# Influence of the electrode-electrolyte interface on electrochemical CO2 reduction reaction and hydrogen evolution reaction

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# Chapter 1

# Introduction

## 1.1 General Introduction

The imperative transition toward renewable energy is both a contemporary obligation and an enduring journey that traces its urgency to the historical industrial reliance on fossil fuels. This shift is driven by increasing global awareness of climate change, aggravated by excessive $CO_2$ emissions resulting from industrial activities. Since the beginning of the industrial era, $CO_2$ emissions have dramatically increased, leading to considerable environmental disruptions. This has prompted a global shift towards renewable energy sources that are less detrimental to our planet. Anchored by a global commitment to achieve carbon neutrality, underscored by key climate agreements such as the Kyoto Protocol and the Paris Agreement, this shift highlights the global imperative to achieve carbon neutrality within specified timelines.

Given the achievement of low-cost electricity from renewable sources like solar and wind, electrochemistry emerges as a pivotal element in this global energy transition. It is directed to a transformation of electrical energy into chemical bonds and vice versa, promoting the development of modern energy storage and conversion technologies. Ever since Galvani’s discovery of “animal electricity” and Volta’s pioneering battery, numerous innovations have emerged in the field of electrochemistry, pacing the rhythm of progress across centuries. A key milestone in this journey is the launch of the lithium-ion battery technology, recognized by the 2019 Nobel Prize in Chemistry. This breakthrough marked the beginning of a new era in portable electronics, electric vehicles, and efficient storage for renewable energies, thus foregrounding electrochemistry's vital role in moving towards a fossil fuel-free future.

Over the past decades, electrochemically converting carbon dioxide ($CO_2$) into fuels, chemicals and building materials has drawn substantial attention as a strategy to “close the carbon cycle”. Such a cycle is shown in Figure 1.1. By utilizing renewable electricity, this process reduces the $CO_2$, a byproduct of industrial activities, to value-added products. If these value-added products replace fossil resources, it could indeed close the carbon cycle. Up to now, the achievements in electrochemical $CO_2$ reduction ($CO_2$RR) have been notable, including the successful conversion of $CO_2$ into a wide array of products, from simple molecules like carbon monoxide and formic acid to more complex multi-carbon products.[1] These successes demonstrate the feasibility of using $CO_2$ as a feedstock for renewable fuel and chemical production.

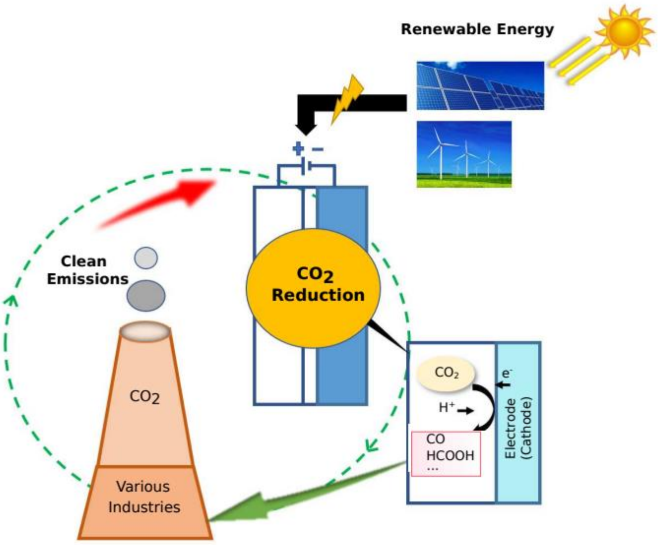

**Figure 1.1** Schematic overview of a carbon neutral cycle including the electrochemical $CO_2$ reduction reaction[2]

Despite these achievements, the $CO_2$RR confronts numerous technical challenges that hinder its application on an industrial scale, including low selectivity and activity for desired products, the rapid deterioration of electrocatalysts, and low overall energy efficiency.[1] Therefore, the future of $CO_2$RR rests on overcoming these technical challenges that currently limit its scalability and economic viability. This includes the developments of more efficient and selective electrocatalysts, improved understanding of reaction mechanisms, and the engineering of electrolyzers to optimize $CO_2$RR performance. This thesis will concentrate on these challenges and explore how to optimize $CO_2$RR performance from different aspects. In this chapter, we will first introduce some general concepts associated with the $CO_2$RR.

## 1.2 Electrochemical $CO_2$ Reduction Reaction

The device that enables the electrochemical conversion of $CO_2$ is known as an electrolyzer, which utilizes electricity to drive a chemical reaction that would not occur spontaneously under standard conditions. Figure 1.2 illustrates a typical electrolyzer comprising a cathode and an anode submerged in an electrolyte, an electrically conducting medium containing cations and anions.[3] A separator, typically a membrane, may be placed between the cathode and the anode. This membrane selectively permits species to move from one electrolyte compartment to another, thereby preventing secondary reactions and separate the products generated at the two different compartments. Prior to the $CO_2$RR, $CO_2$ is supplied to the electrolyzer, such as by dissolving it in the electrolyte, or by supplying it through the gas phase in a so-called gas diffusion electrode (GDE). Upon application of an electric potential between the cathode and the anode, electrons are provided to the cathode, while a positive charge is generated on the anode by extraction of electrons. At both electrodes, if the driving electrical energy is higher than the reaction activation energy barrier, the electrical energy is converted into chemical energy. As depicted in Figure 1.2, electron transfer at the cathode initiates an electrochemical $CO_2$ reduction reaction (Equation 1.1), whereas the electron extraction at the anode results in an electrochemical oxidation of $H_2O$ to oxygen (Equation 1.2). Simultaneously, ions in the electrolyte migrates between the cathode and the anode to balance the transfer of charges at both electrodes, thereby completing the electric circuit.

Despite the great potential of $CO_2$RR to generate fuels and chemicals, the processes at electrodes remain kinetically limited for multi-charge transfer reactions.[4] To address this limitation, the introduction of an electrocatalysts is essential. In the field electrochemistry, the electrocatalysts are a specific form of catalysts that function at electrode surfaces or, most commonly, may be the electrode surface itself, which can accelerate the transfer of electrons between electrode and reactants, and/or facilitate to an intermediate chemical transformation described by an overall half-reaction. Therefore, electrocatalyzing $CO_2$ reduction is directed to chemical reactions happening at the electrode-electrolyte interface.[5]

Cathode: $x\,CO_2 + n\,H_2O + ne^- \rightarrow product + y\,OH^-$ Equation 1.1

Anode: $2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^-$ Equation 1.2

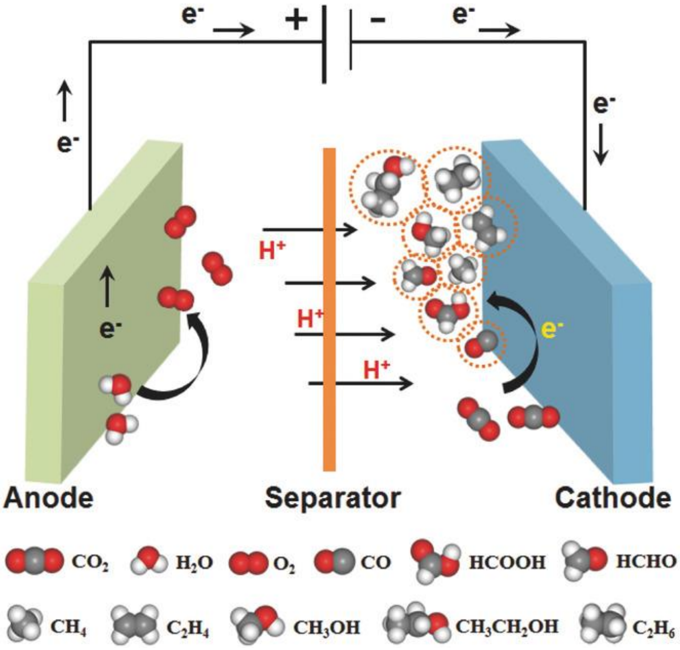

**Figure 1.2** Schematic overview of a $CO_2$ electrolyzer[3]

Extensive experimental and theoretical work has been dedicated to develop efficient electrocatalysts for $CO_2$RR.[1, 6-17] Among these, metal-based electrocatalysts have been extensively studied due to their superior catalytic performance. The nature of the metal catalysts has an important effect on the activity and selectivity of $CO_2$RR.[6-8, 10, 12-13] For instance, of the monometallic catalysts, Cu exhibits a unique selectivity to methane and various multi-carbon products such as ethylene, ethanol, and propanol.[8, 12] Precious metal catalysts such as Au and Ag show high selectivity toward CO.[6-7] Platinum group metals are also selective for CO formation but are affected by CO surface poisoning.[14-17] Pd-based catalysts can reaching a Faradaic efficiency of 95% for CO generation at negative potentials (-0.8 $V_{RHE}$),[15] while delivering a high Faradaic efficiency toward HCOOH (close to 99%) with a small overpotential of 0.1 V[14]. In addition, other factors, such as surface structure, surface morphology as well as catalyst particle size, are also crucial to the performance of the electrocatalyst for $CO_2$RR. Up to now, many approaches including alloying, nanostructuring as well as functionalization by organic additives, have been employed to the rational design of robust, active, and selective electrocatalysts for $CO_2$RR.[1]

In addition to the electrocatalysts, electrolyte composition including cation identity, anion identity, electrolyte pH and buffer capacity have been shown to have a strong impact on the $CO_2$RR activity and selectivity.[1] Earlier studies show metal cations in the electrolyte affect the electrode-electrolyte interface by modification of the local electric field, buffering of the interfacial pH or stabilization of reaction intermediates, thereby influencing the selectivity and activity of $CO_2$RR.[18-20] For instance, Singh et al. propose that cations affect the $CO_2$RR by buffering of the interfacial pH,[19] which is in agreement with the result of pH measurement at a gold–electrolyte interface using attenuated total reflection surface-enhanced infrared spectroscopy based on the ratio between the integrated intensity of the $CO_2$ and $HCO_3^-$ bands, showing that larger cations are better buffers and lead to lower pH changes at the interface.[21] Electrolyte pH as well as buffer capacity impacts the local dynamic equilibria of $CO_2$ (aq.) as well as other reacting species ($H_3O^+$, $HCO_3^-$ and $H_2O$) near the electrode-interface,[22] and thereby influencing the $CO_2$RR performance. For example, ethylene formation with high selectivity (70% faradaic efficiency) can be achieved by operating the $CO_2$RR in an alkaline electrolyte.[23]

Recent efforts have shifted toward the engineering of the electrolyzer itself to improve the activity and efficiency of $CO_2$RR.[23-24] In a traditional $CO_2$ electrolyzer, a known limitation is the low solubility of $CO_2$ in the electrolyte, especially in aqueous media, and consequently the low concentration of $CO_2$ at the electrode-electrolyte interface. This limitation can be overcome by utilizing a flow cell equipped with a GDE. The flow cell enables continuously electrolyte supply across the electrode surface and the porous structure of the GDE allows continuous $CO_2$ supply from the gas phase to the catalyst-electrolyte interface, therefore greatly improving local $CO_2$ concentration near the electrode during $CO_2$RR and enabling high current densities (e.g. greater than 200 $mA\ cm^{-2}$) even at ambient conditions.[24-29] However, stability of the GDE remains an issue. Rapid electrode degradation was observed in highly alkaline electrolyte,[27, 30] with one of the degradation mechanisms being carbonate precipitation resulting from the reaction between $CO_2$ and KOH.[30-32] To overcome this shortcoming, recently acidic electrolytes have been employed in $CO_2$RR electrolyzers.[25, 33] With the fast kinetics of proton reduction, rational design of the electrolyte/electrode interface becomes extremely important to achieve a good $CO_2$RR performance.

## 1.3 Hydrogen Evolution Reaction (HER)

The hydrogen evolution reaction is an electrochemical process that generates hydrogen ($H_2$) from protons, water, or other proton sources. It serves not only as a half reaction in water electrolysis but also as a competing side reaction during $CO_2$RR. Therefore, understanding HER is fundamentally important for the development of both water and $CO_2$RR electrolyzers, which both play significant roles in the energy transition towards a fossil fuel-free future.

Extensive work has been dedicated to gain mechanistic insights of the HER process.[18, 34-45] Traditionally, the significant variations in HER rates observed across different electrodes have been correlated to differences in the free energy of hydrogen adsorption.[46-47] However, this adsorption energy-based descriptor fails to describe the sluggish kinetics of HER in alkaline media and does not accurately reflect the influence of electrochemical environment at the electrode-electrolyte interface on HER under these conditions,[41, 48] where water dissociation is a prerequisite for generating adsorbed hydrogen. As a result, other descriptors such as the interfacial field strength, the oxophilicity of the surface sites and the cation solvation energy have been identified. These descriptors contribute to a more comprehensive understanding of the HER mechanism under alkaline conditions.[35, 38, 40, 49-50] Among these descriptors, the interfacial electric field is recognized as an important factor due to its impact on both the structure and composition of the electric double layer, thereby affecting the electrode-electrolyte interface in multiple manners.[38] Nonetheless, the specific role of the interfacial electric field in tuning the HER activity remains elusive. Therefore, further studies are necessary to gain a deeper understanding of the activity trend and reaction mechanisms of HER.

## 1.4 Outline of This Thesis

The goal of this thesis is to understand how interfacial parameters, such as the addition of organic additives, bulk pH or metal cations of the electrolyte, affect the relevant electrocatalytic reactions, i.e. electrochemical $CO_2$ reduction reaction or hydrogen evolution reaction. In the following chapters, we will present in-depth studies on the role of these interfacial parameters in tunning $CO_2$RR and HER under practical reaction conditions. Our study provides more fundamental insights of $CO_2$RR and offers guidelines to optimize $CO_2$RR performance for further industrial application of $CO_2$RR.

In chapter 2, we first investigate the influence of organic additives on $CO_2$RR activity and selectivity and explore how organic additives impact the interfacial environments during $CO_2$RR. We show improved selectivity and activity of $CO_2$RR towards formic acid production on poly(4-vinylpyridine) (P4VP) modified copper and gold electrodes. By using in situ ATR-SEIRAS and contact angle measurements, we attribute the altered selectivity towards formic acid over CO on both copper and gold electrodes to the hydrophobic nature of P4VP, which influences mass transport dynamics at the electrode-electrolyte interface and thereby promotes a surface hydride mechanism leading to an improved formic acid production.

In chapter 3, we closely examine the role of metal cations on $CO_2$RR on a well-defined surface, a palladium monolayer modified Pt(111) surface ($Pd_{ML}$Pt(111)), in a pH 3 electrolyte. We show the onset potential for formic acid and carbon monoxide formation shift positively with the increasing cation concentrations, with a stronger effect observed on HCOOH formation. Density functional theory simulations indicate that cations facilitate both hydride formation and $CO_2$ activation by polarizing the electronic density at the surface and stabilizing $*CO_2^-$. The simulations further suggest that high CO coverage prevents the formation of hydrides, leading to the quick decrease of HCOOH selectivity at high applied potentials. The result highlights the crucial importance of cations and the overall microenvironment design in $CO_2$RR.

Understanding the competing HER is relevant for optimize $CO_2RR$ performance. Therefore, in chapter 4, we further study the role of metal cations on HER in pH 3 electrolytes. We show that on a polycrystalline Pt surface, while cations do not kinetically influence proton reduction at low potentials, an increase in cation concentration notably enhances water reduction, suggesting the promotional effect of cations on water dissociation. In addition, we identify a non-negligible migration current under mass transport limited conditions in electrolytes with low cation concentration. To minimize this migration current component, electrolytes with sufficient conducting cations and anions are required. We thereby employ electrolytes with mixtures of $Li^+$ and $K^+$ cations to explore specific cation-promotion effects on HER, showing that adding strongly hydrated cations ($Li^+$) to a $K^+$-containing electrolyte leads to a less negative onset potential of water reduction. Interfacial pH measurements show that the interfacial pH at the platinum electrode, at potential where water reduction occurs, remains consistent across different cationic electrolytes. This result indicates that the variation in the onset potential of water reduction across different cationic electrolytes does not result from interfacial pH effect caused by cation hydrolysis near the electrode. Based on these findings, we propose that this difference arises from the more favorable promotion of water dissociation by strongly hydrated cations ($Li^+$) compared to weakly hydrated cations ($K^+$) under our experimental conditions. Our results hint at the potential benefits of utilizing weakly hydrated cations ($K^+$) for $CO_2RR$ on Pt based catalysts in mild acidic media, offering valuable insights for catalyst-electrolyte design in renewable energy technologies.

In chapter 5, we expand the study on $CO_2RR$ under more industrially relevant conditions. Specifically, we investigate the influence of bulk electrolyte pH on $CO_2RR$ product distribution using a copper gas diffusion electrode (Cu GDE) in both a traditional bicarbonate electrolyte and a mildly acidic electrolyte. We observe inhibited hydrogen formation in the mildly acidic electrolyte at low current densities, while the $CO_2RR$ product distribution remains consistent in both electrolytes at high current densities. In addition, SEM images, along with EDX elemental mapping, indicate a less stable catalyst layer on the Cu GDE, resulting in electrode degradation over long electrolysis in acidic media compared to the bicarbonate electrolyte. Our findings highlight the positive prospects of acidic media in the field of $CO_2$RR, while also indicating new challenges of employing acidic media in $CO_2$RR electrolyzers.

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