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Unveiling the electrolyte effects of CO₂ electroreduction to CO and H₂ evolution from the interfacial pH perspective

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Citation

Liu, X. (2025, February 6). *Unveiling the electrolyte effects of CO₂ electroreduction to CO and H₂ evolution from the interfacial pH perspective*. Retrieved from <https://hdl.handle.net/1887/4178928>

Version: Publisher's Version

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Chapter 1

Introduction



1.1 Electrochemistry bridging electricity and chemical power

Electrochemistry is the branch of chemistry that investigates redox reactions in which electrons are transferred from the reductant (increasing valence of the elements) to the oxidant (decreasing valence of the elements). Redox reactions are universal and widely utilized in our daily lives e.g. combustion of fuels, corrosion of metals, and photosynthesis and respiration in plants. Energy can be stored or released *via* an electrochemical process, making electrochemistry one of the most promising alternatives for relieving the energy crisis.

Dating back to the 16th century, electrochemistry originates from the exploration of magnetism and static electricity. William Gilbert, known as "The Father of Magnetism," discovered multiple methods for producing and strengthening magnets and made a principal contribution to the distinguishing between static electricity and magnetism. In fact, the English word "electricity" was derived from Gilbert's 1600 Neo-Latin "electricus", meaning "like amber in its attractive properties". The 18th century marked the birth of electrochemistry with experiments by Charles François de Cisternay Du Fay. Inspired by the invention of the first gas-discharge lamp by Francis Hauksbee in 1705, and the demonstration of conductivity of electricity by Stephen Gray and Jean Desaguliers in the 1730s, Charles François de Cisternay Du Fay discovered two forms of static electricity and proposed that like charges repel each other whilst unlike charges attract. Later, in 1799, a significant advancement was made by Alessandro Volta's ¹ invention of the first modern electric battery, the voltaic pile, which output a continuous electric current. Volta's work challenged Luigi Galvani's theory of animal electricity and for the first-time correlated electricity production with chemical power, which was further confirmed by the electrical theory of chemical affinities by Humphry Davy. By using the electric power supplied by the voltaic pile, Humphry Davy discovered several new elements such as sodium, potassium, and calcium, with the electric power converted to the chemical power. Noteworthy, water electrolysis was accomplished and properly interpreted even before the invention of the voltaic pile, in 1789. Without a stable current offered by the voltaic pile, a Dutch merchant Adriaan Paets van Troostwijk and his friend Johan Rudolph Deiman produced hydrogen and oxygen out of water by the electric discharge with a electrostatic generator.²

Throughout the 19th and 20th centuries, with the development of physical and chemical theories, mathematical methods, and experimental techniques, the investigations of electrochemistry notably thrived and largely enhanced the popularity and accessibility of electric power, which in turn boosted the industrial productivity and spawned the industrial revolution. In recent decades, electrochemistry has become a hot research area of versatile applications, contributing to advancements in batteries, ³ fuel cells, ⁴ electrolysis, ⁵

corrosion prevention,⁶ wastewater treatment,⁷ and biosensing.⁸

1.1.1 The electrochemical cell

A redox process generally consists of two half-reactions, involving a reduction reaction and an oxidation reaction. Separating the half-reactions in space by immersing two electronic conductors (the electrodes) in an electrolyte solution and connecting them externally by a conductor (commonly a metal wire), an electrochemical cell is constructed. An electrochemical cell consists thereby of two electrodes, namely a cathode where the reduction reaction takes place and an anode where the oxidation reaction takes place, and two charge transport paths, namely electronic transport through the wire and ionic

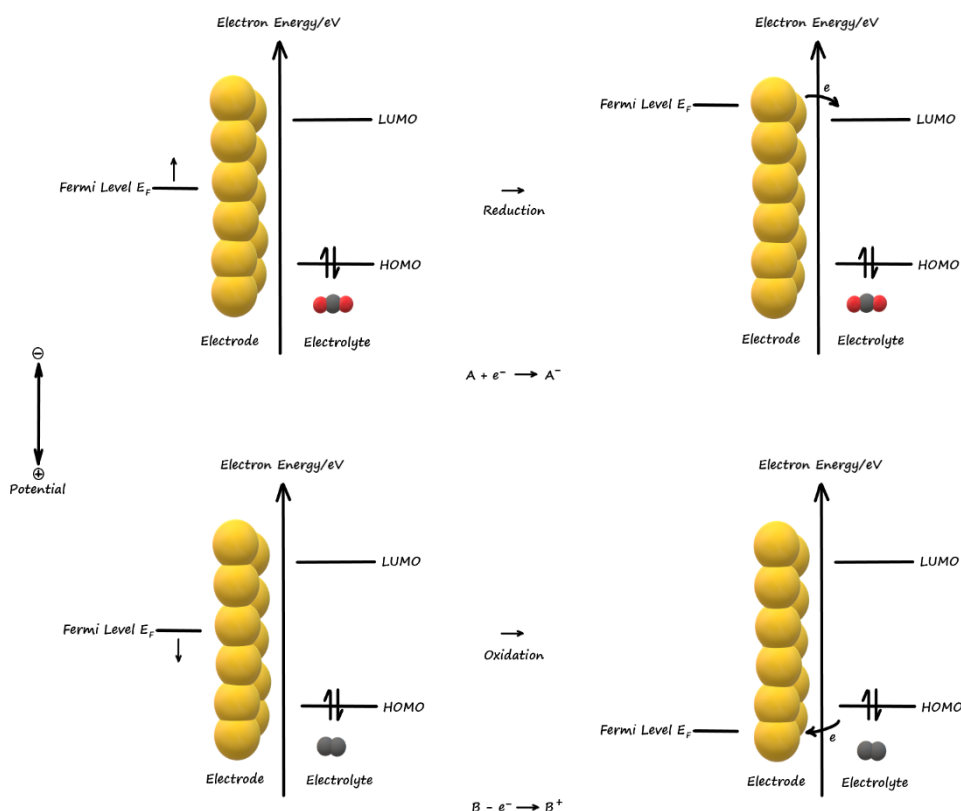


Figure 1. Representation of the heterogeneous electron transfer process between the Fermi energy level of the electrode and the molecule orbitals of the reactive species of a reduction reaction of A and a oxidation reaction of B respectively.

transport through the solution. Depending on the Gibbs free energy (G) difference between the reagents and the products, there are two types of electrochemical cells. In a galvanic cell, the G of the reagents is larger than that of the products, the redox reactions occur spontaneously, generating a faradaic current and releasing the chemical energy mostly into electric energy. On the other hand, an external energy supply is needed to drive the redox process in the opposite direction in a so-called electrolytic cell. The transfer of electrons occurs between the highest filled orbital of the electrode, known as the Fermi Energy Level (E_F) of a metal electrode, and the molecular orbitals of the reactant in the solution. By adjusting the electrode potential, the E_F of the electrode is adjusted with respect to the orbital energy levels in solution, to control the direction and extent of the reaction. As Figure 1 depicts, when negatively shifting the electrode potential, the energy of the electrons is lifted to reach the Lowest Unoccupied Molecular Orbital (LUMO) of the reagent, resulting in the electron transfer from the electrode to the reactant and a reduction current flow. In contrast, when the electrode potential is shifted in a positive direction, the energy of the electrons is lowered to approach the Highest Unoccupied Molecular Orbital (HOMO) of the reagent, leading to the electron transfer from the reactant to the electrode and an oxidation current flow. In commercial applications, galvanic cells are often employed as power sources such as batteries while the electrolytic cells are involved in the electrosynthesis process e.g. the production of chlorine or hydrogen, and in electroplating.

In an electrochemical process, the charge transferred is related to the extent of the chemical reaction. According to the Faraday's law (eq. 1):

$$Q = nFN \quad (1)$$

where Q is the charge transferred (C, 1 C is equivalent to 6.24×10^{18} electrons), n is the stoichiometric number of electrons transferred in the corresponding redox reaction, F denotes the Faraday's constant 96485 C/mol, and N (mol) is the amount of the reactants being consumed or the products being formed. In a single electron transfer reaction, the passage of 96485 C in the circuit brings about 1 equivalent of reaction (e.g., consumption of 1 mole of reactant or production of 1 mole of product). The current i , as defined in eq. 2:

$$i = \frac{dQ}{dt} \quad (2)$$

is the time derivative of the charge, where a current of 1 ampere (A) is equivalent to 1C/s.

By combining eqs. 1.1-1.2, the current is linearly related to the reaction rate $\frac{dN}{dt}$ (eq. 1.3):

$$v = \frac{dN}{dt} = \frac{dQ}{nFdt} = \frac{i}{nF} = \frac{i}{nFA}$$

(3)

Hence the current i and current density j are direct measures of the reaction rate of an electrochemical process. In fact, for a unimolecular elementary reaction (eq. 4):



the net reaction rate is:

$$v_{net} = v_f - v_b = k_f C_O - k_b C_R = \frac{i}{FA} \quad (5)$$

where v_f , k_f and v_b , k_b denote the reaction rate and reaction rate constant of the forward and the backward reactions, respectively, and C_X is the concentration of species X. The reaction rate constant is determined by the Arrhenius Equation (eq. 6):

$$k = Ae^{-E_A/RT} \quad (6)$$

where A is the frequency factor, E_A is the activation energy, R is the universal ideal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), and T is the temperature. As illustrated in the diagram of Figure 2, showing the free energy of the reaction as a function of the reaction coordinate, a change of electrode potential causes the movement of the “ $A + e$ ” free energy curve, leading to a corresponding change in the activation energy. This means that the electrode potential tunes the activation energy, thereby modulating the reaction rate and the current density. By plotting the current or current density as a function of the electrode potential, a polarization (i vs. E) curve of the electrode process is obtained, which is ubiquitous in electrochemical studies. These curves can be quite informative about the nature of the underlying process, and how it depends on the electrolyte and electrode, and further analysis of the polarization curves discloses qualitative or quantitative details about the thermodynamics and kinetics of the reaction processes taking place on the electrode.

In the study of an electrochemical half-cell reaction, a three-electrode set-up as shown in Figure 1.3 is commonly employed, constituting of a working electrode, a reference electrode, and a counter electrode. The working electrode is the electrode where the reaction of interest takes place. The reference electrode is an electrode with a known and well-defined potential which approaches an ideally nonpolarizable electrode under small current passage, so that it serves as the reference of the electrode potential of the working electrode. The Reversible Hydrogen Electrode (RHE), saturated calomel electrode (SCE, $\text{Hg}/\text{Hg}_2\text{Cl}_2$) and Ag/AgCl electrode (Ag/AgCl) are frequently used as a reference electrode in practical studies. Since the absolute value of the electrode potential is unknown, the

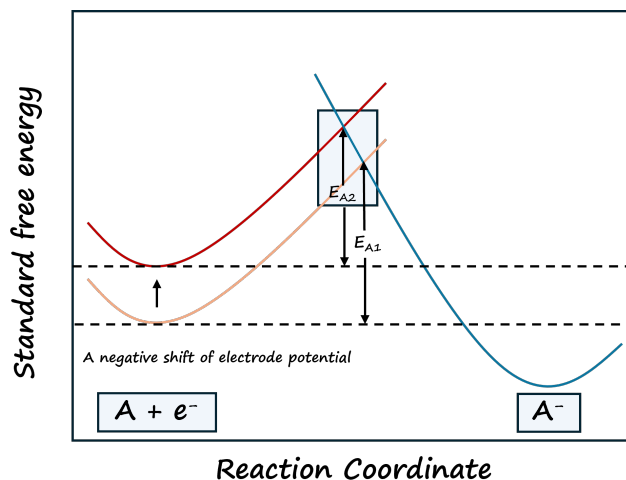


Figure 2. Schematic free energy diagram of the effects of a negative potential shift on the standard free energies of the partners in a redox reaction, and the corresponding changes in activation energy

potential of Standard Hydrogen Electrode (SHE, Pt/H_2 ($a=1$)) is standardized to be 0 V, and the potential of RHE, SCE, and Ag/AgCl are $-0.059 \cdot \text{pH}$ (the bulk pH of the electrolyte), 0.241 V, and 0.197 V vs SHE respectively. Current passes between the working electrode and the counter electrode to avoid any perturbation of the (potential of the) reference electrode. Investigations of the electrochemical behavior usually acquire valuable insights about the thermodynamic, kinetic, analytical, and other relevant aspects of the system by recording the excitation and response variables and applying an appropriate model to disentangle the information. They often proceed by keeping certain variables of the electrolysis cell constant while observing how other variables, e.g. current, potential, and species concentration change in response to controlled variables. For instance, chronoamperometry experiments during which the potential is kept constant while the current changes with time are often performed when studying the nucleation and growth process of electrodeposition and when testifying the stability and durability of the electrocatalyst. Another way to investigate an electrochemical process is to monitor how the system responds to a perturbation. The electrochemical cell is subjected to a specific excitation function, and a specific response function is recorded, while all other system variables are kept constant. For example, Figure 3 illustrates a cyclic voltammetry (CV) measurement, which is one of the most used potential sweep methods in electrochemical research, in which the input electrode potential is ramped linearly with time in periodic

phases, leading to corresponding time-dependent current. CV curves usually exhibit so-called redox peaks. The shape and potential of these peaks provide information about the redox species, while the difference between the forward and backward scans indicates the kinetic reversibility of the redox couple.⁹

1.2 Electrochemical Interface

In contrast to homogeneous reactions, which occur in a single medium, electrochemical reactions take place heterogeneously at the electrode-electrolyte interface.¹⁰⁻¹¹ The characteristics of the interface impact the electrochemical performance importantly. At the interface, charge transfer and mass transport meet, in conjunction with potential and concentration gradients extending from the electrode surface to the bulk electrolyte. Understanding (the complexity of) this interface is therefore of paramount importance in electrochemical studies.

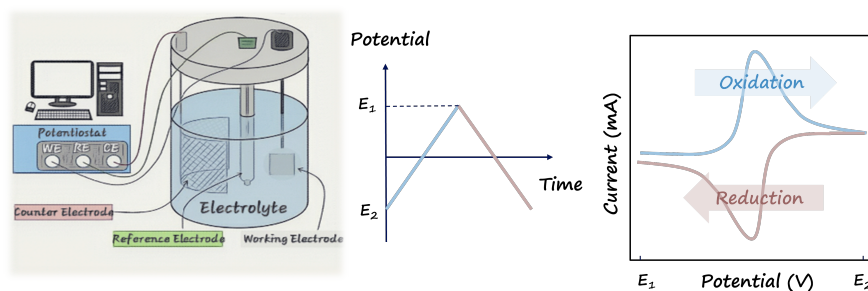


Figure 3. Schematic of a typical three-electrode electrolytic cell set-up and the cyclic voltammetry measurement where the blue curve denotes the forward scan where the electrode potential shifts positively and thus (typically) generating a positive current, while the red curve represents the

1.2.1 Electric double layer

The Electric Double Layer (EDL) is considered the core of the electrochemical interface. EDL corresponds to the spatial ordering of charge in the electrolyte that counters the surface charge on the electrode.¹² It is typically considered to consist of several layers of charged species, as shown in Figure 4, the first of which is located at the centers of the specifically adsorbed species at the electrode surface, known as the Inner Helmholtz Plane (IHP). This is also the location where catalytic reaction intermediates e.g. $^*\text{CO}$ in CO_2 electroreduction and $^*\text{H}$ in H_2 evolution reside. The second layer contains the solvated ions, their closest plane of approach known as the Outer Helmholtz Plane (OHP), where the solvated species reorganize their conformation prior to electron transfer. Due to the thermal motion in the

electrolyte, a third layer of charged species is distributed diffusely into the bulk electrolyte, known as the diffuse layer. The earliest EDL model was proposed by Helmholtz in the 19th century, who suggested a simple, rigid layer of ions adhering to the electrode surface. This model predicts a linear electrostatic potential profile across this interface leading to a constant capacitance. However, the model does not agree with the real EDL behavior as the capacitance varies with electrode potential. Later, Gouy and Chapman introduced the concept of a diffuse layer, where a Boltzmann distribution of the counterions was considered, resulting in the ions spreading out into the bulk electrolyte and a corresponding potential drop across the EDL. The Gouy-Chapman predicts a potential-dependent differential capacitance, with a minimum capacitance at the potential where the surface charge is zero. However, the Gouy-Chapman model does not explain the approximately constant capacitance observed at a highly polarized electrode surface. Stern integrated the ideas of the rigid adsorbed Helmholtz layer with the diffuse layer, which explains better the experimental observations of electrochemical interfaces. More advanced models have included the incorporation of ion size effects and solvent structure into EDL models. These considerations have led to the development of more complex models like the modified Gouy-Chapman-Stern model¹³⁻¹⁴ and the Bockris-Devanathan-Müller (BDM) model,¹⁵⁻¹⁶ which account for the finite size of ions and the orientation of solvent molecules, respectively.

The ongoing research in the field of EDL is focused on achieving a comprehensive

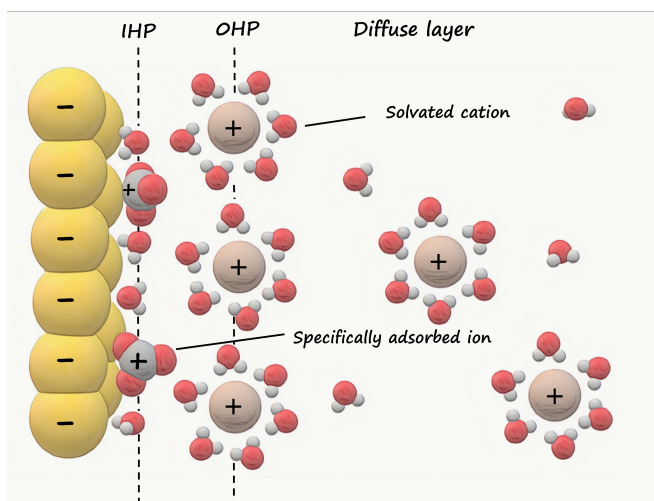


Figure 4. Schematic of the electric double layer region in aqueous solution including a negatively charged electrode surface and specifically adsorbed ions in the Inner Helmholtz Plane (IHP). OHP =

understanding of the interfacial phenomena at the molecular level, using advanced computational and experimental techniques like molecular dynamics simulations and in-situ spectroscopy. These studies aim to unravel the complexities of the EDL, such as the specific adsorption of ions,¹⁷ the role of solvent molecules,¹⁸ and the impact of electrode surface morphology¹⁹ on the EDL properties. The insights gained from these investigations are expected to accelerate the development of more reliable EDL models, which will further benefit the study of electrochemical processes and systems.

1.2.2 Electrode surface effect

As a vital component of the electrode-electrolyte interface, the electrode surface plays an indispensable role in electrochemical processes. When a reactive species arrives in the proximity of the electrode surface, it interacts with the surrounding solvent species and with the electrode surface itself. Depending on the interactions between the reactant and the electrode, the electrode surface functions differently in heterogeneous reactions. When the interaction is relatively weak, the reactant reorients the configuration of its solvation shell in the OHP but does not contact the surface directly during the reaction. This is known as the outer sphere electron transfer reaction, of which the redox reaction of $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ would be a classic example, where the electrode surface merely serves as an electron reservoir and the nature of the electrode surface barely impacts the reaction. These reactions tend to proceed comparatively fast as there is no adsorption or bond formation or breakage occurring during the process. In contrast, if bond rearrangement or adsorption is involved in an electron transfer reaction, the reactive species partially loses its solvation shell and comes into direct contact with the surface in the IHP. Such processes are referred to as inner-sphere electron transfer reactions; electrocatalytic reactions belong to this class. In this scenario, the composition and the structure of the electrode surface markedly influence the electrochemical performance.

Considerable research efforts have been dedicated to revealing the relationship between the reaction performance and a certain parameter of the electrode or the active sites, such as the work function (E_F),²⁰ the strength of the metal-hydrogen bond,²¹⁻²² and the presence of the empty d-band orbitals.²³ One of the most distinguished empirical models is Sabatier's principle,²⁴ which correlates the reaction rate to the adsorption energy between the key catalytic intermediate binding to the electrode surface. A proper catalyst is expected to bind with the reaction intermediate with an intermediate strength. A strong interaction between the intermediate and the surface hinders the subsequent desorption and deactivates the reaction sites, while a weak interaction slows down the initial adsorption process. For instance, the Sabatier principle aids in interpreting the dependence of the CO_2

electroreduction reaction rate on the metal identity. Cu and Cu alloys²⁵ are the most promising metal materials capable of producing multi-carbon species from CO₂ electroreduction, as they bind to the primary intermediate *CO appropriately. Strong adsorption of CO, such as with Pt, hampers the reaction performance, while weak adsorption of CO, as seen with Au, impedes subsequent reduction and mainly generates CO.

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Electrode surface modification customizes the composition and characteristics of the electrode surface, hence tuning its electronic structure to optimize the electron transfer rate of the reaction process. Research has shown that modifying the surface properties through strategies such as alloying,^{25,27} doping,²⁸⁻²⁹ or creating roughness³⁰⁻³¹ can enhance the efficiency and selectivity of CO₂ electroreduction. The presence of certain metals or dopants in the catalyst can alter the electronic properties of the surface, thus affecting the reduction pathway and the energy barrier of the reaction. Specific surface facets provide distinctive active sites that promote the selectivity and activity for desired products. The activity of silver for CO₂ electroreduction, for example, has been reported to be strongly facet dependent.³² Additionally, surface reconstruction and modification strategies, such as using surfactants, can significantly improve electrode performance. Studies reported that the electrode modified with Cetyltrimethylammonium bromide (CTAB) surfactant³³⁻³⁴ exhibited a marked increase in CO₂ reduction activity and selectivity for CO production. This improvement was attributed to the formation of a favorable modified electrode/electrolyte interface with CTAB. Similarly, carbon-based electrodes functionalized with molecular organometallic complexes are beneficial to the dispersion of active components and facilitate the heterogeneous electron transfer, which further enhances the CO₂ electroreduction performance.³⁵⁻³⁶

1.2.3 Mass transfer condition

During the (fast) electron transfer reaction at the interface, concentration gradients of the species involved in the reaction will develop from the electrode surface into the bulk electrolyte. This means that the interfacial concentration of the reactive species deviates considerably from the bulk value, which is due to the mismatch between the rate of charge transfer and mass transfer. Mass transfer is the result of gradients in the electrochemical potential, or the movement of solution by spontaneous or applied convection. Depending on different driving forces, there are three common modes of mass transfer, namely diffusion, migration, and convection. Diffusion denotes the movement of a species driven

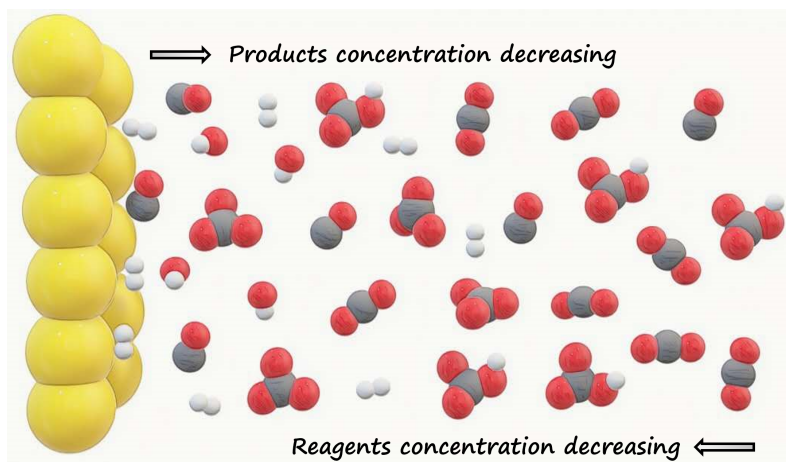


Figure 5. Schematic of the concentration gradients near the electrochemical interface where the product concentration increases from the electrode surface to the bulk phase while the reactant concentration decreases from the bulk phase to the electrode surface.

by a chemical potential gradient i.e. a concentration gradient. Migration involves the movements of a charged species driven by an electrical potential difference, while convection occurs due to stirring or hydrodynamic transport. The contribution of migration of the reactant can be neglected by using an excess of supporting electrolyte species in the solution, while convection can be ignored in a stagnant solution. Figure 5 illustrates that with the consumption of the reactant and generation of the products by the reaction, concentration gradients are formed, resulting in the transport of reactant from the bulk electrolyte to the surface and the product moving in the opposite direction. Under a mass transfer-controlled condition, the slower mass transfer compared with the electron transfer results in the incapability to replenish the consumed reactant and eliminate the accumulated product. In the absence of convection, the thickness of the diffusion layer grows over time and the current continuously decays, but in a convective system, it quickly reaches the steady-state value.

To study fast reaction kinetics, various methods can be used to control and increase the mass transfer rate, such as the Rotating-Disk-Electrode (RDE) and the Ultramicroelectrode (UME). RDE is a powerful and widely-used electroanalytical tool in electrochemical studies, which controls hydrodynamic

environment and generates well-defined mass transfer conditions for electrode kinetics investigations. It consists of a conductive disk, typically made of noble metal or glassy carbon, and an inert polymer shroud. Since the electrode is rotating during the measurements, a mass transfer contribution is brought about by the forced convection. Once the reactant is exhausted by the electrochemical reactions at the surface, the limiting current density is reached, which represents the largest current density under the given mass transfer-controlled conditions. By solving the relevant convective-diffusion equation displayed in eq. 7 (for one dimension):³⁷

$$\frac{\partial C_j}{\partial t} = D_j \frac{\partial^2 C_j}{\partial y^2} - v_y \frac{\partial C_j}{\partial y} \quad (7)$$

where on the right-hand side, the first and the second terms represent diffusion and convection respectively, the concentration profile can be calculated and the limiting current density is then given by the Levich equation (eq. 8):³⁸

$$i_l = 0.62nFAD^{2/3}\omega^{2/3}\nu^{2/3}C^* \quad (8)$$

where D is the diffusion coefficient of the electroactive species, ω is the rotation rate of RDE, ν is the kinematic viscosity, and C^* is the bulk concentration of the electroactive species.

Understanding mass transfer is extremely important in electrochemical studies. Mass transfer causes concentration polarization, making the characteristics of the interface remarkably different from those in the bulk phase. With the development of numerical simulation and in-situ spectroscopy techniques in modern electrochemistry, we now have the opportunity to visualize the details of mass transfer with the necessary resolution. Notably, the ring electrode in the Rotating Ring-Disk electrode can be used as an in-situ sensor to examine the interfacial environment under well-defined mass transfer conditions, without any interference to the reaction process.

1.2.4 Electrolyte effect

The interfacial electrolyte is an important part of the electrochemical interface. Inert electrolyte species are involved in the electrochemical current flow as charge carriers to establish the conduction path in the solution. However, at the interface, due to the influence of the electric field and the heterogeneous electron transfer process, electrolyte species in close vicinity of the electrode may interact with the electroactive species and the electrode itself. Although electro-inactive by themselves, they might hence impact the electron transfer in an implicit way.³⁹ An idealized single electron transfer process comprises mass transfer of the reactant, adsorption, electron transfer, desorption, and mass transfer of the product (outer sphere reactions taking place without adsorption and

desorption). However, in practical studies, the reactant and/or the product might undergo chemical reactions with the electrolyte species before or after the electrochemical reactions, resulting in complex reaction pathways e.g. CE reaction (with a preceding chemical reaction), EC reaction (with a subsequent chemical reaction). The hydrolysis of the hydrated cation, the interaction of the cation with the reaction intermediate, the homogeneous reactions of anions, and the resulting variation of interfacial pH all impose profound influences on the reaction process, which will be elaborated and demonstrated in the next few chapters.

1.3 CO₂ reduction reaction

Carbon is the pivotal element of all life on Earth. It is stored and circulated within the atmosphere, the ocean, the ecosystem, and the lithosphere, during thousands of years, which forms the Natural Carbon Cycle (NCC).⁴⁰ CO₂ is released into the atmosphere by the respiration of plants, consumption of organic carbon by animals and decomposition of organic matter by microorganisms, while it is solidified and stored as organic carbon *via* photosynthesis of plants and as lithosphere in the long term. Alternatively, the scientific community has been dedicated to the development of the anthropogenic carbon cycle (ACC), which is based on the capture, fixation, and temporary storage of CO₂ followed by the conversion of CO₂ into commercial products. Compared with NCC, the anthropogenic carbon cycle can be industrially scaled up to produce sustainable, renewable, and environmental-friendly carbon sources. Here, CO₂ is treated as a valuable industrial C1 raw material to produce valuable products, instead of a greenhouse gas that does harm to the global environment.

CO₂ is a linear and centrosymmetric molecule, with two C=O bonds which require 800 kJ mol⁻¹ to dissociate. This endothermic CO₂ reduction reaction can be powered by biomass energy,⁴¹ photon energy,⁴² thermal energy,⁴³ and electricity.⁴⁴ In comparison with other techniques, electrochemical CO₂ reduction reaction (CO₂RR) in aqueous solution is simply carried out through the passage of a current under a moderate reaction condition. Importantly, when coupled with renewable energy e.g. solar energy, wind energy, and hydropower, CO₂RR produces carbonaceous feedstock with zero carbon emission. The early examples of CO₂RR dates back to 1900s,⁴⁵⁻⁴⁶ in which CO₂ was reduced on mercury electrode, followed by enlightening studies by Hori et al of CO₂RR on Cu electrode.⁴⁷⁻⁴⁸ Since then, investigations have been focused on the development of a highly efficient and selective electrocatalyst system. In the past decade, impressive breakthroughs have been made in the exploration of selective reaction pathways for C₂₊ products,⁴⁹⁻⁵¹ which is based on the understanding of the CO₂ activation mechanism, guided by the Sabatier principle. With the progressive advancement of nanoscience, material science, and computer science,

great progress has been achieved in catalyst design,^{39,52} reaction understanding,⁴⁴ electrolyzer construction²⁶ and industrialization.^{35,53} However, there are still challenges, including improving the current density and the catalyst durability to a real industrial scale. Therefore, further innovation is needed in catalyst selectivity, activity, and cost-effectiveness, as well as enhancements in energy efficiency and system stability for the transition from lab setting to industrial application. CO₂RR is a promising technology to contribute to environmental concerns and energy demands to realize carbon neutrality. The future should be targeting to devise a sustainable and highly efficient electrochemical system to convert CO₂ into other value-added products with an acceptable cost and a simple downstream treatment.

1.4 H₂ evolution reaction

The current energy landscape still highly counts on fossil fuels, which imposes significant worldwide challenges, such as greenhouse gas emissions and energy crisis. The move to renewables is picking up momentum, among which green hydrogen, as a clean energy carrier, is a promising alternative to fossil fuels due to its high energy density and zero-emission character. Despite the abundance of hydrogen elements on Earth, it is combined in various compounds, making its production energy demanding. Unfortunately, the principal and least expensive technique of hydrogen production still relies on reforming fossil fuels or other multi-carbon compounds, due to the low energy cost, although it causes massive pollutant emissions (i.e. CO₂) and needs further purification of hydrogen from other by-products e.g. CO₂ and CO. Alternatively, hydrogen can also be produced by water electrolysis,⁵⁴ thermochemical process,⁵⁵ photoconversion,⁵⁶ or photobiological processes,⁵⁷ from which water electrolysis is the most affordable, pollution free, and efficient. More importantly, when coupled with electricity derived from renewable sources such as solar and wind power, water electrolysis is highly sustainable with a minimal carbon footprint. This is in alignment with the goal of a low-carbon economy, where green hydrogen could play a critical role in decarbonizing the chemical industry, in energy storage and serve as a power source for various applications.

Hydrogen Evolution Reaction (HER) is a critical component of water splitting, laying the cornerstone of electrocatalysis. The efficiency of the HER is highly dependent on the electrode material. Design, synthesis, and analysis of these HER electrode materials have been the subject of extensive research.⁵⁸⁻⁶⁰ Pt-group catalysts are noted for their high activity and stability for HER, but their scarcity and high cost largely impede their application⁶¹⁻⁶². Recent advancements have focused on the exploration of alternative non-precious metal catalysts, including transition metal sulfides, phosphides, and selenides such as iron,

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cobalt, and nickel-based complexes.⁶³⁻⁶⁵ These materials offer an excellent combination of good activity and affordability, which is necessary for large-scale implementation. Since HER is a typical inner sphere (catalytic) reaction that is highly surface sensitive, the performance of the catalyst is heavily influenced by the electrode surface properties e.g. such as electronic structure, surface morphology, and interaction with the electrolyte. Tuning the structure of the catalyst enhances HER performance by providing more active sites,^{60,66} while doping catalysts with other elements introduce local heterostructures that can modify the electronic structure, thereby improving the catalytic activity.^{63,67-68}

Elucidating complex reaction mechanisms is of great importance for HER, especially under alkaline conditions where the kinetics are slower compared with acidic media. Studies have demonstrated the prominent influence of the electrolyte species.⁶⁹⁻⁷⁰ Disclosing the role of these electro-inactive species in the interface and their interaction with the reactant and the reaction intermediates during HER can make an eminent contribution to the fundamental understanding of HER. Besides, reaction parameters such as the adsorption energies of certain intermediates and the potential dependence of the reaction rate have been investigated as interfacial descriptors of the HER, offering valuable insights and principles for the rational design of electrocatalysts.^{62,71-72}

The integration of the HER process with renewable energy is a viable path to produce sustainable hydrogen. The declining costs of renewable electricity render water electrolysis an attractive candidate for industrial hydrogen production. However, challenges remain in improving the efficiency and reducing the cost of electrolyzers. Coupling electrochemistry with the advanced techniques such as in-situ spectroscopies, molecular simulations, can assist in progressing the understanding of the interfacial environment of HER at a molecular level, eventually contributing to a more sustainable, efficient and affordable production of green hydrogen.

1.5 Scope of this thesis

During the heterogeneous electron transfer process, the electrochemical interface provides a non-uniform environment for the reactive species, in which the inert electrolyte species are part of the molecular micro-environment and have a profound influence on the reaction process. Interfacial pH plays a decisive role among these interfacial parameters. The main goal of this thesis is to develop an in-depth understanding of the interplay between the interfacial pH and other electrolyte effects and evaluate its impact on CO₂RR and HER.

In **Chapter 2**, we devise a reliable and highly sensitive interfacial pH sensor using RRDE coupled with a voltammetric redox couple, to visualize the variation of interfacial pH during HER under well-defined mass transport conditions. Protic anions are shown to impact the

interfacial pH through homogeneous reactions with the electrogenerated OH^- , i.e. the buffering acid-base reaction. **Chapter 3** demonstrates the influence of CO_2 , HCO_3^- , the alkali cations, and mass transport on the interfacial pH during CO_2RR . We find that the buffering capacity increases in the order $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+ < \text{HCO}_3^-$. The interfacial pH in turn impacts the speciation near the interface, the electrochemical reaction, and the competition between CO_2RR and HER. Inspired by these results, in **Chapter 4**, CO_2RR is carried out in mildly acidic media, where the CO_2RR is capable of competing with proton reduction under proper conditions. By adjusting the interfacial environment *via* the protic anion HSO_4^- , the weakly hydrated alkali cations e.g. Cs^+ , and mass transfer, the Faradaic Efficiency of CO_2RR can reach over 80%, even under acid conditions. Finally, **Chapter 5** demonstrates the impact of HSO_4^- and the weakly hydrated alkali cations on the steady state current of HER. The limiting current density increases with the concentration of these inert electrolyte species. The linear variation of the Koutecký-Levich Slope with respect to the concentration of these species is revealed, out of which valuable thermodynamic information is extracted through mathematical analysis.

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