficient), which varies between 0 and 1 and in doing so, gives the symmetry of the energy barrier for the reaction in the forward and backward direction. In principle, in going from an outer sphere to an inner sphere electron transfer reaction the energy barrier becomes more asymmetric, thus resulting in the deviation from the assumed value of 0.5 for α.[16, 24-25] Moreover, for $|\eta|$>>RT/F the Butler-Volmer expression reduces to the well-known Tafel equation: η = a+b·$\log j$ where b = 2.303RT/αF gives the Tafel slope.[16, 26] This way of plotting the current-overpotential relationship is called Tafel analysis and it is often used to determine the operative mechanism for a multi-electron transfer reaction. In principle, the Butler-Volmer expression can be used to fit both outer and inner sphere electron transfer reactions, where in the former case j_o will vary only with the concentration of the species in the bulk while in the latter case it should also depend on the catalyst material (among other things). However, similar to the Marcus theory, this model suffers from certain limitations which also stem from the lack of consideration for the near-surface environment at the electrode-electrolyte interface. One such limitation arises due to changes in the near-surface concentration of the electroactive species with respect to the bulk.[16, 27] These concentration gradients can result in unreliable Tafel analysis as the applied overpotential is no longer a true measure of the activation energy of the reaction and it has additional contributions from mass transport effects. Moreover, electrostatic and chemical interactions at the electrode-electrolyte interface are also neglected within the Butler-Volmer model, both of which require further corrections.[28-29]

Hence, in order to completely describe the kinetics of electrocatalytic reactions, or more specifically inner-sphere electrocatalytic reactions, it is important to look more closely at the electrode-electrolyte interface.

1.3. Electrostatic and chemical effects of adsorption in electrocatalysis

The idea that the electric double layer structure affects the kinetics of electrocatalytic reactions was put forward already in the early 1930s by Frumkin.[16, 28] In his work, Frumkin argued that in the absence of any specific ion adsorption, the reaction plane of a heterogeneous reaction will be the outer-Helmholtz plane of the electric double layer. Hence, the effective electrode potential that will affect the kinetics of an electrocatalytic reaction is not the electrochemical potential E at the electrode surface but instead $E - \varphi_{O.H.P.}$ i.e. the potential in the outer-Helmholtz plane. Additionally, he also argued that while considering the rate of a reaction the concentration of the electroactive species in the outer-Helmholtz plane has to be considered, instead of its bulk concentration. However, the former responds to the changing potential gradient within the double layer. Accounting for these double layer effects is the so called Frumkin correction, that addresses some of the experimental anomalies that are not accounted for by the previously described models. For instance, the dependence of the heterogeneous rate constant on the identity and the concentration of the supporting electrolyte. However, in most cases, this is still not sufficient.[30] That is, for most electrocatalytic reactions the chemical effects of adsorption at the interface also need to be considered in addition to the electrostatic effects.[29-30] Only then the true role of the electrode-electrolyte interface in tuning the kinetics of a reaction can be captured.

Specific adsorption at the interface has profound impact on the kinetics of an electrode reaction.[29, 31] One of the effects is the change is in the position of the reaction plane itself which changes from the outer-Helmholtz plane (O.H.P.) to the inner-Helmholtz plane (I.H.P) in the event of specific ion adsorption of the electroactive species. Consequently, the effective potential that drives a reaction also changes from $E - \varphi_{O.H.P.}$ to $E - \varphi_{I.H.P.}$. Moreover, when an electroinactive species (i.e. supporting electrolyte) adsorbs at the interface instead of the reactive species, the potential gradient within the double layer is still impacted, even though the reaction plane itself does not shift. In this event the required Frumkin correction for the system changes. However, even more important than these electrostatic effects are the surface coverage effects at the electrode surface associated with surface-adsorbate interactions. These effects alter both the rate and the mechanism of an electrode reaction and establish a direct correlation between electrocatalysis and heterogeneous catalysis.[32]

Adsorption in electrocatalysis proceeds via the discharge of an ionic species at the electrode surface to form a neutral species, which is bound to the surface via a direct chemical bond. This neutral species has a certain coverage (θ) at the electrode surface and its adsorption behaviour can generally be modelled by using modified versions of the well-known adsorption isotherms that are generally employed in heterogeneous catalysis (such as Langmuir, Frumkin and Temkin isotherms).[16] These modifications essentially account for the fact that in electrocatalysis the surface coverage θ of an adsorbed species also depends on the applied electrode potential. Hence, in electrochemistry, an adsorption isotherm gives the relationship between the coverage of the adsorbed species, the activity of the species in the bulk of the electrolyte and the electrode potential, at a constant temperature. For a general electrochemical reaction involving adsorption: $X_{sol}^{+} + e^{-} + M \overset{K}{\leftrightarrow} X - M$, if we assume a Langmuir type adsorption (no lateral interactions and no surface heterogeneity), we can write (eqn. 2):

$$\frac{\theta}{1-\theta}=\frac{\Gamma_X}{\Gamma_{max}-\Gamma_X}=K_{ads}\,[X^+_{sol}]\,e^{\left(\frac{-\Delta G^o_{ads}(E_o)}{RT}\right)}\,e^{\left(\frac{-F(E-E_o)}{RT}\right)}\approx K'_{ads}\,[X^+_{sol}]\,e^{\left(\frac{-F(E-E_o)}{RT}\right)} \qquad (2)$$

where Γ_X is the surface concentration of species X (in mol cm^{-2}), Γ_{max} is the maximum (saturation) surface concentration, K_{ads} is the equilibrium constant of adsorption, $[X^+_{sol}]$ is the bulk concentration of X and $\Delta G^o_{ads}(E_o)$ is the standard Gibbs energy of adsorption at a fixed potential E_o (generally $E_o = 0$ against an arbitrary reference electrode) and K'_{ads} is the apparent equilibrium constant of adsorption $\left(K'_{ads} = K_{ads}\,e^{\left(\frac{-\Delta G^o_{ads}(E_o)}{RT}\right)}\right)$.

The $\Delta G^o_{ads}(E_o)$ term in eqn. 2 expresses the ability of a given catalyst material to adsorb species X and it is generally used to compare the activity of different materials for a given reaction involving the same reaction intermediate.[33-34] This follows directly from Brønsted-Evans-Polyani relationship which states that the kinetics of a reaction involving adsorption/desorption i.e. its activation energy ($\Delta G^\#$) is linearly related to the thermodynamics of adsorption/desorption at the catalyst surface i.e. the standard Gibbs free energy of adsorption (ΔG^o_{ads}).[35-36] Hence, an increase in the adsorption energy results in a proportional decrease in the activation energy of the reaction. This in-turn implies that at a fixed overpotential, the rate constant of an electron transfer reaction involving adsorption will increase with increasing adsorption energy:

$$k_o \propto j_o \propto e^{\left(\frac{-\beta\Delta G^o_{ads}(E_o)}{RT}\right)} \qquad (3)$$

In electrocatalysis, this is often represented by lnj_o vs ΔG^o_{ads} or lnj_o vs lnK'_{ads} plots where lnj_o represents the activation barrier for the reaction.[33-34, 37-39] These plots generally take a curved shape otherwise known as the volcano relationship which signifies that there is an optimal adsorption energy for a reaction intermediate that results in optimal activity for that reaction. If the adsorption energy increases beyond this optimal value, it results in the over-stabilization of the adsorbed intermediate at the catalyst surface, thereby resulting in a situation in which the desorption step of the reaction becomes rate limiting. This observation harkens back to the well-known Sabatier principle of heterogeneous catalysis which states that optimal catalytic activity is achieved when the catalyst-reactant interaction is neither too weak nor too strong.[40] Essentially, this means that with increasing adsorption energy, as the activation barrier for the reaction decreases, there is a simultaneous increase in the surface coverage of the reactive intermediate at the electrode surface. This leads to the "blocking" of the active sites at the catalyst surface, thereby resulting in a volcano relationship between the activity and the adsorption energy. This can be modelled in the kinetic eqns. for the adsorption step by accounting for the slower rate of adsorption at X covered sites of the catalyst surface (θ) compared to the pristine sites (1-θ).

We note here that another important implication of the surface-adsorbate interactions described above is the effective potential dependence of the heterogeneous rate constant itself.[29, 41] It was first elucidated by Parsons by introducing an activity coefficient term for the surface bound transition state of the reaction (inspired by Eyring).[29] Parsons showed that this activity coefficient is related to the potential dependent surface coverage θ term. This in-turn results in a potential dependence of the heterogeneous rate constant and in doing so, shows a better agreement with the experimental data than the Frumkin modified Butler-Volmer expression.[30]

The fundamental insights on how the surface-adsorbate interactions shape the electrode-electrolyte interface, as discussed above, have not only shaped the laws and theories of electrocatalysis but they have also assisted in understanding the kinetic behaviour of different electrochemical reactions, both actively and retroactively. Moreover, these insights have also led to the recognition of an important activity descriptor, namely, adsorption free energy of reaction intermediates, that has long acted as the central parameter for discerning and tailoring electrocatalytic behaviour. It has helped in understanding the observed catalytic trends (Volcano plots) for important electrochemical reactions such as HER and at the same time it has also assisted in the rational synthesis of new catalytic materials.[37, 39, 42-43]

However, even though these insights have been crucial to the theoretical and practical knowledge of electrode reactions, gaps remain in our molecular level understanding of the near-surface reaction environment.[44-47] This is also reflected by the fact that often times additional descriptors/parameters are required to fully capture the reaction kinetics across different electrode-electrolyte combinations, especially for more complex reactions. In the next sections we will discuss some of these descriptors/parameters, specifically for the case of CO2RR and HER, and show that the kinetics of electrocatalytic reactions can be altered by a myriad of additional effects that go beyond the realm of adsorption.

1.4. Electrochemical CO_2 reduction reaction: an overview

Electrochemical reduction of CO_2 into value added products, such as CO, formate, methane, ethylene and alcohols, provides a unique opportunity to close the anthropogenic CO_2 cycle while solving the intermittency issue of renewable electricity.[8, 48] This is because electrochemical reduction of CO_2 offers the possibility of storing renewable electricity as infrastructure friendly carbon-based fuels, that are easy to store and transport. One of the most straightforward strategies to do this is to carry out electrochemical CO_2 reduction reaction (CO2RR) in the aqueous media, as water can act as a continuous source of protons for the reaction. However, at present, many challenges remain that need to be resolved in order to make this process economically viable. Most of these challenges arise due to issues related with low energy efficiency and poor product selectivity of CO2RR, both of which are partially related to the fact that a complex reaction network has to be navigated in order to achieve a desired CO2RR product, especially in the aqueous media. This reaction inherently has a bad selectivity as it often leads to concurrent C1, C2 and in some cases even C3 products, due to the comparable equilibrium potentials of the different reaction pathways.[49-50] Moreover, the low energy efficiency of this process also stems from the fact that in aqueous electrolytes CO2RR is inevitably accompanied by a concomitant hydrogen evolution reaction (HER) which is kinetically more facile than the multi-electron reduction of CO_2.[51-52] HER can also be detrimental towards certain CO2RR products as it can influence the electrolyte composition at the electrode-electrolyte interface. More specifically, by tuning the proton availability that affects the reaction pathways of CO2RR.[52] Hence, significant efforts have been put towards understanding the reaction mechanism of CO2RR on the surface of different catalysts, so that key reaction intermediates for the different reaction products can be identified, and novel catalysts with optimal binding energies can be synthesized. In this respect, Hori and coworkers did some of the most seminal work in the late 1980s.[53-57] They identified different classes of metallic catalysts for obtaining different CO2RR products, based on how the electronic properties of the metals influence the species binding energies. This prompted a lot of follow-up research,[50, 58-60] both practical and theoretical, towards the development of optimized catalytic materials by following the broad template outlined by Hori and coworkers. However, CO2RR activities thus obtained have not shown much improvement. One reason for this is the existence of linear scaling relationships for the binding energy of different reaction intermediates associated with different CO2RR reaction pathways.[52, 61] Consequently, any changes in the electronic properties of the catalysts lead to simultaneous modification of the binding energies for different possible reaction pathways. Thus, making it difficult to obtain optimal selectivity towards one desired product. Moreover, while a lot of focus has been put on the optimization of CO2RR on a given catalyst surface, studies on understanding and selectively suppressing the competing HER reaction under the conditions of CO2RR have been very limited.[62-65] This has contributed to the low energy efficiency and Faradaic selectivity for CO2RR on the surface of most new catalysts that have been synthesized by solely taking the adsorption energies of CO2RR intermediates into account.

Recently, it has been recognized that in addition to the catalyst material, the electrolytes employed for CO2RR also have a profound impact on the activity/selectivity of this reaction.[64-69] This is because the electrolyte identity can tune the near-surface reaction environment both by altering the structure/composition of the electric double layer and by impacting the local dynamic equilibria of CO_2 (aq.) and other reacting species (HCO_3^-, H_3O^+ and H_2O) in the electrolyte. Thus, going beyond the adsorption-based activity descriptors and understanding the role of electrolyte properties (such as cation identity, anion identity, local electrolyte pH and solvent identity) in tuning CO2RR can be a viable strategy for boosting the energy efficiency as well as the product selectivity of this reaction.[70] In the next section, we will discuss the possibilities offered by one such electrolyte parameter, namely, electrolyte pH, in tuning the CO2RR activity.

1.4.1. pH effect on CO2RR

It is well known that electrolyte pH has a profound impact on the kinetics of different CO2RR pathways.[64, 68-69, 71-72] Depending on the rate determining step (RDS) for a certain CO2RR product i.e. whether it involves a proton coupled electron transfer (PCET) or simply an electron transfer (ET), it can either be (bulk) pH dependent or independent. Thus, if we consider the most widely accepted RDS for different CO2RR products:

Carbon monoxide: $CO_2(aq.) + e^- \rightarrow CO_2^{\delta -}{}_{ads}$ (4)

Methane: $CO_{ads} + H^+ + e^- \rightarrow CHO_{ads}$ (5)

Ethylene, Ethanol: $CO_{ads} + CO_{ads}/CHO_{ads} \rightarrow OCCO_{ads}/OCCHO_{ads}$ (6)

The reaction in eqn. 5 is an example of a reaction that is dependent on the bulk pH, whereas the reactions in eqns. 4 and 6 are independent of electrolyte pH. That is, the Butler-Volmer eqn. for these reactions will either include the term for bulk proton concentration or not. This can be exploited to tune the selectivity towards certain products by changing the bulk pH or the buffer strength of the electrolyte. In fact, Mul and coworkers reported that by optimizing the electrolyte pH they could achieve ethylene formation with high selectivity (up to 44%) and suppress methane formation (around 2%) on rough Cu electrodes.[73] Moreover, this strategy has also been employed with gas diffusion electrode set-ups to carry out CO2RR in alkaline electrolysers, where very high selectivity for ethylene (up to 69%) could be obtained.[74-77]

However, beyond these bulk pH effects, the local changes in the electrolyte pH can also affect CO2RR selectivity by tuning the concentration of different reactive species near the electrode-electrolyte interface.[67-68, 78] During CO2RR in the aqueous media, the local pH becomes more alkaline than the bulk due to the constant generation of OH^- ions near the surface during CO2RR (for example: $CO_2 + 2e^- + H_2O \rightarrow CO + 2OH^-$) and the competing HER ($H_2O + 2e^- \rightarrow H_2 + 2OH^-$) reaction. These changes in the local pH can directly impact the kinetics of the reactions that are implicitly dependent on the electrolyte pH (as described above). In addition to these effects, local pH changes can also impact the reaction kinetics by influencing the local concentration gradients for the different reactive species at the electrode surface. It follows that any changes in the local electrolyte pH trigger corresponding changes in the homogeneous equilibria between CO_2 (aq.), HCO_3^- and CO_3^{2-} species that are present in the electrolyte:

$CO_2\,(aq.) + OH^- \leftrightarrow HCO_3^-$ (7)

$$HCO_3^- + OH^- \leftrightarrow CO_3^{2-} + H_2O \qquad (8)$$

which results in certain concentration gradients for these species that can have a huge impact on the partial current densities of different CO2RR products as well as H_2 formation, the side product due to HER. In principle, the homogeneous consumption of CO_2 (eqn. 7), as triggered by the increasing local pH at the surface can result in the suppression of CO2RR due to increasing mass transport limitations for the reaction. Hence, changes in the buffering capacity of the electrolyte via bicarbonate concentration changes, CO_2 partial pressure changes as well as by the introduction of other buffering ions, can all contribute to the enhancement/suppression of CO2RR by changing the local CO_2 (aq.) concentration.[63, 79] Moreover, mass transport conditions can also be tuned either by changing convection control or by tuning the morphology of the catalysts than can either introduce or alleviate concentration gradients at the electrode surface.[80-82]

Notably, these changes in the local concentration gradients can also impact the kinetics of competing HER reaction, either due to the changes in concentration of the proton donor species at the electrode surface (such as HCO_3^-) or due to explicit pH effects on the kinetics of HER (discussed in detail in the following sections). Needless to say, these changes in the HER activity can in-turn influence the Faradaic selectivity of CO2RR.

However, even though the role of local pH changes in tuning the competition between HER and CO2RR is being increasingly recognized, the studies that have been conducted to investigate these effects have been inconclusive thus far. One of the strategies that has been employed to investigate the role of local pH effects in tuning CO2RR is the use of nanoporous catalysts. Introducing nanoporous structuring at the catalyst surface results in the generation of additional diffusional gradients and these gradients can be tuned by controlling pore diameter and pore length. In Table 1 we show a comparison of some of these studies on monometallic nanoporous catalysts, specifically for the case of CO2RR towards CO formation. We see that even under relatively similar experimental conditions drastically different Faradaic selectivities for CO formation are achieved.[81-89] Hence, it appears that in order to understand the role of local pH gradients in tuning CO2RR selectivity, first there is a need to study these effects under well-defined conditions where the local concentration gradients can be tuned systematically. Additionally, care has to be taken in comparing catalytic activities for similar catalysts when different electrolyte parameters are used, as changes in the electrolyte identity are directly reflected in the bulk as well as the local pH at the interface.[73, 90] Hence, similar catalyst morphologies studied under different electrolyte conditions can also result in varying CO2RR selectivities.

All the studies shown in Table 1 were performed by conducting long-term bulk electrolysis measurements coupled with a gas chromatography (GC) set-up. In such measurements, depending on the sampling time, cell geometry and electrolyte flow conditions, variable concentration gradients can be generated even with similar catalyst morphologies, thus resulting in varying Faradaic selectivities. It is therefore important to study these effects with online techniques so that the interplay between the heterogeneous consumption of reactants/ production of hydroxyl ions and the corresponding changes in the homogeneous equilibria can be tracked in real time without any convolutions due to time-based concentration polarization effects.

Table 1 An overview of CO Faradaic efficiency during CO2RR that have been reported in the literature on different monometallic porous catalysts (prepared with different techniques). Some of the important reaction parameters, such as pore diameter, bicarbonate concentration and the applied potential where the Faradaic efficiency is measured are also listed.

Group/Year	**Catalyst-Substrate**	**Pore diameter**	**Electrolyte (M)**	**Potential (V vs RHE)**	**Faradaic efficiency (%) for CO**
Lu et al. 2014[83]	Ag (free standing)	Few hundred nm	0.5 M $KHCO_3$	< - 0.5	92
Sen et al. 2014[85]	Cu-Cu polished	15-72 µm	0.1 M $KHCO_3$	- 0.4	27
Surendranath et al. 2015[82]	Au-Au coated glass slide	200 nm	0.1 M $KHCO_3$	- 0.4	75
Surendranath et al. 2016[81]	Ag-Au coated glass slide	200 nm	0.1 M $KHCO_3$	- 0.6	80
Zhang et al. 2016[84]	Ag-Ag foil	30-50 nm	0.5 M $KHCO_3$	- 0.4	82
Wang et al. 2017[89]	Cu-Cu foil	120- 300 nm	0.1 M $KHCO_3$	- 0.8	55
Cheng et al. 2017[88]	Au-Ag foil	Few hundred nm to few µm	0.1 M $KHCO_3$	- 0.39	90.5
Chen et al. 2018[86]	Au-Cu wire	250-500 nm	0.1 M $NaHCO_3$	- 0.6	95.9
Luo et al. 2019[87]	Zn-Cu mesh	30-80 µm	0.1 M $KHCO_3$	- 0.95	95

In order to unambiguously elucidate the role of local pH effects in tuning CO2RR it is important to separately study the role of mass transport conditions, electrolyte effects and catalyst morphology effects, so that general guiding principles can be derived for the selective optimization of CO2RR.

Moreover, it is also important to understand the activity trends for HER under CO2RR reaction conditions. So that this parasitic side reaction can be selectively suppressed and higher CO2RR efficiencies can be obtained. In the current literature, while a lot is understood about HER in acidic media, there are many ambiguities regarding the activity trends for HER under CO2RR relevant near-neutral/alkaline reaction conditions. Hence, understanding HER trends is not only important due to its relevance for hydrogen generation/storage but also for other renewable technologies (such as CO2RR), where it can act as a parasitic side reaction. And given that near-surface environment also plays an important role in tuning HER, in the next sections we will shift the focus to this reaction.

1.5. Electrochemical hydrogen evolution reaction: an overview

Hydrogen evolution reaction (HER) is perhaps the most well studied reaction in electrocatalysis. In fact, water splitting reaction to form hydrogen and oxygen is the earliest known experiment involving the chemical conversion of electricity.[32] Many of the theories in electrocatalysis, some of which have been touched upon in the previous sections, were either developed to explain the empirically observed trends for HER or HER was used as a test reaction to develop more advanced theories of electrocatalysis. Additionally, this two-electron transfer reaction is also an important piece in the energy transition puzzle,[9] as green hydrogen generated by water electrolysis is vital for achieving a carbon-neutral energy system and establishing the so-called hydrogen economy – a vision Bockris put forward already in the early 1970s.[91]

In this respect, most of the early studies on HER focused on understanding the mechanism and the activity trends for this reaction in acidic media.[37-39, 92-94] This resulted in the identification of Pt as the best catalyst and of the adsorption free energy of hydrogen as the key descriptor for HER activity. Ultimately, this led to the commercialization of proton exchange membrane (PEM) electrolysers, which employ Pt based catalysts for the cathodic half reaction (i.e. HER) of water splitting.

However, the activity trends for HER in alkaline media differ significantly from the trends obtained in the acidic media and catalysts such as Ir and Ni show superior activity under alkaline conditions, even though they bind hydrogen less optimally than Pt.[95-97] In practice, this is what makes alkaline water electrolysers more cost effective than PEM electrolysers as they can be operated with cheaper Ni-based catalysts. However, the energy efficiency of alkaline electrolysers remains inferior to PEM electrolysers, since the HER activity always decreases in going from acidic environment to alkaline environment, regardless of the catalyst employed.[98] This has led to significant research efforts in the recent years, towards understanding the activity descriptors that govern the HER kinetics in alkaline media, with the goal of optimizing this reaction under alkaline conditions.

In-fact it is widely recognized now that the hydrogen binding energy (HBE) at the catalyst surface is an incomplete descriptor for HER, especially under alkaline conditions. HBE cannot explain many of the experimentally observed trends for HER, including the (non-Nernstian) pH dependence of the reaction[44, 99-100] as well as the activity trends on different catalytic materials under alkaline conditions.[47, 101-102] This in-turn points to a fundamental change of the nature of HER when going from acidic media to alkaline media. This is also shown in Table 2, where we see that in acidic media, a hydronium ion (H_3O^+) undergoes discharge and forms an adsorbed hydrogen atom at the electrode surface. Instead, a neutral water molecule has to dissociate at the electrode surface in alkaline media. This essentially results in an additional barrier for the reaction in alkaline media, which is reflected by the fact that under alkaline conditions the first ET (Volmer step; see Table 2) is invariably the rate RDS, regardless of the employed catalyst. Consequently, the reaction rate of HER in alkaline media is influenced by additional parameters that can tune the interaction of the reactants (H_2O_{ads}) and the products (OH_{ads}, OH^-) of the RDS at the metal-electrolyte interface.

Table 2 Mechanism of HER under acidic conditions and under alkaline conditions where the rate determining step can either be Step I (Volmer step) or Step II (Heyrovsky/Tafel step).[103]

HER Reaction	Step I	Step II
Acidic media: $2H_3O^+ + 2e^- \rightarrow H_2 + 2H_2O$	Volmer step: $H_3O^+ + e^- \rightarrow H_{ads} + H_2O$	Heyrovsky step: $H_{ads} + H_3O^+ + e^- \rightarrow H_2 + H_2O$ Or Tafel step: $H_{ads} + H_{ads} \rightarrow H_2$
Alkaline media: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	Volmer step: $H_2O + e^- \rightarrow H_{ads} + OH^-$	Heyrovsky step: $H_{ads} + H_2O + e^- \rightarrow H_2 + OH^-$ Or Tafel step: $H_{ads} + H_{ads} \rightarrow H_2$

In the recent years, various important interfacial parameters have been identified that have been shown to influence the rate of HER in alkaline media, such as, the cation identity in the electrolyte, oxophilicity of the reactive sites and the interfacial electric field at the surface.[47, 101, 104-106] Among these, interfacial electric field is an especially important parameter as it can affect both the structure and the composition of the electric double layer and hence, influence the near-surface reaction environment for HER in multiple ways. In the next section, we will discuss some of these ways in which the electric field effects impact the HER kinetics in alkaline media.

1.5.1. Electric field effect on HER

At an electrode-electrolyte interface, the interfacial electric field is determined by the applied potential and the potential of zero charge of the electrode material i.e. $\Delta E = E - E_{pzc}$.[16] The potential of zero charge (*pzc*) represents the potential at which there is net zero surface charge density at the electrode surface ($E_{pzc} = E_{\sigma=0}$).[107] Hence, at potentials more negative than the *pzc,* the net interfacial electric field at the surface is negative and cations are expected to have preferential electrostatic interactions at the interface. On the other hand, at potentials more positive than the pzc, the net electric field is positive and the anions preferentially interact at the surface. We note that in reality, on most electrode surfaces, the net surface charge density is not zero at the *pzc* as there is always some degree of specific adsorption irrespective of the employed supporting electrolyte.[108-110] This results in a net charge at the surface even at the *pzc*, due to the chemical bonds formed between the specifically adsorbed ions and the electrode surface. Hence, a distinction has to be made between the potential of zero free charge (*pzfc*) which represents the *pzc* in the absence of any specific adsorption and the potential of zero total charge (*pztc*) which represents the potential where the net charge at the surface is zero both due to electrostatic interactions and chemical interactions.[107] And, while the *pzfc* is only dependent on the electrode material (more specifically, the work function ϕ of the electrode), the *pztc* is dependent on both the electrode material and the electrolyte identity.[111] Consequently, at the same applied potential, varying interfacial electric field strength can be obtained depending on the nature of the electrode-electrolyte interfaces, which is in turn determined by the catalyst identity/structure as well as the composition of the bulk electrolyte.[112-114]

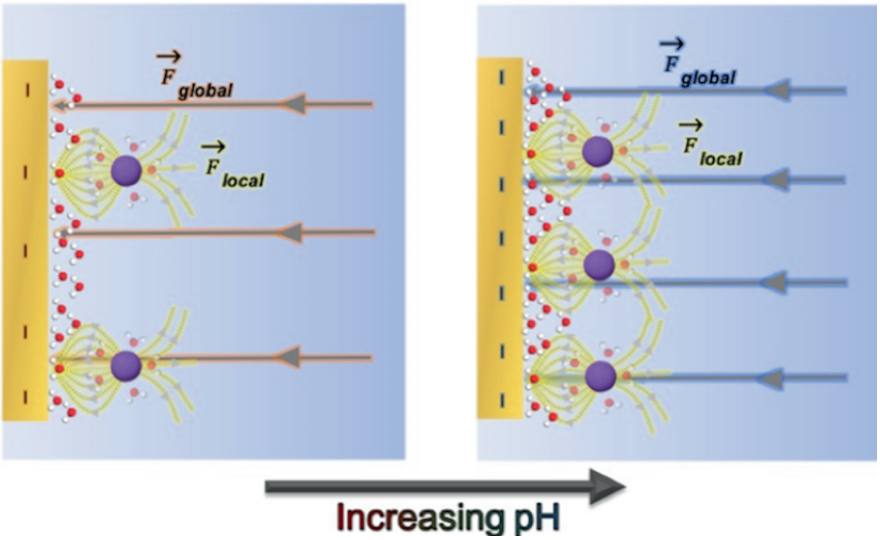

Figure 1 A schematic representation of the pH dependent global interfacial electric field at the electrode surface which affects the solvent (water) structure at the interface as well as the local composition of the double layer, such that an increasing global electric field strength results in a higher reorganization energy for the interfacial water network and a higher near surface cation concentration. Additionally, the cations near the interface also exert a local electric field aligned with the dipole of the reacting water molecule at the electrode surface.

This interfacial electric field can influence the rate of an electrocatalytic reaction in a number of ways. For instance, by influencing the solvent dynamics at the interface, by tuning the polarizability of the reaction intermediates and/or by tuning the composition of the electric double layer, which can in-turn influence the chemical/electrostatic interactions of the adsorbed intermediates in the reaction plane.[15] In a recent study, our group showed that for Pt(111), the changes in the solvent dynamics with changing interfacial electric field tune the rate of HER in alkaline media.[104] We proposed that the interfacial water network has the highest mobility when the interfacial electric field is the weakest and this mobile water network can facilitate the transport of ions such as H_3O^+, OH^- within the double layer, thus facilitating HER. On the other hand, as the interfacial electric field becomes stronger (more negative), the water network at the surface becomes more rigid, thus, hindering the transport of ions near the interface. Moreover, based on the previous works by Feliu and coworkers, the interfacial electric field on Pt(111) is expected to become more negative (vs reversible hydrogen electrode) with increasing electrolyte pH.[115] Hence, the loss in the HER activity on Pt(111) with increasing electrolyte pH can be reconciled with the changes in the interfacial water structure with changing interfacial electric field.

Additionally, the interfacial electric field is also directly intertwined with another important parameter for HER kinetics, namely the extent of cation adsorption at the electrode surface and/or the cation concentration in the O.H.P.[15, 116-117] It has been shown previously that the HER activity in alkaline media is very sensitive to the identity of the alkali metal cations in the electrolyte.[47, 106] Markovic and co-workers have shown that on Pt based catalysts, the HER activity increases in the order $Cs^+ < K^+ < Na^+ < Li^+$ which they correlate to the stronger interaction of the Li^+ ions with the dissociating water molecule in the rate determining Volmer step (see Table 2).[101-102, 118] However, the surface coverage of the alkali metal cations at a given surface is in-turn dependent on the interfacial electric field strength. This is because a stronger interfacial electric field can stabilize the surface dipole generated by a specifically adsorbed cation, thus resulting in a larger cation coverage at the surface and/or a higher near-surface cation concentration in the O.H.P. Hence, in addition to the solvent dynamic effects, the interfacial electric field can also influence the HER kinetics by tuning the near-surface cation concentration at the interface. Moreover, it should be noted that in the above discussions, the interfacial electric field has been considered to be uniform everywhere within the reaction plane (parallel to the electrode surface). However, due the presence of ions in the electric double layer, there will be an additional "local" electric field associated to these ions (as shown in Fig. 1).[119] These local changes in the interfacial electric field can also influence the HER reaction rate as the electrostatic interactions between the adsorbed reaction intermediates and the cations can also tune the reaction energetics at the interface.

However, even though the effect of the interfacial electric field on the near-surface cation concentration has been studied to some degree in the literature, its role in tuning the HER activity remains elusive. Given that, these cation-associated field effects have been shown to influence the activity of other electrocatalytic reactions such as CO2RR,[119-120] it can be expected that these effects can also have a profound impact on the rate of HER.

1.6. Scope of the thesis

The scope of this thesis lies in understanding the role of near-surface environment in tuning electrocatalytic reactions by the means of interactions that go beyond the traditional adsorption-based activity descriptors. In the preceding sections we have outlined some of the shortcomings of such adsorption-based descriptors and the classical theories that are generally used to simulate the kinetics of electrocatalytic reactions. Especially, when considering the activity trends for CO2RR and HER, under practical reaction conditions. In the following chapters, we will present in-depth studies on some of these additional reaction parameters that can tune CO2RR and HER and elucidate some of the molecular complexities that underlie these reactions.

In chapter 2, we will first discuss the development of an online rotating ring disk electrode (RRDE) set-up that allowed us to bypass the issues that were discussed in section 1.4.1.[80] Briefly, the RRDE technique allows for hydrodynamic convection control at the electrode surface which in-turn results in well-defined near-surface concentration gradients. Hence, by using the RRDE technique, the role of concentration (pH gradients) in controlling the CO2RR activity can be studied under well-defined conditions. Moreover, the RRDE technique also gives the possibility to separate the contributions due to mass transport effects and intrinsic kinetics of the reaction, thus improving upon one of the limitations of the Butler-Volmer model (as discussed in section 1.2 and 1.3). Moreover, we restricted this study to the polycrystalline Au surface in order to simplify the system. That is, we avoid additional convolutions due to the internal competition between different CO2RR pathways, as CO2RR on Au electrodes yields only CO as the main product for this reaction. Thus, we focused our study on the role of local pH gradients in tuning the competition between CO2RR and HER. Interestingly, we found that CO2RR shows only a slight improvement with increasing mass transport (decreasing local pH), while the changes in the local pH at the Au surface mainly affected the kinetics of the competing HER. Essentially, we observe a significant improvement in HER activity with increasing local pH at the surface. To emphasize: an increase in the local pH with increasing mass transport rate leads to the suppression of CO2RR Faradaic selectivity, even though the kinetics of CO formation is not significantly impacted by the changing local concentration gradients.

In chapter 3, we elucidate the pH dependence of the HER kinetics on Au electrodes further.[121] In doing so, we shed light on the role of the pH dependent interfacial electric field in tuning HER activity. We show that with increasing strength of the interfacial electric field, the near-surface cation concentration also increases. This increase in the near-surface cation concentration in-turn results in the enhancement of HER, as cations near the surface can decrease the activation barrier for the reaction. This is because the cations can favorably interact with the transition state of the rate determining Volmer step ($^*H\text{--}OH^{\delta-}\text{--}cat^{+}$). Interestingly, this cation assisted enhancement of HER kinetics saturates and even becomes inhibitive as the local cation concentration increases beyond a threshold concentration. This shows that while an initial increase in the cation concentration decreases the activation barrier for the reaction, at some point the metal-cation interactions start to inhibit the HER reaction, either due to double layer crowding or due to blocking effects. These results clearly show that the electrolyte pH and the near surface cation concentration are two interrelated parameters, that have a similar effect on the HER kinetics. Moreover, we confirm that the interfacial electric field is indeed an important parameter in tuning the HER kinetics in alkaline media and it not only alters the structure (solvent dynamics) of the double layer but also the composition of the near-surface reaction environment. Hence, its role in tuning the near-surface reaction environment is even more convoluted than was previously hypothesized in the literature (as discussed in section 1.5.1). In chapter 4, we reconcile the results presented in Chapter 2 and Chapter 3 by further elucidating the role of local pH gradients in tuning the HER kinetics on Au electrodes. We point out that while the changes in the interfacial electric field with the changing bulk pH can tune the near-surface cation concentration (chapter 3), the local pH effects on HER kinetics, as observed in chapter 2 are different than these bulk pH effects. Instead, we demonstrate that the changes in the local pH with changing rotation (mass transport) rate tune the local cation concentration due to the need to satisfy local electro-(neutrality) conditions. Hence, even though the changes in the bulk pH and the local pH seem to influence the HER kinetics on Au electrodes in a similar fashion, there is a distinction in the underlying cause for these effects. The former effect is due to the changes in the local cation concentration with changing interfacial electric field, while the latter results from the need to satisfy local electro-(neutrality) which results in increasing local cation concentration with increasing local hydroxyl concentration.

Lastly, in chapter 5, we extend the understanding gained from the previous chapters to further elucidate the role of near-surface reaction environment in tuning CO2RR and HER on nanoporous Au catalysts. We present a systematic study on the role pore parameters (pore diameter and pore length) in tuning the Faradaic selectivity for CO2RR by employing differential electrochemical mass spectrometry (DEMS). The latter is a powerful online and *in situ* technique that allowed us to quantify the formed amounts of H_2 and CO and bypass the limitations that have resulted in convoluted trends in the previously reported literature on nanoporous catalysts (as discussed in section 1.4.1). We find that similar to the flat polycrystalline Au electrodes, the changes in the local pH gradients with changing pore parameters mainly affect the rate of the HER reaction. However, the changing pore parameters also tune the CO2RR activity due to the changes in the number of active sites at the catalyst surface and due to the presence of additional Ohmic drop effects within the porous channels.

In summary, we show in this thesis that the near-surface reaction environment is a dynamic entity that can be tuned by varying the electrolyte parameters. Here, we discuss the role of the electrolyte pH, the cation identity and cation concentration. Furthermore, we demonstrate that mass transport conditions (via convection control or catalyst morphology) is an important tuning handle for controlling the near-surface reaction environment. With this thesis we reveal that the kinetics of different electrocatalytic reactions can be tuned by defining the near-surface environment through various means. In doing so, we venture beyond classical theories of electrocatalysis, that fail to consider the intertwined effects of bulk/local electrolyte composition and local electric field on inner sphere reactions.

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