EFFECTS OF ELECTROLYTE CATIONS 
ON ELECTROCHEMICAL CO₂ 
REDUCTION VIA ANALYSIS OF THE 
ELECTRODE-ELECTROLYTE 
INTERFACE

by

Zhuoqun Zhang

A dissertation submitted to The Johns Hopkins University 
in conformity with the requirements for the degree of 
Doctor of Philosophy

Baltimore, Maryland 
August, 2021

© 2021 Zhuoqun Zhang 
All rights reserved
Abstract

Urgent actions are required to protect the environment from catastrophic climate change; to accomplish this we need to decrease our dependence on fossil fuels and reduce the CO₂ concentration in the atmosphere. The electrocatalytic CO₂ reduction reaction (CO₂RR) is a promising solution for converting CO₂ to energy-dense chemical fuels from intermittent renewable energy. Copper-based materials are widely explored for electrochemical CO₂RR since it is the only metal that is capable of catalyzing CO₂ reduction to a wide range of hydrocarbons. However, it is still challenging to achieve an appreciable conversion rate and selectivity for large-scale CO₂ conversion in industrial applications. The hydrogen evolution reaction (HER) is a competitive side reaction that reduces the performance of CO₂ conversion. The HER occurs during CO₂RR because it has a lower onset potential and lower kinetic barrier than the potentials required to reduce CO₂. Therefore, this thesis aims to understand how cations in electrolyte affect the performance of CO₂RR and HER on copper electrodes via analysis of the electrode-electrolyte interface.

Surface-enhanced infrared absorption spectroscopy (SEIRAS) can be used to track surface-adsorbed species on the electrode and sketch a profile of electrical double layer (EDL) under reaction conditions. The replacement
of a significant fraction of interfacial water and the perturbation of surface-adsorbed CO are caused by the presence of cationic CTAB, an amphiphilic ionic organic molecule, which leads to the enhanced performance of CO$_2$RR and HER suppression. The interplay between various alkali cations and CTAB was investigated during electrochemical CO$_2$RR on copper electrodes. Alkali cations coexist with CTAB within the double layer which gives rise to an improved formate generation.

This work demonstrates a significant correlation between interfacial cations and the performance of electrochemical CO$_2$ conversion, which also provides fundamental insights for understanding reaction pathways. Findings in this work are valuable for designing efficient routes for CO$_2$RR and other electro-catalytic reactions.

**Primary Reader and Advisor:** Anthony Shoji Hall

**Secondary Reader:** Chao Wang
Acknowledgments

I am grateful to my advisor, Prof. Anthony Shoji Hall, for introducing me to electrochemistry and catalysis, and for his support along the road of my Ph.D. study. I also appreciate him for giving me the freedom to explore different research ideas and conduct research through trial and error, which inspired me to shape my independence in work and life.

I am thankful to our collaborators, Prof. Van Sara Thoi and her student Soumyodip Banerjee, for their generous exchange of new ideas and thoughtful discussions through our work. I would also like to express my gratitude to Prof. James B. Spicer and Prof. Mingwei Chen for serving as the committee in my thesis proposal and GBO examination, and to Prof. Susanna Thon, Prof. Jonah Erlebacher, Prof. Chao Wang, Prof. David Gracias for serving as the committee in my GBO examination.

Besides, I am grateful to my dear lab mates: Du Sun, Yunfei Wang, Fufei An, Chunsong Li, Hamdan Alghamdi, Hyun Woo Chung, Yaming Ma, Cheng Fang, Matthew Lee, Ty Gong, Jiaxin Gao, Nick Zhang, and Jenna Carton, who made this long journey enjoyable and full of good memories. I would also like to acknowledge all the administrative and technical staff in the Department of Materials Science and Engineering, Department of Chemistry, Integrated
Imaging Center, and Department of Physics & Astronomy.

Last but not the least, I want to express my gratitude and love to my family, my best friends, and my boyfriend for sharing all my happiness and sadness and always being supportive, no matter how far we were from each other. Without them, I could not make this marathon-like journey to the end. Together with them, I have grown and progressed to who I am and where I am.
Table of Contents

Abstract ii

Acknowledgments iv

Table of Contents vi

List of Tables ix

List of Figures x

1 Introduction 1

1.1 Catalysis and electrocatalysis ................................. 1

1.1.1 Catalysis .................................................. 1

1.1.2 Electrocatalysis .......................................... 5

1.1.3 Electrochemical CO₂ reduction ........................... 10

1.2 Electrode-electrolyte interface ............................... 13

1.2.1 Electric double layer .................................... 13

1.2.2 Cations impacts on electrocatalytic processes via the
electric double layer ........................................... 14
1.2.3 Investigations on interfacial water and adsorbed intermediates of electrochemical CO\textsubscript{2} reduction .... 19

1.3 Summary ..................................................... 27

2 Methods and characterizations for electrochemical CO\textsubscript{2} reduction 42

2.1 Sample preparation ........................................ 42

2.2 Electrocatalysis of CO\textsubscript{2} reduction in aqueous solution .... 44

\hspace{1em} 2.2.1 Experimental Set-up .................................. 44

\hspace{1em} 2.2.2 Product analysis ........................................ 46

\hspace{1em} 2.2.3 Partial current density and Faradaic efficiency for each CO\textsubscript{2} reduction product ......................... 47

2.3 Surface-enhanced infrared absorption spectroscopy for analysis of the electrode-electrolyte interface ........... 48

3 The effects of cationic surfactant additives on the electrocatalytic CO\textsubscript{2} reduction over Cu electrodes 55

3.1 Introduction .................................................. 55

3.2 Electrocatalytic performance of CO\textsubscript{2}RR and HER in an electrolyte with the addition of CTAB ............ 57

3.3 Dynamics of interfacial species in the electric double layer with potential dependence via in-situ spectroscopic detection .... 61

\hspace{1em} 3.3.1 Infrared spectroscopy for interfacial water orientation . 62

\hspace{1em} 3.3.2 Infrared spectroscopy for CTAB orientation ............ 65
3.3.3 Infrared spectroscopy for the dynamics of water, electrolyte anions, and CTAB at the electrode-electrolyte interface .............................................. 66
3.4 Influence of interfacial CTAB on the reaction rate of HER and \( \text{CO}_2 \text{RR} \) ................................................................. 71
3.5 Summary ................................................................. 76

4 Combined effects of alkali metal cations and surfactant cations on the electrocatalytic \( \text{CO}_2 \text{ reduction over Cu electrodes} \) 85
4.1 Introduction ......................................................... 85
4.2 Electrocatalytic performance of \( \text{CO}_2 \text{RR and HER in CTAB-containing alkali metal electrolytes} \) ......................... 86
4.3 Dynamics of water and CTAB in the electric double layer with time dependence via in-situ spectroscopic detection ............. 91
4.4 CTAB perturbation on hydrated alkali cations in the electric double layer ................................................................. 94
4.5 Summary ................................................................. 95

5 Summary and outlook 101
5.1 Summary ......................................................... 101
5.2 Outlook ......................................................... 103
List of Tables

1.1 Thermodynamic conversions during electrochemical CO₂ reduction. ................................................. 12
List of Figures

1.1  Schematic representation of the Gibbs energy profile for a catalyzed and an uncatalyzed reaction  ......................................... 4
1.2  Illustration of electrochemical devices ........................................ 9
1.3  Illustration of the electric double layer at cathode ....................... 15
1.4  Electric field distribution of a plane parallel to the electrode surface ................................................................. 16
1.5  Free-energy diagram for CO\textsubscript{2} (g) reduction to CO ............. 18
1.6  Alkali cations effect on electrochemical CO\textsubscript{2} reduction on Cu electrode ................................................................. 19
1.7  Infrared absorption spectroscopy of interfacial water with potential dependence ................................................................. 22
1.8  Configuration of interfacial water with potential dependence . .... 23
1.9  Alkali cations effect on the IR peak frequency of CO adsorption as a function of potential .......................................................... 25
1.10 Quaternary ammonium cations effect on surface-adsorbed CO   26
2.1 Schematic representation of the homemade H-cell for electrochemical CO$_2$RR. 45
2.2 Schematic path of IR beam in ATR-FTIR. 50
3.1 CTAB effect on electrochemical HER and CO$_2$RR with potential dependence on Cu 59
3.2 CTAB effect on the selectivity of electrochemical CO$_2$RR with potential dependence on Cu 60
3.3 Illustration of an in-situ ATR-FTIR setup with a home-made electrochemical device 62
3.4 Infrared absorption spectroscopy of interfacial water and CTAB with potential dependence 64
3.5 Infrared absorption spectroscopy of surface-adsorbed CO with potential dependence and CTAB effect 67
3.6 Integrated band intensities of OH, OCO, and CH IR absorption as a function of potential 69
3.7 Concentration effect of CTAB on the IR absorption of interfacial water and the reaction rate of HER 73
3.8 CTAB effect on the IR absorption of surface-adsorbed CO and the reaction rate of CO production 75
4.1 CTAB effect on the reaction rate and Faradaic efficiency of HER on Cu under the influence of alkali cations 87
4.2  CTAB effect on the reaction rate and selectivity of CO$_2$RR on Cu under the influence of alkali cations .......................... 89
4.3  Alkali cations effect on the reaction rate of HER and CO$_2$RR as a function of the concentration of CTAB ................................. 90
4.4  CTAB effect on the IR absorption spectroscopy of interfacial water with time dependence under the influence of alkali cations 92
4.5  Alkali cations influence on the IR absorption spectroscopy of CTAB with time dependence ................................. 94
4.6  Combining effect of CTAB and alkali cations on the electrical double layer ................................................................. 96
Chapter 1

Introduction

1.1 Catalysis and electrocatalysis

1.1.1 Catalysis

Catalysis describes a phenomenon in which the rate of a chemical reaction is accelerated by the addition of a reagent which is not consumed during the reaction. This reagent is known as the catalyst which opens up a route between reactants and products with a lower activation barrier than the uncatalyzed reaction. The term “catalysis” was brought up by Jöns Jacob Berzelius in 1836, who summarized the findings of several scientists in the late 18\textsuperscript{th} and early 19\textsuperscript{th} centuries [1]. For example: Gottlieb Sigismund Constantin Kirchhoff found that the promoted conversion of starch into sugar in heated mineral-acid solutions, without consumption of the acids; the report from Humphry Davy that the combustion of a gaseous mixture of oxygen and coal gas was initiated on platinum and palladium without a chemical change to the metals; and the observation by Thenard that hydrogen peroxide in acid solution decomposed under the influence of alkali metals and manganese...
dioxide, silver, platinum, gold, but without activity loss on these substances. Nowadays, more than 85% of all chemical products involve the assistance of catalysts at some stage during the manufacturing process [2]. In industrialized countries, 15-20% of their economic activities rely on catalyzed processes [3]. For example, ammonia is one of the most highly demanded industrial chemicals worldwide, its production involves multiple catalytic processes for hydrogen generation and ammonia formation (also known as the Haber-Bosch process) in modern ammonia-producing plants. Therefore, it is useful to understand the principles of catalysis science.

In a catalyzed reaction, the catalyst plays a key role in increasing the reaction rate, but a catalyst cannot alter the direction of the equilibrium. In other words, catalysts won’t help to make a thermodynamically unfavorable reaction happen. According to the second law of thermodynamics, the balance between two sides of a chemical reaction is determined by the Gibbs free energy difference between products and reactants [4]. The chemical balance lies in an equilibrium of a reaction described by the equilibrium constant, which is the ratio of products to reactants in the form of pressure or concentration, once the reaction has reached equilibrium. The equilibrium constant of a reaction is related to the Gibbs free energy difference as shown in equation 1.1:

\[
K = \exp(-\Delta G/RT)
\]

(1.1)

Where \( K \) is the equilibrium constant, \( \Delta G \) is the Gibbs free energy difference between two sides of the reaction, \( R \) is a gas constant, \( T \) is temperature. Therefore, the equilibrium constant is determined by the reactants, products and
their states (temperature, pressure, or concentration), but it is not dependent on the catalyst.

As the reaction proceeds, reactant molecules come into contact, distort, and begin to exchange or discard atoms. During this process, an activated complex at the maximum Gibbs free energy occurs in the space between reactants and products. This crucial configuration at the peak of the reaction coordinate is also called the transition state of the reaction [4]. Once the clusters of reactants pass through this transition state, they continue to progress to become products. Therefore, the transition state creates an energy barrier that must be overcome before reactants can reach their final state. If the transition state shifts to a lower energy or if it consists of multiple states with smaller energy differences from the reactants, then the reaction will proceed more quickly to products (i.e. improved kinetics). A schematic representation in Figure 1.1 shows how different reactions progress with and without a catalyst [2, 5]. In the catalyzed reaction, the original transition state at a high Gibbs energy can be altered to consist of multiple transition states with much smaller energy barriers, of which two states are at lower Gibbs energy levels than the reactants. This new set of transition states allow the clusters of reactants to pass through each transition state quicker before reaching the final product. Therefore, more reactants are able to convert to products with the assistance of a catalyst in the same period in comparison to an uncatalyzed reaction.

Reactions can be classified as homogeneous catalysis or heterogeneous catalysis based on the phase of the catalysts and reaction mixture [4]. A homogeneous catalyst is in the same phase as the reactants (usually gaseous or liquid),
Figure 1.1: Schematic representation of the Gibbs energy profile for a catalyzed and an uncatalyzed reaction. Reproduced with permission from [2]. Copyright 2012 American Chemical Society.

which is soluble in the reaction mixture. For example, hydrogen peroxide in an aqueous solution will rapidly decompose into water and oxygen gas in presence of iodide ions which act as a homogeneous catalyst [6]. A heterogeneous catalyst is in a different phase from the reactants, which is not separated from the reaction mixture. The decomposition of hydrogen peroxide in an aqueous solution, it can be catalyzed by various metals and solids such as platinum, silver, and manganese oxide [6, 7]. Homogeneous catalysts are easier to tailor for specific purposes than heterogeneous catalysts because they are in the same phase with the reaction mixture. However, homogeneous catalysts have separation problem since they cannot be easily removed from the products; this makes it inconvenient for continuous operation. On the
contrary, using heterogeneous catalysts is a way to solve the separation issue, since in the heterogeneous catalysis, the reactants need to adsorb onto the surface of the catalyst. A wide range of effects will play a role in heterogeneous catalysis because of the phase boundary, such as the surface property of the catalyst, environmental properties in the immediate proximity of the catalyst interface, and interactions between reactants and catalysts. It’s worth mentioning enzymes can serve as a biocatalyst, which is an intermediate type between homogeneous and heterogeneous catalysts, are very specific in biological reactions [4]. This type of catalysts won’t be expanded in detail due to the scope of this thesis.

1.1.2 Electrocatatalysis

Electrocatalysis is a transformation that takes place at an electrified solid-solution interface. Electrochemical reactions can be broken up into two half reactions: an oxidation reaction and a reduction reaction. At the anode the reactant is oxidized by the loss of electrons to the electrode. At the cathode the reactant is reduced by gaining electrons from the electrode. Ionic molecules from the electrolyte move between the electrodes to complete the circuit. [4, 8].

Consider the reaction shown below:

\[ A + B \rightarrow AB \]

which is composed of two half reactions:

oxidation: \[ A \rightarrow A^+ + e^- \], with equilibrium potential \( E_1^0 \) at standard condition

reduction: \[ B + A^+ + e^- \rightarrow AB \], with equilibrium potential \( E_2^0 \) at standard
condition

The equilibrium potential values ($E_1^0$ and $E_2^0$) can be looked up in the table of standard reduction potentials. Therefore, the cell potential of this electrochemical reaction is calculated by:

$$E_{cell}^0 = E_{(cathode)} - E_{(anode)} = E_2^0 - E_1^0$$  \hspace{1cm} (1.2)

According to the work of a German chemist, Walther Nernst, who extended Gibbs’ theory to electrochemistry. He established the relationship between the Gibbs free energy of an electrochemical reaction and the cell potential, described as below:

$$\Delta G^0 = -n \times F \times E_{cell}^0$$  \hspace{1cm} (1.3)

$$\Delta G = -n \times F \times E_{cell}$$  \hspace{1cm} (1.4)

Where equation 1.3 is at standard condition, $n$ is the number of electrons transferred per mole of the reaction, $F$ is the Faraday constant. From the second law of thermodynamics, we have:

$$\Delta G = \Delta G^0 + R \times T \times \ln(Q)$$  \hspace{1cm} (1.5)

Where $R$ is the gas constant, $T$ is temperature and $Q$ is the reaction quotient as a function of the activities or concentrations. Therefore, the well-known Nernst equation for a complete electrochemical reaction is derived from equation 1.3,
\[ E_{\text{cell}} = E^0_{\text{cell}} - R \times T / [n \times F \times \ln(Q)] \]  \hspace{1cm} (1.6)

Similar to a conventional reaction, kinetic barriers are also common in electrochemical reactions. Specifically speaking, kinetic barriers occur for half-reactions at the interface between the electrode and the electrolyte. Considering equations 1.1 and 1.4, the reaction rate of an electrochemical reaction is determined by its cell potential. When at open circuit, no current is passing through the electrode, the current half-cell potential is assumed to be at the reversible potential \( E_{\text{rev}} \). Each half reaction needs to overcome a kinetic barrier to proceed; therefore, a potential larger than the equilibrium potential is required for the reaction to proceed in a specific direction. This extra potential, called overpotential (\( \eta \)), is defined as the difference between the actual potential applied (or measured, \( E \)) and the reversible potential.

\[ \eta \equiv E - E_{\text{rev}} \]  \hspace{1cm} (1.7)

An electrochemical reaction involves two half-reactions occurring at the interface between the electrode and the electrolyte; it can be attributed to three causes: 1) activation overpotential \( \eta_{\text{ac}} \) is the potential difference across the electrode interface generated by the passing current, which reflects the extra Gibbs energy of activation in the electrochemical reaction (or half-reaction); 2) resistance overpotential \( \eta_{\text{iR}} \) is the residual potential drop \( (iR) \) in the electrolyte; 3) concentration overpotential \( \eta_{\text{conc}} \) is the result from concentration gradient of
ionic species from the bulk electrolyte to the region near the electrode surface, which is influenced by the rate of mass transport of those ions. In summary, the overpotential can be written as the sum of the above three terms:

\[ \eta = \eta_{ac} + \eta_{iR} + \eta_{conc} \]  

(1.8)

An increased overpotential requires more energy consumed to keep a constant current density. Hence, all three overpotentials should be controlled as low as possible to avoid energy being wasted in an electrochemical reaction. The overpotential is related to the reaction rate, which is determined by the inherent kinetics of the reaction and the mass transfer efficiency of the reactants and products.

The electrode serves as a heterogeneous catalyst which can increase the current density at a given overpotential or decrease the overpotential needed to reach a given current density. Electrochemical devices enable the direct conversion between chemical and electrical energy with minimal energy lost to heat. For example, fuel cells have been used as an alternative method for recovering stored chemical energy. Fuel cell device enables the large-scale conversion of chemical energy into electricity at room temperature. A schematic device of a hydrogen fuel cell is shown in Figure 1.2 a), in which hydrogen gases is oxidized at the anode releasing electrons to generate electricity. The two half-cell reactions are the oxidation of hydrogen gas at the anode to protons and the reduction of oxygen gas at the cathode combining protons into water [9–11]. Platinum-based catalysts and other metal catalysts (such as silver, gold, palladium, nickel, iridium, etc.) are commonly used as electrocatalysts at the
Another important application of electrocatalysis is the electrolyzer, which performs non-spontaneous transformations under mild conditions. Reactions of this type include chlorine production from a sodium chloride solution and large-scale hydrogen generation from water [12–17]. A schematic device of water electrolysis cell is shown in Figure 1.2 b), in which water decomposes into hydrogen and oxygen with the help of an electrocatalyst. Hydrogen production in this way provides an opportunity for a CO$_2$-free renewable process and is also a clean fuel source for hydrogen fuel cell systems. The half-cell reactions are the oxidation of water molecules at the anode to oxygen...
gas and the reduction of protons at the cathode to hydrogen gas. With a supply of electrical energy and the assistance of electrocatalyst, an endergonic reaction ($\Delta G > 0$) is accomplished in an electrolyzer towards products at a higher Gibbs free energy than reactants.

### 1.1.3 Electrochemical CO$_2$ reduction

Alternative energy applications are being investigated to improve environmental sustainability. Otherwise, climate change will intensify in the near future. The increasing global temperature has already given rise to wildfires in California, relatively low temperatures in Texas, and hurricanes in the southern regions, which had a broad destructive impact. In the 2014 report of the Intergovernmental Panel on Climate Change, 76% of greenhouse gas emissions which cause global warming was from carbon dioxide (CO$_2$) that accumulated through forestry, fossil fuel combustion, and industrial processes $^{[18]}$. Therefore, it has become urgent to decrease the generation of CO$_2$ and maintain a low atmospheric concentration to mitigate catastrophic climate change. Electrochemical CO$_2$ reduction has attracted significant interest since it provides an opportunity to convert excess CO$_2$ to high-energy-dense fuels in a sustainable way. This process couples readily with electricity under mild conditions as an effective way to store renewable electricity from intermittent natural sources $^{[19-24]}$. However, CO$_2$ is highly stable, which makes it challenging to achieve decent conversion and controlled selectivity towards energy-dense fuels using electrocatalysis.

The electrolysis potentials for CO$_2$ reduction are usually more negative than
the equilibrium potentials since the generation of intermediates with higher Gibbs energy than the reactants requires more energy during the process. For example, the first electron transfer to CO₂ forms radical CO₂⁻, which is a key intermediate that forms at a very negative potential (-2.21 V vs saturated calomel electrode) [25]. In addition, the overpotential for CO₂ reduction varies for each product, and products which require more electrons to be transferred to CO₂ have larger kinetic barriers. The electrochemical conversions of CO₂ with thermodynamic equilibrium potentials are shown in Table 1.1, where the electrochemical equilibria of water and proton are considered since CO₂ reduction occurs in aqueous solution [25, 26]. We can see that the equilibrium potentials of CO₂ reduction are close to the potential of hydrogen evolution reaction (HER), which means that HER can occur in parallel with electrochemical CO₂ reduction. HER takes up active sites of the catalyst which interferes and competes with CO₂ reduction, leading to decreased Faradaic efficiencies of CO₂ reduction products [27–30]. Therefore, suppressing HER is equally important to improving the electrochemical kinetics of CO₂ reduction.

Copper (Cu) is the most versatile catalyst for CO₂ reduction since it is capable of producing a wide range of hydrocarbon products [22, 23, 31, 32]. To explain the selectivity of CO₂ reduction products in experiments, theoretical calculations are widely applied to propose the reaction mechanism of C₁ and C₂ productions [31, 33–36]. The formation of *CO₂⁻ intermediate is the rate-limiting step to generate formate (HCOO⁻) on Cu, which is a separate pathway than other products. It has been determined that *CO is a key intermediate
Half-cell reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$E^0$ vs RHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2H^+ + 2e^- \rightleftharpoons H_2$</td>
<td>0.00</td>
</tr>
<tr>
<td>$CO_2 + H^+ + 2e^- \rightleftharpoons HCOO^-$</td>
<td>-0.02</td>
</tr>
<tr>
<td>$CO_2 + 2H^+ + 2e^- \rightleftharpoons CO + H_2O$</td>
<td>-0.10</td>
</tr>
<tr>
<td>$CO_2 + 6H^+ + 6e^- \rightleftharpoons CH_3OH + H_2O$</td>
<td>0.03</td>
</tr>
<tr>
<td>$CO_2 + 8H^+ + 8e^- \rightleftharpoons CH_4 + 2H_2O$</td>
<td>0.17</td>
</tr>
<tr>
<td>$2CO_2 + 7H^+ + 8e^- \rightleftharpoons CH_3COO^- + 2H_2O$</td>
<td>-0.26</td>
</tr>
<tr>
<td>$2CO_2 + 12H^+ + 12e^- \rightleftharpoons C_2H_4 + 4H_2O$</td>
<td>0.08</td>
</tr>
<tr>
<td>$2CO_2 + 12H^+ + 12e^- \rightleftharpoons C_2H_5OH + 3H_2O$</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Table 1.1: Thermodynamic conversions during electrochemical CO$_2$ reduction. Reactions are listed in an order with an increasing number of electron transfers.

during the process of CO$_2$ reduction to hydrocarbons. Following the initial formation of *CO, *HCO is formed with subsequent hydrogenation and electron transfer and finally is reduced to CH$_4$ (major) or CH$_3$OH (minor). On the other hand, C-C coupling via *CO and *CHO or direct CO dimerization from *CO is a crucial step to form C$_2$ species. It has been reported that C$_1$ and C$_2$ species are preferentially formed on different facets of the catalysts. Furthermore, C$_1$ formation shows a different pH dependence than C$_2$ formation [35, 37–40]; which indicates that different reaction mechanisms are associated with C$_1$ and C$_2$ generation. More experimental evidence is needed to decipher details on the intermediates involved during specific reaction pathways. Therefore, strategic designs on the structure of catalysts, the proton concentration, and the composition of electrolytes are beneficial to gain fundamental insight of electrochemical CO$_2$ reduction.
1.2 Electrode-electrolyte interface

1.2.1 Electric double layer

The microenvironment near the electrode surface can have a substantial impact on the performance of an electrocatalytic reaction. Reactants need to diffuse through the solution and adsorb onto the electrode surface before the reaction can proceed. During this process, the reaction kinetics will be affected by the distribution of the electric field, dynamics of electrolyte ions, and solvents (water molecules in aqueous solution) at the electrode-electrolyte interface. Therefore, environmental effects on electrocatalytic processes in an aqueous solution will be discussed in the following sections.

An electrical double layer (EDL) is formed when the electrode surface is placed into solution; counterions from the solution are attracted to the electrode surface to neutralize the interfacial charge \([41, 42]\). A classic model of the electric double layer, the Gouy-Chapman-Stern (GCS) model, is popular for analyzing the electrochemical phenomena at the electrode surface \([8, 43–47]\). Herein, key elements of the model were depicted for the subsequent discussion of this thesis, as shown in Figure 1.3. The electrode describes a negatively charged metal in contact with the aqueous solution. Hydrated cations migrate toward the electrode to neutralize its negatively charged surface, which leads to a depletion of the hydrated anions near the interface. The plane passing through the centers of cations in the first monolayer is called the inner Helmholtz plane (IHP). Close to the first layer of adsorbed ions, the second layer of solvated cations approaching the electrode is assumed to
be in a region called the outer Helmholtz plane (OHP). Both IHP and OHP are in parallel to the electrode surface. Lastly, the region of the double layer beyond the OHP is the diffuse layer, which is filled loosely with hydrated ions, cations are migrating toward the electrode and anions are moving toward the other side. Due to differences in the structure and charge distribution in the compact part (IHP & OHP) and the diffuse part (diffuse layer) within the EDL, the electric potential at the electrode surface drops exponentially with the distance from the surface. The differential capacitance of the EDL is related to the applied potential, which is dependent on the ion-ion interactions and the nature of the electrode surface [8, 46, 48–51].

Based on the EDL model, the concentration and the distribution of cations in the EDL are affected by the applied potential, electrode properties, pH, and interactions with anions of the electrolyte [53–61]. Therefore, cations of the electrolyte are likely to play a crucial role in influencing the rates and selectivity of electrocatalytic processes at the cathode.

1.2.2 Cations impacts on electrocatalytic processes via the electric double layer

The classic double layer models do not consider interactions among discrete ions and interfacial water, and their impact on the profile of the local electric field. With recent developments of electrocatalysis for wise utilization of energy resources, the nature of the electric double layer was explored under electrochemical conditions [62–70]. Due to the discrete nature of the ionic charge, the potentials at the OHP are localized. This fact was supported by density functional theory calculations for the cation-induced electric fields

14
Figure 1.3: Simplified schematic model of the electric double layer at a cathodic electrode (negatively charged metal electrode). The electric potential in the double-layer region as a function of distance from the electrode surface was described as the yellow curve. Reproduced with permission from [52]. Copyright 2019 AIP Publishing.
Figure 1.4: Electric field distribution of a plane parallel to the electrode surface, which includes K cations (large circles, outlined in black) and *CO$_2$ in its vicinity (small circles, outlined in black). One cell of electrode metal atoms (parallelogram in light gray) and solvent atoms (dashed light gray circles) are represented. Reproduced with permission from [62]. Copyright 2016 American Chemical Society.

near the center of adsorbed CO$_2$ on the Ag (111) surface with solvated K cations at coverage of $\frac{1}{36}$ (Figure 1.4). The electric field distribution is highly heterogeneous within the plane, which is localized by the ions. A large electric field on the order of $-1$ V/Å was calculated in the vicinity of the K cation and decayed to zero quickly beyond a distance of 5 Å from the K cation. Hence, only adsorbed CO$_2$ close to the ion would experience the maximum ion-induced electric field.
Furthermore, the electric field effect on the electrochemical reaction was investigated, since many intermediates of the reaction are expected to have large dipoles or polarizabilities at an electrified surface. The free-energy diagram for CO\(_2\) reduction to CO on the Ag electrode faceted with (111) at \(-0.11\) V vs RHE was simulated by DFT methods. The differences of the Gibbs free energies involved in multiple steps along the reaction were observed between the condition with no electric field and the condition with an interfacial electric field of \(-1\) V/Å (Figure 1.5). The presence of the interfacial electric field helped to stabilize the adsorbed CO\(_2\) and COOH intermediates by reducing the Gibbs free energies, which decreased the thermodynamic barriers associated with these high-energy intermediates. The electric field facilitated the CO\(_2\) reduction to CO on Ag and other weakly adsorbing metals via facile formation of *CO\(_2\) and *COOH intermediates. The effect of the interfacial electric field in alkali metal electrolytes successfully led to CO\(_2\) reduction to HCOO\(^-\), C\(_2\)H\(_4\), and C\(_2\)H\(_5\)OH productions on Cu electrodes [71]. The solvated alkali cations created a dipole field on the order of \(-1\) V/Å that stabilized the surface adsorbed intermediates (*CO\(_2\), *CO, *OCCO) with large dipole moments. The electric field stabilization can be improved as the cation size increases, since large cations are more energetically favored at the OHP, leading to a higher coverage with increased cation size (Figure 1.6). Therefore, the cation-induced interfacial electric field is an important driving force for the kinetics and selectivity of electrochemical CO\(_2\) reduction at various metal electrodes.
Figure 1.5: Free-energy diagram for CO\textsubscript{2} (g) to CO (g) without (blue) and with (yellow) the effects of electric field on Ag (111) at the equilibrium potential of the overall reaction (−0.11 V vs RHE). Reproduced with permission from [62]. Copyright 2016 American Chemical Society.
Figure 1.6: Partial current densities of electrochemical CO$_2$ reduction productions on Cu(100) at $-1.0$ V vs RHE as a function of the electrolyte metal cation (Li, Na, K, Rb, Cs). Reproduced with permission from [71]. Copyright 2017 American Chemical Society.

1.2.3 Investigations on interfacial water and adsorbed intermediates of electrochemical CO$_2$ reduction

When the metal electrode is charged, the electric double layer is formed with a compact layer of solvated ions and polarizable species via direct (or specific) adsorption and electrostatic adsorption (Helmholtz layer). The vibrational mode of the functional group in a molecule is affected by its chemical environments, such as the bonding configuration with the substrate, interactions with surrounding molecules, and the strength of an external electric field if the molecule has a dipole moment [72–74]. Hence, vibrational spectroscopy of interfacial adsorbed species has provided information on the nature of the EDL and the dynamics of those species at the electrochemical interface, as a
tool for understanding electrocatalytic processes [75–83]. Several studies have shown that water molecules adsorbed at the electrode surface exhibited different behaviors from bulk water [84–93]. Due to the important role of interfacial water as the primary proton donor source for electrochemical reactions in aqueous solution, and the interplay of its dipole moments with the surrounding chemical environment under an electric field; the structure and dynamics of interfacial water at electrode surfaces was investigated [94–103]. The in-situ infrared absorption spectroscopy with surface-vibration enhancement was developed by Osawa, which enabled molecular scale observations of the metal electrode surface with very high sensitivity and without interference from the bulk solution [104–109].

From a study on the reorientation of interfacial water with applied potentials by surface-enhanced infrared absorption spectroscopy (SEIRAS) [94], OH vibrational modes (ν-OH, δ-HOH) of adsorbed water molecules were observed in the potential-dependent infrared spectra of a highly ordered Au(111) surface in 0.5 M HClO₄ solution. This study demonstrated that the spectra of interfacial water differs from bulk water (Figure 1.7). The ν-OH absorption frequency of bulk water in 0.5 M HClO₄ without applied potentials was observed between 3400-3250 cm⁻¹ (Figure 1.7 b-d). Different types of water molecules were present at 3612, 3507, and 3460-3200 cm⁻¹, which suggested that the hydrogen-bonding of interfacial water varied with applied potentials. The change of the water molecule’s hydrogen-bonded network was expected around the potential of zero charge (pzc) of the Au electrode at 0.55 V vs RHE [110–112]. At 0.12 V, the surface was negatively biased, IR absorption of ν-OH
at 3507 $\text{cm}^{-1}$ showed a decrease of hydrogen-bonding in interfacial water compared to 3400-3250 $\text{cm}^{-1}$ for bulk water [113]. At higher potentials such as at 0.77 and 1.22 V, the IR absorption of $\nu$-OH at 3460-3200 $\text{cm}^{-1}$ from interfacial water overlapped with the $\nu$-OH region of bulk water, which indicated the interfacial water with strong hydrogen-bonding was weakly adsorbed on the positively charged electrode. The appearance of a sharp peak at 3612 $\text{cm}^{-1}$ and a broad peak at 3200 $\text{cm}^{-1}$ for interfacial water at 0.77 V suggested the presence of non-hydrogen bonded OH as well as an ice-like structure of water at the surface [114–119].

The overview of the IR spectra has shown changes of water structure from weakly hydrogen-bonded, to ice-like, and strongly hydrogen-bonded water with increased applied potential. As shown in Figure 1.8, the integrated intensities of the $\delta$-OH band of interfacial water were plotted as a function of applied potential. Since $\nu$-OH frequencies for each type of water structure did not shift with potentials, the change in integrated peak intensities can be used to determine the relative populations of different types of interfacial water. At potentials below the pzc, water orients with hydrogen atoms pointing toward the surface. When the potential is increased to the pzc, water reorients to a flat-lying configuration, which allows a plane parallel to the surface to pass through the centers of all three atoms. Beyond the pzc, water molecules in an ice-like structure have an orientation with hydrogen atoms towards the solution, which is convenient to form hydrogen bonding with the above layer of water molecules. At higher potentials than 0.8 V, water molecules further reorient with hydrogen atoms pointing towards the solution in the
Figure 1.7: a) Potential-dependent infrared absorption spectra of a highly ordered Au(111) electrode surface in 0.5 M HClO₄, reference spectrum was collected at 0.62 V, b) selected spectra from left spectra in a) at 0.12 V (a), 0.77 V (b), 1.22 V (c), and a transmission spectrum of 0.5 M HClO₄ (d). The strongest bands of all four spectra are rescaled to be equal. Reproduced with permission from [94]. Copyright 1996 American Chemical Society.
direction normal to the electrode surface, which resulted from the coadsorption of perchlorate anions with interfacial water that interrupts the previous hydrogen-bonding in orientation C (Figure 1.8). With the knowledge of the water dynamics at electrified surfaces, we can gain fundamental insights on the pathways of electrochemical reactions. Similar methods can also be applied to study other interfacial species at the electrode-electrolyte interface. Investigations on the configuration and dynamics of the adsorbed CO at the electrode surface were performed to understand the rate and selectivity of
the electrochemical CO$_2$ reduction [53, 120–127]. In the work by Shao et al., SEIRAS was utilized to probe adsorbed CO on Pd and Pd-Au nanowires as electrocatalysts for CO$_2$ reduction [120]. The formation of the weakly adsorbed CO with a linear bond to the metal was facilitated on the Pd-Au surface, compared to the Pd surface with most CO adsorbed strongly in the bridge bonded configuration. This observation helped explain how the rate of CO$_2$ reduction was accelerated on Pd catalysts after incorporation with Au. Moreover, adsorbed CO was used as a probe to reveal the effect of alkali cations on electrocatalytic CO$_2$ reduction [126, 127]. The difference in the peak frequency of linearly bonded CO was observed in different alkali metal electrolytes (Figure 1.9). The slope of the frequency change of adsorbed CO with the applied potential was approximately the same in all three electrolytes, which rules out dipole-dipole coupling effects on the frequency difference in different electrolytes. Hence, this observation suggested the surface-adsorbed CO experienced a larger interfacial electric field with increasing cation size, resulting in a higher frequency of CO in the Li-containing electrolyte than it in the K- and Cs-containing electrolytes. This conclusion is consistent with our earlier discussions in section 1.2.2 that the cation-derived interfacial electric field of the double layer increased with cation size as found by DFT calculations [71, 128]. Furthermore, the IR absorption frequencies of CO stretching mode from surface-adsorbed CO in the presence of different quaternary alkylammonium cations on Cu electrodes [53] provided information on the structure and width of the electric double layer (Figure 1.10 a). The reaction pathway for C$_2$H$_4$ production was facilitated by the formation of hydrogen bonding between water and adsorbed CO (Figure 1.10 b).
Figure 1.9: Peak frequencies of CO stretching band from the linearly bonded CO as a function of applied potential in 0.1 M MHCO$_3$ (M = Li, K, Cs) with CO saturated. Reproduced with permission from [127]. Copyright 2017 Royal Society of Chemistry.
**Figure 1.10:** a) Peak frequencies of CO stretching band from the linearly bonded CO as a function of applied potential in the presence of different cations as indicated. b) The adsorbed CO coupling mechanism on Cu(100) as proposed by Bagger et al. [129] was modified in the presence of methyl$_2$N$^+$ (above in red circles) and ethyl$_2$N$^+$ cations (below in large yellow circles). Reproduced from [53]. Copyright 2019 PNAS.
1.3 Summary

Electrochemical devices are promising for the generation and storage of renewable electricity. The greenhouse effect on climate change may be moderated by utilizing fuel cell devices to decrease the dependence on fossil fuels and by using electrolyzer to convert CO$_2$ to chemical fuels. It’s urgent to improve the conversion rate and the selectivity of electrochemical CO$_2$ reduction, which can be used to achieve large-scale CO$_2$ conversion for industrial applications. Experimental data and theoretical calculations have shown the electrocatalyst’s surface structure and electrolyte composition have significant impacts on the electrocatalytic performance of CO$_2$ reduction. However, a deeper understanding of the reaction mechanism is important for designing conditions for promoting the activity and selectivity of electrochemical conversions. By studying the properties of EDL, its profile including the structure, electric field, and cation’s distribution can exhibit a significant correlation with the performance of electrochemical CO$_2$ conversion. The dynamics of interfacial water and adsorbed intermediates at the electrified surface are deciphered with SEIRAS, which provides fundamental insights into the reaction pathways. Therefore, tracking the profile of EDL and the dynamics of surface adsorbed species during the reaction are valuable strategies for designing efficient electrocatalysts and optimum reaction environments for electrochemical CO$_2$ conversion.
References


[54] Shayne A Sorenson, Joel G Patrow, and Jahan M Dawlaty. “Solvation reaction field at the interface measured by vibrational sum frequency generation spectroscopy”. In: Journal of the American Chemical Society 139.6 (2017), pp. 2369–2378.


DM Kolb and J Schneider. “Surface reconstruction in electrochemistry: Au (100-(5×20), Au (111)-(1×23) and Au (110)-(1×2)”. In: Electrochimica Acta 31.8 (1986), pp. 929–936.


JE t Bertie and E Whalley. “Infrared Spectra of Ices Ih and Ic in the Range 4000 to 350 cm—1”. In: The journal of chemical physics 40.6 (1964), pp. 1637–1645.


[126] AS Malkani, J Li, NJ Oliveira, M He, X Chang, B Xu, and Q Lu. “Understanding the electric and nonelectric field components of the cation effect on the electrochemical CO reduction reaction”. In: Science advances 6.45 (2020), eabd2569.


Chapter 2

Methods and characterizations for electrochemical CO$_2$ reduction

In this chapter, we will introduce our experimental methods for the electrolysis of CO$_2$ and the analysis of the electrode-electrolyte interface during the reaction as shown in Chapters 3 & 4. To gain an understanding of our experimental system and to have an objective comparison between the results shown in the following two chapters. Peer studies on electrochemical CO$_2$ reduction, materials, preparation methods, materials’ characterization for the electrolysis of CO$_2$ and surface-sensitive spectroscopy techniques are provided in this chapter.

2.1 Sample preparation

*Working electrode preparation for electrochemical experiments*

Copper foil (99.999%, Alfa Aesar) was cut into the desired size and polished with 800 grit abrasive paper for at least 5 min until a mirror finish was achieved. The foil was sonicated in Milli-Q water for 5 min to remove any residual
particles and dried under N\textsubscript{2} flow before use \cite{1, 2}. The copper electrode can also be prepared by electropolishing pieces of copper foil (99.999\%, Alfa Aesar) in ortho-phosphoric acid (85\% in water, Fisher Scientific) at 50 mA/cm\textsuperscript{2} versus a graphite rod (Alfa Aesar, 99.9995\%) as counter electrode for 60 seconds. The foil was rinsed with Milli-Q water for 5 min and dried under a stream of N\textsubscript{2} \cite{3–5}.

\textit{Copper film preparation for infrared spectroscopy measurements}

The copper film was prepared by physical vapor deposition using a thermal evaporator. Before Cu deposition, a Si prism (60-degree Si face-angled crystal purchased from PIKE Technologies) was polished with 1 \(\mu\text{m}\), followed by 0.05 \(\mu\text{m}\) alumina slurries respectively to clean the surface. Alumina was rinsed off with Milli-Q-filtered water (>18.2 M\(\Omega\) cm, TOC < 4 ppb) and wiped clean by Kimwipes. Then the clean silicon surface was etched by a 40 wt\% NH\textsubscript{4}F solution for several minutes to remove the silicon oxide layer before deposition. 25-nm of copper was deposited at 0.01-0.02 nm/s at a base pressure of \(\sim 10^{-6}\) torr on a silicon prism. The copper film surface was cleaned and activated electrochemically in the test electrolyte by repeating potential scans between 0 and 0.5 V vs RHE before performing surface-sensitive infrared spectroscopic measurements \cite{5–11}. 

43
2.2 Electrocatalysis of CO₂ reduction in aqueous solution

2.2.1 Experimental Set-up

CO₂ reduction was performed in a homemade H-cell (Figure 2.1) with an Autolab PGSTAT204 (Metrohm Autolab). Cu film coated on Si wafers and copper foils were used as working electrodes. Cu-films coated on Si were prepared as described in the Cu thin film preparation section, except it was performed on Si wafers, the samples were used as received. A leakless Ag/AgCl electrode (eDAQ) and a graphite-rod (Alfa Aeser, 99.9995%) was used as reference and counter electrode, respectively. Electrode potentials were converted to the reversible hydrogen electrode (RHE) scale using the following equation:

\[ E(\text{vsRHE}) = E(\text{vsAg/AgCl}) + 0.210 + 0.0591 \times pH \]

0.05 M Na₂CO₃ (Alfa Aeser, 99.999%) solution purified with Chelex was saturated with CO₂ (research grade 99.999%, Airgas) to prepared for 0.1 M NaHCO₃ electrolyte (\(pH = 6.8\)). The proper volume of the electrolyte was filled in the cathodic compartment and anodic compartment of the homemade H-cell, respectively. Potentials were corrected for uncompensated Ohmic loss (iRu) via positive feedback. Surfactant additives (CTAB) were added to the CO₂-saturated electrolyte for the appropriate experiments. To inhibit soap suds forming from surfactant addition to the solution, the gas sparging tube was lifted above the solution to keep the system blanketed in CO₂ once the surfactant was added [1, 5].
Figure 2.1: Schematic representation of the homemade H-cell for electrochemical CO$_2$RR.
2.2.2 Product analysis

Techniques for the detection of gaseous or liquid phase products are introduced here:

*Gas Chromatography-Mass Spectrometry (GC-MS)*

GC-MS is a powerful analytical method for the analysis of gaseous products and identifying unknown compounds [12–14]. The GC-MS instrument combines the function of GC, which can separate each compound from a mixture of gas phase components, with the function of MS, which can identify each compound passing through the GC and quantify their amounts. The gas products analysis of the electrochemical CO\(_2\) reduction performed with the online set-up can take several minutes or longer to complete a run [15–17].

*Nuclear Magnetic Resonance (NMR)*

NMR is a physical phenomenon that the nuclei with an odd number of protons and/or neutrons will generate an electromagnetic signal with a resonance frequency when it is in a strong constant magnetic field. The characteristic of the electromagnetic signal produced from the nuclei is related to the chemical environment, hence this signal can be utilized to identify the structure of molecules (liquid or solid) with the detectable nucleus. The liquid products of CO\(_2\) reduction are hydrocarbons, which exhibit a characteristic chemical shift of the resonance frequency. Therefore, the identity and quantitative analysis of those liquid products can be achieved by using the NMR technique [18].

For specific measurements carried out in this thesis, gaseous CO\(_2\)RR products
were analyzed by a GCMSQP2010 SE instrument from Shimadzu. This instrument contains a quadrupole mass spectrometer and a gas chromatograph (GC-2010 Plus) instrument equipped with Rt-Q-bond (ID: 0.25 mm, 8-µm thickness, 30-m length) column from Restek. The GCMS was operated at 25 keV to allow for the detection of H₂. Gas products were collected every 10 min, while CO₂ was continuously sparged at a flow rate of 20 sccm. The GC method was updated by an independent calibration from the standard gas mixture before measurements. The liquid products were analyzed by Bruker 400 MHZ NMR, using DMSO as an internal standard. The 1D ¹H spectrum was measured via water suppression by a pre-saturation method.

2.2.3 Partial current density and Faradaic efficiency for each CO₂ reduction product

1) Partial current density \( j_p \) of gas product is calculated from GC analyses:

\[
j_p = \left( \frac{[c] \times \text{flow rate} \times n \times F \times P_0}{R \times T \times \text{electrode area}} \right)
\]

\([c]\) is the ppm value of the gas product measured from the GC run, the flow rate is the purging gas CO₂ flow rate through the reaction electrolyte, \( n \) is the number of electrons transferred to generate one mole of the product, \( n = 2 \) (H₂), 2 (CO), 6 (CH₄), 8 (C₂H₄); \( F \) is Faraday’s constant, \( R \) is the molar gas constant, \( P_0 \) and \( T \) is the standard pressure and temperature at 1 atm and 273.15 K.

2) Partial current density \( j_p \) of liquid product is calculated from NMR analyses:
\[ j_p = (\text{[m]} \times n \times F) / (\text{reaction time} \times \text{electrode area}) \]

\([m]\) is the mole value of the liquid product generated from the electrochemical reaction, which was calculated from the NMR analysis using an independent calibration curve and DMSO as an internal standard, \(n\) is the number of electrons transferred to generate one mole of the product, \(n = 2\) (HCOO\(^{-}\)), 4 (acetate), 8 (ethanol), 12 (n-propanol); reaction time is the total reaction proceeding time before the collection of liquid products.

3) Partial Faradaic efficiency \((F_p)\) is determined by the division of the partial current density \((j_p)\) to the total current density \((I)\):

\[ F_p = j_p / I \]

2.3 Surface-enhanced infrared absorption spectroscopy for analysis of the electrode-electrolyte interface

Surface-enhanced infrared absorption spectroscopy (SEIRAS) was used to collect information of surface adsorbed species, and species that are present in the double layer during electrocatalysis [19–24]. SEIRAS is based on the attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy; the key difference is that SEIRAS exhibits enhanced signals from surface plasmon resonances of nanostructured thin films. To perform ATR-FTIR, the IR beam passes through an internal reflection crystal with a relatively high refractive
index \((n_1)\) and reflects from the crystal surface at an incident angle \((\theta)\) larger than the critical angle (Figure 2.2). Based on Maxwell’s theory, an evanescent wave is generated at the surface when light undergoes total internal reflection \((\theta > \text{critical angle})\). The electric field intensity of the evanescent wave decays exponentially with the distance perpendicular to the crystal surface, the penetration depth \((d_p)\) can be determined by:

\[
d_p = \frac{\lambda}{[2\pi \times \sqrt{(n_1^2 \times \sin^2(\theta) - n_2^2)}]}
\]

where \(\lambda\) is the wavelength of the incident beam, \(n_2\) is the refractive index of the sample. Usually, \(d_p\) is at a micrometer scale. The intensity of the evanescent field decays exponentially with the penetration depth given by:

\[
E = E_0 \times \exp(-z/d_p)
\]

Where \(E\) is the electric field amplitude at a penetration distance \(z\), \(E_0\) is the initial electric field amplitude at the crystal surface. Therefore, only species within the penetration depth can absorb the radiation from the evanescent wave, giving rise to an infrared spectrum with surface sensitivity.

The electric field of the evanescent wave can be enhanced via the excitation of localized plasmon of the metal particles in contact with the crystal. Molecules adsorbed on the metal particles exhibit significantly enhanced infrared absorption, which provides a promising analytical method to study the structure and dynamics of surface adsorbed molecules [20, 23]. The enhancement of surface-enhanced absorption is proportional to \(\frac{1}{r^6}\) \((r\) is the relative distance from the
electrode surface), therefore the sensitivity is restricted to the surface \([20, 25]\). As a result, this method is suitable for analyzing the electrode-electrolyte interface, since the infrared radiation will interact with interfacial species without the interference from the bulk solution. To observe that SEIRAS-effect, the metal sample needs to be a nano-scale thin film consisting of coalesced metal particles with an island structure. The synthesis parameters, such as the metal deposition rate, and thickness of the metal thin film needs to be controlled carefully to observe the surface-enhanced effect.

In-situ SEIRAS Measurements in this thesis:

The copper film coated on a prism was compressed tightly at the bottom of a homemade H-cell assembled with a VeeMax III variable angle ATR sampling accessory from PIKE. 30-mL of 0.05 M \( \text{Na}_2\text{CO}_3 \) (Alfa Aeser, 99.999%) solution purified with Chelex (\(pH = 6.8\)) was saturated with \( \text{CO}_2 \) (research grade 99.999%, Airgas) in the cathodic compartment of the cell, and the anodic compartment was filled with a 10-mL of the same solution. CTAB was added to the \( \text{CO}_2 \)-saturated electrolyte for experiments involving \( \text{CO}_2\text{RR} \) promotion.
by CTAB. The SEIRAS spectra of interfacial species were recorded using a Bruker Tensor II FTIR spectrometer with a HgCdTe (MCT) detector. The spectrometer was operated at a scan rate of 30 kHz. Spectra were acquired with a spectral resolution of 4 cm\(^{-1}\), and 32 interferograms were coadded for each spectrum. The aperture size was set for 4 mm. All spectra were shown in absorbance units defined as \(-\log(I/I_0)\), where \(I\) and \(I_0\) represent the sample and reference spectra. Reference spectra were collected in the same electrolyte conditions as sample spectra collections [2, 5].
References


Chapter 3

The effects of cationic surfactant additives on the electrocatalytic CO₂ reduction over Cu electrodes

3.1 Introduction

The electrocatalytic CO₂ reduction reaction (CO₂RR) is a promising method for producing high energy density fuels from intermittent renewable energy [1–4]. The electrolysis of CO₂ requires high overpotentials to reach appreciable current densities and suffers from poor product selectivity. Cu is one of the most promising electrode materials for reducing CO₂ to CO, HCOO⁻, C₂H₄, CH₄, and higher-order hydrocarbons at substantial rates [3, 5–8]. However, the promotion of CO₂RR performance is reduced by the parasitic hydrogen evolution reaction (HER) [9, 10]. It is meaningful to reduce the overpotential of CO₂RR and avoid the HER.

In chapter 1.2, it has been mentioned that cations have significant impacts on the interfacial electric field and reaction species in the electric double-layer region, hence the reaction rate and selectivity of CO₂RR will be improved
by tuning the electrolyte compositions via cations. Recently, the identity of cations in the electrolyte has been shown to impact the rate of CO$_2$RR and/or the HER rate [11–15]. For example, the rate of HCOO$^-$, C$_2$H$_4$, and C$_2$H$_5$OH production were increased over Cu electrode by changing the alkali metal cation from Li$^+$ to Cs$^+$ [12, 14]. Larger cations such as Cs$^+$ have been thought to promote CO$_2$RR by increasing the CO$_2$ concentration at the electrode surface and/or by stabilization of reaction intermediates from the electrostatic interaction with interfacial solvated cations [7, 11, 12, 14, 16]. Some studies have shown that molecular additives can also improve the performance of various electrode materials for CO$_2$RR by modifying the microenvironment of the electric double layer. For example, surface modification of electrodes by polymeric films prepared by electropolymerized pyridinium molecules, N-heterocyclic carbenes, and the addition of molecular additives into the electrolyte, such as amphiphilic surfactants, ionic liquids, n-alkylammonium salts, and pyridine, have been found to improve CO$_2$RR [13, 17–24]. The molecular promotors for these systems have, in most cases, been observed to promote the rate of CO$_2$RR while simultaneously suppressing HER.

Recent spectroscopy has been used to gain a better understanding of how cations impact CO$_2$ reduction [25, 26], but few spectroscopic studies succeeded in explaining cations effect on HER suppression during the electrocatalysis of CO$_2$RR. H$_2$O is most likely the proton donor for both CO$_2$RR and HER processes. Surendranath et al. and Palmore et al. have shown that CO$_2$ reduction displays a strong dependence on porosity, and Wang et al. have shown that the concentration of H$_2$O in water-in-salt electrolytes directly
impacts the rate of CO$_2$RR and HER [9, 27, 28]. Furthermore, a recent report by Koper et al. has shown that the rate of CO$_2$RR and HER on group 11 metals exhibited a dependence on the electrode rotation rate in Ar- and CO$_2$-saturated 0.1 M NaHCO$_3$, suggesting that H$_2$O is a facile proton donor under these reaction conditions [29, 30].

Herein, in the following sections of this chapter, we will demonstrate the enhancement of CO$_2$RR and suppression of HER in presence of cetyltrimethylammonium bromide (CTAB) by using in-situ SEIRAS. Several studies have shown that CTAB can promote CO$_2$ reduction on Cu and Ag electrodes [13, 24], but molecular level insights of this effect are not known. CTAB is a particularly interesting molecular promotor because it is commercially available in large quantities at low cost. The structure of CTAB is a quaternary ammonium group linking with a sixteen-carbon alkyl chain via a C-N bond. This fundamental study is expected to provide a route for improving CO$_2$RR performance.

### 3.2 Electrocatalytic performance of CO$_2$RR and HER in an electrolyte with the addition of CTAB

The electrochemical measurements were performed on Cu electrodes (Cu foils and Cu-coated Si prisms) in 0.1 M NaHCO$_3$ electrolytes (pH 6.8) purified with Chelex to remove trace metal contamination and used a leakless Ag/AgCl reference electrode (eDAQ) [31, 32]. The activity and selectivity of CO$_2$RR was evaluated on Cu foils with and without 67 µM of CTAB, and Faradaic efficiency (FE) of the products and their current densities were plotted in Figures 3.1 and
3.2. It was observed that the HER FE decreased by \( \sim 30 \) to \( 60\% \) and the CO\(_2\)RR FE increased by \( \sim 40 \) to \( 60\% \), depending on the applied voltage (E) (Figure 3.1 a,b). Suppression of the HER current density for E more negative than \(-0.5\) V vs the reversible hydrogen electrode (RHE, henceforth all voltages will be referenced to RHE unless otherwise noted) and an enhancement of the CO\(_2\)RR current density at all voltages demonstrated the impact of CTAB on the rates of both reactions (Figure 3.2 c,d). The primary product for CO\(_2\)RR was HCOO\(^-\) with 50 to 60% FE and CO with \( \leq 15\% \) FE in the CTAB-containing electrolytes at all voltages (Figure 3.1). In CTAB-free electrolytes, up to 90% H\(_2\) and \(< 10\%\) HCOO\(^-\) was produced until \(-1.0\) V, where \( \sim 15\% \) FE for hydrocarbon products (CH\(_4\) and C\(_2\)H\(_4\)) was observed. The Faradaic efficiency and partial current densities for the CO\(_2\)RR on the Cu foil control samples measured in the absence of CTAB are comparable to samples collected in NaHCO\(_3\) electrolytes in other reports [12, 14]. It is reasonable to postulate that the accumulation of CTAB near the electrode can alter the reaction pathway. Cu-coated Si prisms were tested as a control for CO\(_2\)RR to verify the samples used in SEIRAS were active catalysts. Indeed, this material exhibited similar trends for CO\(_2\)RR enhancement and HER suppression as Cu foils.

The accumulation of CTAB was supported by a reduction of the double-layer capacitance, derived from electrochemical impedance spectroscopy (EIS) experiments by Banerjee [13]. Their observations also suggested that the distribution of the ions at the electrode-electrolyte interface was altered by the addition of CTAB in the electrolyte. Dawlaty et al. reported that CTAB adsorption onto a nitrile-modified electrode can produce large interfacial electric
Figure 3.1: Potential dependence for the Faradaic efficiency of a) hydrogen evolution reaction (HER) and b) CO$_2$ reduction reaction (CO$_2$RR). Potential dependence of electrochemical active surface area normalized (ECSA) current density of c) HER and d) CO$_2$RR. All data were collected in a CO$_2$-saturated 0.1 M NaHCO$_3$ electrolyte on a Cu foil with 67 µM CTAB or without CTAB. Reproduced with permission from [33]. Copyright 2020 American Chemical Society.
fields up to $-1.25 \text{ V/nm}$, as probed by vibrational Stark shift spectroscopy under noncatalytic conditions [13, 23, 24, 34]. Based on the analysis of the EIS and vibrational Stark shift spectroscopy measurements, they proposed the surfactant CTAB orientation at the electrode, which exhibited the ammonium head group pointing toward the electrode and the methyl side as the tail pointing toward the bulk solution. Taken together, we hypothesized that the hydrophobic backbone of CTAB modified the concentration of interfacial water and that large interfacial electric fields suppressed the HER rate and the enhanced CO$_2$RR rate, respectively.
3.3 Dynamics of interfacial species in the electric double layer with potential dependence via in-situ spectroscopic detection

To investigate the structure and dynamics of interfacial water and adsorbed intermediates in the presence of CTAB, a suitable surface-sensitive spectroscopic technique is required to detect the O-H vibrations of water and vibrational modes of the adsorbed species. As discussed in chapter 2.3, SEIRAS can detect adsorbates present within the first several monolayers of the electrode surface without interference from the bulk solution, hence this technique is ideal for probing species within the double layer [35–37].

SEIRAS measurements were collected on face-angled Cu-coated Si prisms in contact with CO$_2$-saturated electrolytes to investigate the potential dependence of species near the electrode surface. A graphical representation shows the set-up for the in-situ spectroscopic measurements in Figure 3.3. CO$_2$RR was performed in an H-type cell with the Cu-coated prism mounted at the bottom of the cell. The infrared (IR) spectra data were collected with $\sim$10-second resolution per spectrum and measured simultaneously by sweeping the voltage between 0.2 to $-1.0$ V at a 10 mV/s scan rate. As a result, the potential interval between one spectrum and its successive spectrum is 100 mV. Reference spectra for the SEIRAS measurements were recorded at 0.2 V in CO$_2$-saturated 0.1 M NaHCO$_3$ electrolyte with or without CTAB; the final spectra presented were subtracted from the reference spectrum collected in the same electrolyte, unless otherwise noted. All spectra were in absorbance units defined as $-\log(I/I_0)$, where I and $I_0$ represent the intensity of the sample and
3.3.1 Infrared spectroscopy for interfacial water orientation

In-situ IR spectra were measured during a linear sweep voltammogram at a 10 mV/s scan rate. All IR spectra collected from the cathodic scan from 0.2 to −1.0 V were put together to observe the change of interfacial water and CTAB with potentials (Figure 3.4). We observed vibrational bands between 3800 to 2800 cm$^{-1}$, which contained modes for interfacial water and the C-H bonds of CTAB [38–43]. The upward and downward peaks indicate the absorption and desorption of the species, respectively. The stretching mode (ν-OH) and bending mode (δHOH) of adsorbed water molecules increased in intensity during the cathodic potential sweep (Figure 3.4 a), which may be the result of an increased concentration of interfacial water [41]. According
to previous SEIRAS studies, the OH bonds of water oriented towards the electrode when the surface was negatively charged. The OH bonds of water molecules oriented towards the solution when the electrode surface was positively charged. The change in water orientation is usually accompanied by a shift from a weakly hydrogen-bonded mode (ν-OH ∼3600 cm−1) to a strongly hydrogen-bonded mode (ν-OH ∼3200 cm−1) [38, 39, 44–46]. The increased intensity of ν-OH also suggests the alignment of O-H dipoles of water molecules in an approximate antiparallel direction to the electric field [38, 39].

The ν-OH peaks of interfacial water in the CTAB-containing electrolyte was found to exhibit the desorption of water in (Figure 3.4 b), which is the opposite direction observed in CTAB-free electrolyte (Figure 3.4 a). Desorption bands for ν-OH and δHOH were observed when CTAB was added into the electrolyte at 0.2 V, indicating that these species were displaced by CTAB at the reference potential. This observation is consistent with the fact that CTAB is weakly solvated by water compared to Na+ and likely forms weak ion pairs with electrolyte anions, allowing it to easily liberate its solvation shell and counterion to displace Na+ as the dominant cation at the interface [12, 14, 23, 47]. An increase in the intensity of the ν-OH band, centered at ∼3450 cm−1, was observed between −0.1 to −0.3 V; this observation was similar to what was observed in CTAB-free electrolytes (Figure 3.4 a). However, as the voltage was swept more negative from −0.3 V, a small ν-OH desorption band centered at ∼3600 cm−1 was observed, indicating the desorption of nonhydrogen-bonded (isolated) water molecules at the electrode surface [38,
Figure 3.4: Representative infrared spectra of a) O-H stretching mode of H$_2$O in the electrolyte without CTAB (in blue), and b) O-H stretching mode of H$_2$O and C-H stretching mode of CTAB in the electrolyte with 67 µM CTAB (in green), gray and orange vertical lines denote the C-H groups of CTAB’s head and tail, respectively. Reproduced with permission from [33]. Copyright 2020 American Chemical Society.
For spectra with voltages scanning more negatively than −0.5 V, a broad desorption band centered near \( \sim 3400 \text{ cm}^{-1} \) appeared and grew as the voltage was swept more negatively, suggesting that weakly hydrogen-bonded water desorbed from the interface [38, 39].

### 3.3.2 Infrared spectroscopy for CTAB orientation

The interfacial structure of CTAB was detected over a range of 3000 to 2800 \( \text{cm}^{-1} \) with potential dependence by SEIRAS (Figure 3.4 b). To interpret IR data conveniently, the spectra were plotted separately from the water region in different scales. The figure showed several adsorption bands for C-H stretching modes of the head and tail groups of CTAB. The adsorption bands centered at 3016 and 2959 \( \text{cm}^{-1} \) were assigned to the symmetric and asymmetric C-H vibrational bands of CH\(_3\) in the headgroup (N-CH\(_3\)), and the absorption bands at 2931 and 2855 \( \text{cm}^{-1} \) could be assigned to the asymmetric C-H stretching mode and symmetric C-H stretching mode of CH\(_2\) near the headgroup of the CTAB tail [42, 43, 48, 49]. The desorption bands centered at 2921 and 2846 \( \text{cm}^{-1} \), showed in earlier potential scans, were assigned to asymmetric and symmetric C-H stretching modes of CH\(_2\) near the end of the CTAB tail group, respectively [42, 43, 48, 49]. The adsorption bands for the head groups increased in intensity as the voltage was swept more negatively, while desorption bands from the CH\(_2\) bands of the tail groups were observed. Similar to the analysis of interfacial water structure in section 3.3.1, these changes indicated an increase in the interfacial concentrations of the headgroup, and the reorientation of CTAB with its head pointing toward the electrode as the
voltage was swept negatively.

3.3.3 Infrared spectroscopy for the dynamics of water, electrolyte anions, and CTAB at the electrode-electrolyte interface

Desorption bands that correspond to (bi)carbonate were observed in both CTAB-free and CTAB-containing electrolytes as the voltage was swept negatively (Figure 3.5). The desorption of (bi)carbonate species is in agreement with the interfacial accumulation of CTAB as mentioned above. To quantify the impact of Br⁻, we collected SEIRAS spectra in 0.1 M NaHCO₃ with the addition of 67 µM NaBr. From our results, no significant (bi)carbonate desorption was observed when compared to spectra collected in an additive-free electrolyte (Figure 3.5 a). The adsorption of interfacial water and adsorbed intermediates was barely affected in the presence of 67 µM NaBr. Therefore we can conclude that the interfacial dynamics and the composition of the double layer were disrupted by the presence of CTAB cations (or CTA⁺).

We integrated the bands for the ν-OH of water and the ν-OCO of (bi)carbonate to provide semi-quantitative information on their potential dependence in CTAB-free electrolytes (Figure 3.6, blue traces) and CTAB-containing electrolytes (Figure 3.6, green traces). The δHOH band in CTAB-free electrolytes overlaps with the left tail of the (bi)carbonate desorption band, making it difficult to integrate. Therefore, we will only consider the ν-OH band integration in this discussion. It is worth noting that the potential-dependences of the ν-OH and δHOH band exhibited similar trends. In the forward scan direction (from 0.2 to −1.0 V), the integrated band intensity of ν-OH starts to increase
Figure 3.5: Representative infrared spectra of CO, \( \delta \text{HOH} \), and OCO vibration of (bi)carbonate in CO\(_2\)-saturated a) CTAB- free 0.1 M NaHCO\(_3\), and b) 0.1 M NaHCO\(_3\) containing 67 \( \mu \)M CTAB. Reproduced with permission from [33]. Copyright 2020 American Chemical Society.
at $-0.1$ V before plateauing at $-0.2$ V; then the intensity increased sharply as the voltage was swept negative of $-0.4$ V (Figure 3.6 a). Simultaneously, we observed a desorption band for (bi)carbonate, which grew with potentials before plateauing for $E$ more negative than $-0.4$ V (Figure 3.6 b). The potential of zero charge (PZC) of polycrystalline Cu is around $-0.73$ V (SHE) at pH 5.7; considering a Nernstian shift of $\sim 0.059$ V per pH unit, the PZC of Cu is $-0.4$ V vs RHE at pH 6.8 [50]. The surface of Cu is rendered negatively charged for voltages more negative than the PZC. Therefore, a sharp increase in the $\nu$-OH band intensity at voltages below the PZC was probably caused by an increased amount of water attracted to the electrode surface. However, a plateau of the (bi)carbonate band intensity indicated that the interfacial (bi)carbonate was desorbed from the interface. In the reverse scan direction (from $-1.0$ to $0.2$ V) collected in the CTAB-free electrolyte, the $\nu$-OH band maintained a positive intensity relative to the reference spectra across the entire voltage range, indicating the irreversible adsorption of interfacial water (Figures 3.6 a). This behavior is similar to what was observed in other reports [44]. The $\nu$-OCO band was found to exhibit reversible behavior as the reverse and forward traces nearly overlapped (Figure 3.6 b), which suggested the IR active (bi)carbonates were electrostatically adsorbed in the vicinity of the first adsorbed monolayer on the electrode surface. Moreover, the increase of the $\nu$-OH band intensity and bleach of the (bi)carbonate band supported that the orientation of water changed with potential, and its adsorption occurred with the desorption of (bi)carbonate.

To identify the role of CTAB, the integrated band intensities for the $\nu$-CH band
Figure 3.6: Integrated band intensities of the (a) ν-OH band, (b) ν-OCO band of (bi)carbonate, (c) C-H bands of the CTAB headgroup collected during a cyclic voltammogram with a sweep rate of 10 mV/s starting from 0.2 to −1.0 V in the forward direction (solid lines) and from −1.0 to 0.2 V in the reverse direction (dashed lines) in CO$_2$-saturated 0.1 M NaHCO$_3$ electrolyte with (green trace) and without (blue traces) 67 μM CTAB. The background spectrum was collected at 0.2 V vs RHE in the respective solutions. Black arrows are shown as guides to indicate the scan direction. Reproduced with permission from [33]. Copyright 2020 American Chemical Society.
of CTAB’s headgroup, ν-OH, and ν-OCO were measured in CTAB-containing electrolyte (Figures 3.6, green traces). The forward scan direction showed that the absorption bands of CTAB’s headgroup mirrored the desorption bands for ν-OH at applied voltages more negative than −0.3 V (Figure 3.6 a,b). We also observed a desorption band for (bi)carbonate, which increased for E < 0.2 V before plateauing for E more negative than −0.4 V, similar to what we observed for the CTAB-free electrolyte. The presence of CTAB displaced some of the (bi)carbonate at the reference voltage as shown by the difference in (bi)carbonate band intensity when the reference spectrum was changed from the CTAB-containing solution to a reference spectrum that does not contain CTAB [33]. In the reverse scan direction (Figure 3.6 c), the ν-CH band for CTAB’s headgroup maintained a positive intensity, which barely decreased across the entire voltage range, suggesting that the head-down orientation and interfacial concentration of CTAB was maintained. In the reverse scan, the ν-OH desorption band maintained its negative intensity until the PZC and started to decrease in intensity after passing the PZC. Taking formate as the main product from CO₂RR into account, the ν-OCO band could be convoluted by ν-OCO band of interfacial formate in the reserve scan [33]. The increase of the ν-OCO band to positive adsorption values for E > PZC likely arose from electrostatic adsorption of formate paired with water (enhanced dipoles of OCO) and the accumulation of formate at the electrode surface. In summary, the accumulation and reorientation of CTAB at the interface was irreversible when the electrode was cathodically polarized. The presence of CTAB in the electric double layer was responsible for disrupting water’s hydrogen-bonding network, causing the desorption of water from the interface.
3.4 Influence of interfacial CTAB on the reaction rate of HER and CO₂RR

So far, we have seen the effects of the presence of CTAB on the dynamics and distribution of interfacial species (water, electrolyte anions) at the electrode-electrolyte interface. We correlated the spectroscopy results to the electrocatalytic performance to produce a molecular level picture of CTAB’s promotional effects. In section 3.2, HER suppression was shown in the CTAB-containing electrolyte. We hypothesized that interfacial water was the primary proton donor for the HER reaction.

We correlated the $\nu$-OH band intensity to the HER rate as a function of CTAB concentration at $-0.8$ V with the reference spectrum collected in a CTAB-free electrolyte at $-0.8$ V (Figure 3.7 a, b). The integrated band intensity of $\nu$-OH desorption grew as the concentration of CTAB was increased from 30 to 150 $\mu$M, and then slightly decreased as the concentration increasing to 335 $\mu$M. The slight decrease in the integrated band intensity at 335 $\mu$M is probably from the formation of CTAB micelles, which are known to exhibit a decreased critical micelle concentration (CMC) in an electrolyte solution relative to pure water; additionally, the interfacial CTAB concentration may be higher than the bulk solution concentration [51]. The current density for H₂ production at $-0.8$ V was measured as a function of CTAB concentration (Figure 3.7 c). This curve was compared to the plot of the $\nu$-OH integrated band intensity as a function of CTAB concentration (Figure 3.7 b). The current density of H₂ was reduced by $>2\times$ as the concentration of CTAB increased from 30 to 150 $\mu$M, then slightly increased at 335 $\mu$M CTAB. The intensity change of the $\nu$-OH
desorption bands is consistent with the trend of the current densities of H$_2$ production in response to various concentrations of CTAB, which supports the hypothesis that interfacial water is the primary proton donor for HER. This notion is also supported by various reports that suggested H$_2$O is the source of protons for CO$_2$RR and HER [29, 30]. Solution-based proton donors, such as H$_2$O or HCO$_3^-$, have not been invoked to be part of the rate-limiting step for CO or HCOO$^-$ production during CO$_2$RR; therefore, a reduction in interfacial proton donor concentration would not suppress the formation of these products [9, 10, 52]. In contrast, protons are part of the rate-limiting step for HER; hence, a reduction in the interfacial proton donor concentration will lead to HER suppression [9, 10].

To correlate observations from SEIRAS studies during CO$_2$RR to the rate and selectivity of the reaction, adsorbed CO, the only reaction intermediate detected in the IR spectroscopy, was used to investigate reaction pathways during CO$_2$RR. Usually, CO adsorption modes depend on how the CO bonds to the metal surface and its interaction with environmental species. IR adsorption of atop-CO (CO bonded to a single atom) occurs at frequencies above 1900 cm$^{-1}$, while the adsorption of bridge-bonded CO (CO bonded to multiple atoms) occurs at frequencies in the range of 1800 to 1900 cm$^{-1}$ [44, 45, 53]. Bridge-bonded CO is a kinetically incompetent species on Cu electrodes during CO$_2$RR; hence, it will not be considered in this discussion [16]. We observed two atop-CO bands at 2096 cm$^{-1}$ and 2055 cm$^{-1}$ in CTAB-free electrolytes (Figure 3.5 a). It was proposed that the adsorption of atop-CO bands at different frequencies was from CO bonded to step and terrace sites of the
Figure 3.7: Representative infrared spectra of the water $\nu$-OH band for various CTAB concentrations. (b) Integrated band intensity of the $\nu$-OH band and (c) ECSA normalized current density for HER as a function of CTAB concentration. Dashed lines serve only as a guide to connecting the data points. All data were collected in a CO$_2$-saturated 0.1 M NaHCO$_3$ electrolyte at $-0.8$ V vs RHE with CTAB concentrations of 30, 67, 150, and 335 $\mu$M. All spectra were backgrounded to the CTAB-free electrolyte at $-0.8$ V vs RHE. Reproduced with permission from [33]. Copyright 2020 American Chemical Society.
Cu surface, respectively [53, 54]. An additional band at \(\sim 1998 \text{ cm}^{-1}\) appeared after CTAB addition, suggesting that the local CO-bonded environment is distinct from CTAB-free conditions (Figure 3.5). Notably, the frequency of the atop-CO adsorption bands shifted with potential (Stark tuning), which provides further evidence that these species were specifically adsorbed onto the Cu surface [55]. The lower frequency of the atop-CO band probably was caused by the enhanced interfacial electric field via the ligand effect of CTAB near the interface [23, 53, 56–58], which made this atop-bonded CO more active than others with higher stretching frequencies. Furthermore, we integrated the IR bands of CO intermediates and observed that the atop-CO bands in CTAB-free electrolyte slowly increased in intensity from 0.1 to \(-0.7\) V, before increasing rapidly for E more negative than \(-0.7\) V (Figure 3.8 a, blue traces). In contrast, the band intensity of atop-CO in CTAB-containing electrolyte appeared at \(-0.2\) V but hardly changed until \(-0.6\) V, then it grew rapidly (Figure 3.8 a, green traces). The rapid increase of the integrated band intensity for atop-CO coincided with the increased current density of CO production in CTAB-containing electrolytes (Figure 3.8 b). To conclude our observations, a larger population of atop-CO with the active species at lower frequencies were formed in the presence of CTAB, compared to the electrolyte without CTAB. The CO production and other products via adsorbed CO as a key intermediate during \(\text{CO}_2\text{RR}\) benefited from the presence of CTAB at the electrode-electrolyte interface.
Figure 3.8: (a) Integrated band intensity of atop-CO collected during a linear sweep voltammogram at a 10 mV/s scan rate and (b) partial current density for CO formation collected by constant potential electrolysis in CO$_2$-saturated 0.1 M NaHCO$_3$ electrolyte with and without 67 µM CTAB. The background spectrum was collected at 0.2 V vs RHE in the respective solutions. Reproduced with permission from [33]. Copyright 2020 American Chemical Society.
3.5 Summary

In conclusion, we used SEIRAS to investigate dynamics of interfacial water, electrolyte anions, a molecular promotor (CTAB), and CO intermediates of electrochemical CO$_2$RR over Cu electrodes. Our results suggested that the promotion of CO$_2$ reduction with assistance from CTAB is a combination of the suppressed HER reaction rate and the enhanced CO$_2$RR rate. The frequency change of $\nu$-OH bands has been used to describe the reorganization of water at the interface from the presence of CTAB at the interface. The increased desorption bands of interfacial water indicated a decreased concentration as the voltage was scanned cathodically. The configuration and accumulation of CTAB via electrostatic adsorption near the electrode surface can influence the structure and dynamics of water in the double layer, which gives credence to the assumption that the assembly of the surfactant controls the supply of water to the electrode surface, influencing the supply of protons. The removal of interfacial water is most likely driven by steric and hydrophobic effects from the alkane chain of CTAB. The decreased rate of HER was correlated to the disrupted double layer, specifically the removal of interfacial water. Meanwhile, interfacial water was verified to be a facile proton donor under CO$_2$RR conditions. The perturbed binding mode of CO adsorption and an increased population of CO intermediates during CO$_2$RR with the presence of CTAB provided evidence that CTAB additive plays a key role for promoting electrocatalytic CO$_2$ reduction. Overall, the modification of the electric double layer with a cationic surfactant is a powerful method for enhancing CO$_2$RR performance (rate and selectivity) while simultaneously inhibiting the rate
for HER. Further investigations in various types of molecular modifiers in favor of specific pathways for multi-step reactions are expected to optimize electrocatalytic performance.
References


[26] AS Malkani, J Li, NJ Oliveira, M He, X Chang, B Xu, and Q Lu. “Understanding the electric and nonelectric field components of the cation effect on the electrochemical CO reduction reaction”. In: Science advances 6.45 (2020), eabd2569.


Chapter 4

Combined effects of alkali metal cations and surfactant cations on the electrocatalytic CO\textsubscript{2} reduction over Cu electrodes

4.1 Introduction

The electrolyte plays an important role in the reaction rate and pathway during an electrochemical reaction. As mentioned in Chapters 1.2, cations can impact on the rate and selectivity of electrocatalytic CO\textsubscript{2}RR by modifying the interfacial electric field and interactions of adsorbed species in the double layer. Large alkali metal cations can affect the performance of electrochemical CO\textsubscript{2}RR and simultaneously suppress the hydrogen evolution reaction (HER) [1–3]. Alkali cationic species were reported to affect the hydrocarbon selectivity in electrochemical CO\textsubscript{2} and CO reduction over Cu electrodes [4]. For instance, K\textsuperscript{+}, Rb\textsuperscript{+}, and Cs\textsuperscript{+} ions are weakly hydrated in comparison to smaller cations (Li\textsuperscript{+}, Na\textsuperscript{+}). Bell et. al. hypothesized that weakly hydrated
cations can serve as buffering agents to maintain the pH near the electrode [2, 3, 5]. The near-neutral local pH allows more CO2 to be present near the electrode-electrolyte interface, leading to an increase of CO2RR and a decrease in Faradaic efficiencies (FE) of H2 [3, 6]. The interfacial electric field altered due to solvated alkali cations in the double layer, which provided stabilized sites for key intermediates during CO2RR [2, 7].

Organic cations, molecular additives, and ionic liquids have been shown to modulate the performance of electrocatalytic processes. However, the mechanism of enhancement is distinct in comparison to alkali metal cations [8–15]. One example is the addition of a cationic surfactant - CTAB, which enhances CO2RR and suppresses HER on Cu electrodes [16–18]. In chapter 3, all electrochemical measurements for CO2RR were performed in CO2-saturated 0.1 M NaHCO3 solutions as the electrolyte base. In this chapter, we investigated the impact of CTAB with different alkali cations on CO2RR over Cu electrodes. This study provided insights on the interplay between various alkali cations and CTAB, which can be used as a guide for designing efficient conditions for CO2RR.

4.2 Electrocatalytic performance of CO2RR and HER in CTAB-containing alkali metal electrolytes

The electrochemical measurements of CO2RR were performed on Cu foils using 0.05 M M2CO3 (M = Li, Na, K, Cs) saturated with CO2 (pH 6.8). The Cu foil working electrode and Ag/AgCl reference electrode were placed in the cathode compartment, the graphite rod counter electrode was in the
Figure 4.1: a) Current density and b) Faradaic efficiency of HER over Cu electrodes in CO$_2$-saturated 0.05 M M$_2$CO$_3$ (M = Li, Na, K, Cs) electrolytes with the absence (black) or the presence of 1 mM CTAB (red) at −1.05 V. Reproduced with permission from [19]. Copyright 2020 American Chemical Society.

The anode compartment. The working and counter electrode compartments were separated by a Nafion membrane to prevent products crossover between electrodes. A CTAB concentration of 1 mM was used in all experiments unless otherwise noted. As shown in Figure 4.1, the current density for HER and its FE under the CO$_2$RR condition were plotted from a series of electrolysis in alkali-cation electrolytes with or without CTAB at −1.05 V vs the reversible hydrogen electrode (RHE, henceforth all voltages will be referenced to RHE unless otherwise noted).

The current density for the HER decreased with increasing cation size, from Li$^+$ to Cs$^+$, in CTAB-free electrolytes, which was consistent with previous reports [3, 4]. After the addition of CTAB, the current densities for HER were suppressed (Figure 4.1, red trace). The HER suppression was the largest for Li$^+$ and Na$^+$, while K$^+$ and Cs$^+$ displayed less HER suppression. These changes suggested that CTAB suppressed HER across all alkali metal cations probed, albeit with varied efficiency. Additionally, the rate of HER was suppressed
more by adding CTAB to the Na-electrolyte than by increasing the cation size from Na\(^+\) to K\(^+\). This additional observation supports that HER was suppressed more efficiently by adding CTAB to the electrolyte rather than increasing the alkali cation size. Based on our IR spectroscopic results discussed in chapter 3, HER was suppressed by the removal of interfacial water by CTAB \[18\].

The presence of CTAB does not always improve the selectivity of CO\(_2\)RR, which is also affected by the kind of alkali cations of the electrolyte \[2–4\]. In the CTAB-free electrolyte, larger alkali cations favor the formation of HCOO\(^-\) and C\(_2\)H\(_4\), while smaller cations favor CO or CH\(_4\) production (Figure 4.2, black traces). After adding CTAB to the electrolyte, the rate of CO and HCOO\(^-\) production increased for all the electrolytes (Figure 4.2 a,b; red traces). A significant increase in the rate of HCOO\(^-\) was observed in the Cs-electrolyte under the influence of CTAB. However, the production rates of CH\(_4\) and C\(_2\)H\(_4\) were not improved by the presence of CTAB, except for the C\(_2\)H\(_4\) production in Li- and Na-electrolyte. It was found that the rate of C\(_2\)H\(_4\) production in Cs-electrolyte decreased to a comparable value with the other three electrolytes due to the influence of CTAB. These changes in the selectivity for CO\(_2\)RR indicated that CTAB influences the CO\(_2\)RR differently, depending on the identity of the alkali cation. By recalling discussions in chapter 3, the red-shifted CO adsorption band and increased population of CO intermediates was observed during CO\(_2\)RR in the presence of CTAB, which can explain the enhanced CO production with the help of CTAB in all alkali cations. The change in the current density and Faradaic efficiency for CH\(_4\) was consistent
with the change of H$_2$ production by the influence of CTAB, the same trend for the change in CH$_4$ and H$_2$ production is related to a decreased supply of interfacial water which serves as primary proton donors during the reaction [3, 18]. To proceed with the formation of C$_2$H$_4$ on electrocatalysts, the coupling of two CO molecules has been proposed to be a key intermediate [20–22]. It was reported that the enhanced C$_2$H$_4$ production in alkali electrolytes with large cations was facilitated by stabilizing the C-C bond formation [2]. However, the introduction of CTAB in the electrolyte led to a decrease in the rate of C$_2$H$_4$ production, suggesting that the C-C bond formation was perturbed by the presence of CTAB.

CO$_2$RR was evaluated in blends of CTAB and alkali cations to investigate the cation size dependent behavior and the concentration dependence of CTAB.
Figure 4.3: a) Current density of HER and partial current densities of CO$_2$RR at $-1.05$ V in b) Li-electrolytes and c) Cs-electrolyte by varying the concentration of CTAB in the respective electrolyte. Reproduced with permission from [19]. Copyright 2020 American Chemical Society.

at the interface (Figure 4.3). It was observed in Figure 4.3 a, that the rate of HER was lower in the Li-containing electrolyte than in the Cs-electrolyte under the influence of CTAB, the reverse trend was observed in CTAB-free electrolytes (Figure 4.1). The effect of CTAB was larger in the Li-containing electrolyte since strongly solvated (Li$^+$) was easily displaced by CTAB [2]. CTAB was systematically observed to increase the rate of CO and HCOO$^-$ production in both electrolytes, and a slight increase in the rate of C$_2$H$_4$ was observed in the Li-containing electrolytes (Figure 4.3 b,c). In contrast, the rate of C$_2$H$_4$ production dropped when CTAB was introduced into the Cs-electrolyte (Figure 4.3 c). These findings are consistent with the observations from Figure 4.2. Taken together, the combination of the alkali metal cation and CTAB showed a synergistic effect on enhancing both CO and HCOO$^-$ production, and suppressing HER.
4.3 Dynamics of water and CTAB in the electric double layer with time dependence via in-situ spectroscopic detection

To understand why the combination of the alkali cations and CTAB displayed different behavior on the selectivity of CO$_2$RR, we utilized SEIRAS to probe adsorbed species at the electrode-electrolyte interface. The CO$_2$RR was performed by applying a constant potential at $-1.1$ V on Cu. Each IR spectrum was collected every 10 seconds and the reference spectra were collected at 0.4 V in the same electrolyte. As shown in Figure 4.4 and 4.5, the IR bands of surface-adsorbed species (H$_2$O, CO, and CTAB) were integrated to estimate their interfacial population and to determine its time dependence. We note that the higher CTAB concentration used in this study may facilitate the formation of CTAB micelles [23–25], leading to a lower freely diffusing CTAB cations near the electrode surface compared to our prior work [18]. The IR bands of interfacial water adsorption were suppressed by the presence of CTAB in both alkali electrolytes during the electrolysis of CO$_2$ (Figure 4.4 a-d). The increasing band intensity of interfacial water with time was observed in both alkali electrolytes with no CTAB (Figure 4.4 e,f, black traces), suggesting that water was reorienting with its hydrogen atoms tilted toward the electrode and/or an increase in the concentration of interfacial water due to electrowetting of the charged electrode [26, 27]. The band intensity of interfacial water was maintained with time in Li-electrolyte with CTAB (Figure 4.4 e, red trace), suggesting that the interfacial solvent structure was stable [18]. In contrast, the band intensity of interfacial water increased with time in the Cs-electrolyte.
Figure 4.4: Representative infrared spectra of O-H stretching mode of interfacial water in CO$_2$-saturated 0.05 M Li$_2$CO$_3$ electrolyte with (red) and without (black) CTAB for CO$_2$RR at $-1.1$ V proceeding at a) 0 min and b) 7 min, as well as in CO$_2$-saturated 0.05 M Cs$_2$CO$_3$ electrolyte with (red) and without (black) CTAB for CO$_2$RR at $-1.1$ V proceeding at a) 0 min and b) 7 min. The integrated band intensity of the water peak from conditions of (a-d) in e) Li-electrolyte and f) Cs-electrolyte as a function of reaction proceeding time. Reproduced with permission from [19]. Copyright 2020 American Chemical Society.

with CTAB at a similar rate observed to the CTAB free electrolyte (Figure 4.4 f). This suggests that the interfacial CTAB assembly was disturbed by large-size Cs cations.

The IR bands of the C-H stretching modes of CTAB cations were evaluated to identify the interplay between CTAB and alkali cations in the double layer (Figure 4.5). In Li-electrolyte, we found that the CH stretching mode grew with time, indicating that the CTAB assembly was steadily formed by replacing hydrated Li cations near the negatively charged electrode (Figure 4.5 black traces). As a comparison, a weak IR band of CH stretching mode was detected
in Cs-electrolyte at the beginning of the applied potential at −1.1 V and the CTAB adsorption decreased with time and ended at a lower population than the reference spectrum (Figure 4.5 green traces). This observation was the reverse of behavior in Li-electrolyte, suggesting that the CTAB assembly (0 min) was disturbed by the interfacial adsorption of Cs cations. The accumulation of Cs cations at the OHP was supported by a similar slope of the integrated band intensity of water as a function of time in Cs-electrolytes with and without CTAB; and the slope was higher than it in Li-electrolyte with CTAB (Figure 4.4 e,f). The behavior of CTAB adsorption between Cs\(^+\) and Li\(^+\) exhibited the opposite behavior. Li\(^+\) was easily displaced by CTAB because it is strongly hydrated, which reduces the affinity for Li\(^+\) to adsorb on the electrode surface. In contrast, Cs\(^+\) is weakly solved which enables it to easily liberate its solvation shell and adsorb onto the electrode surface; enabling it to displace some CTAB over time. It was reported that the ethylene evolution involved the adsorbed CO dimer as the key intermediate, which was stabilized by interacting with interfacial water via hydrogen bonding to oxygens [20, 21]. The ethylene production rate was significantly increased when switching Li-electrolyte to Cs-electrolyte, but was decreased when CTAB was added to the electrolyte. The formation of hydrogen bonding between interfacial water and adsorbed CO was probably not favorable when Cs and CTAB cations coexist in the OHP, leading to suppressed C\(_2\)H\(_4\) production. This can be explained by the removal of interfacial water due to the large size of CTAB’s headgroup and the hydrophobic nature of CTAB’s tail.
4.4 CTAB perturbation on hydrated alkali cations in the electric double layer

We measured the change of the double-layer capacitance in alkali-cation electrolytes with various concentrations of CTAB by electrochemical impedance spectroscopy (EIS) [16]. It was shown in Figure 4.6 a, the double-layer capacitance in Cs-electrolyte was similar to what was observed in Li-electrolytes at $-1.1$ V in CTAB free electrolytes. Upon the addition of CTAB to both electrolytes, the double-layer capacitance decreased with the concentration of CTAB, which was caused by the presence of CTAB at the interface. This is expected since CTAB has a lower dielectric constant than water. Furthermore, the different change of the double-layer capacitance in both electrolytes was observed with increasing CTAB concentration. The double-layer capacitance in Cs-electrolyte decreased at a slower rate than it was in Li-electrolyte until CTAB concentration reached 250 $\mu$M. The double-layer capacitances in Cs-electrolyte maintained higher values than they were in Li-electrolyte with
CTAB. These changes indicated that CTAB replaced Li cations easier than Cs cations in the double layer and the Cs cations remained at the double layer even in the presence of 1000 µM of CTAB. Cation hydrolysis decreases with increasing cation size, thus it is more favorable for Cs cations to coexist with CTAB in the double layer than Li cations [1, 3]. It has been reported that the driving force of alkali cations to accumulate at the Outer Helmholtz Plane (OHP) increases with cation size and density-functional theory (DFT) calculations also suggest that hydrated Cs cations form the most compact layer at the electrode-electrolyte interface [2, 28, 29]. The trends of double-layer capacitances by our measurements implied a lower population of CTAB was in the double layer in Cs-electrolytes compared to other alkali cations [19]. Therefore, we proposed a structure of the double layer under the influence of CTAB in Li-electrolyte and Cs-electrolyte (Figure 4.6 b,c).

4.5 Summary

In summary, we demonstrated the reaction rate and selectivity of electro-chemical CO$_2$RR were affected by the introduction of a ternary ammonium surfactant (CTAB) in alkali metal electrolytes. The formation of HCOO$^-$ and CO was enhanced by the introduction of CTAB in alkali metal electrolytes. The high rate of HCOO$^-$ production was observed in Cs-electrolyte, as a consequence of the accumulation of CTAB at the interface. Similarly, the accumulation of CTAB played a dominant role in suppressing HER, since the proton donor concentration was decreased by the removal of interfacial water. However, the CH$_4$ production in Na and K-electrolyte and the C$_2$H$_4$
production in Cs-electrolyte decreased by the introduction of CTAB, indicating that the removal of interfacial water under CTAB perturbation in the double layer inhibited hydrocarbon (CH$_4$, C$_2$H$_4$) production. The investigation of the electrode-electrolyte interface by SEIRAS and EIS measurements proved that the population of CTAB in the double layer depends on the alkali cation size. This fact helps explain that the suppression of C$_2$H$_4$ production in CTAB-containing Cs-electrolytes was because the hydrogen bonding between interfacial water and adsorbed CO intermediates was disturbed by CTAB. These fundamental insights of the cation effects on the performance of electrochemical CO$_2$RR can facilitate the design of electrolytes for improved electrochemical performance.
References

[1] Matthias M Waegele, Charuni M Gunathunge, Jingyi Li, and Xiang Li. “How cations affect the electric double layer and the rates and selectivity of electrocatalytic processes”. In: The Journal of chemical physics 151().


Chapter 5

Summary and outlook

5.1 Summary

This thesis investigated the effect of cations on the performance of CO$_2$RR and HER at copper electrodes via molecular-scale analysis of the electrode-electrolyte interface. SEIRAS based on ATR-FTIR spectrometry is a powerful analytical tool that can be used to track information about surface-adsorbed species on the electrode and sketch the profile of electrical double layer (EDL) under reaction conditions. CTAB is an amphiphilic ionic organic molecule, which shows a promotion effect on CO$_2$RR and suppresses HER at the same time. Through the investigation on interfacial water and CTAB cations via in-situ SEIRAS with potential dependence, the population of interfacial water decreased by cathodically scanning potential because of the accumulation of CTAB at the interface. The reorientation and accumulation of CTAB with potentials observed through IR absorption spectra are determined to influence the dynamics and population of water in the double layer. This study also confirms that interfacial water is as a facile proton donor for the HER. Overall,
it explains HER suppression by the addition of CTAB results from significant water removal in the double layer under the steric and hydrophobic effects of CTAB. Meanwhile, CTAB cations promote not only the coverage of surface-adsorbed CO intermediates, but also the generation of more active CO species, which indicates the enhancement of CO$_2$RR is also related to the presence of CTAB cations at the electrode.

Furthermore, the effect of alkali cations on electrochemical CO$_2$RR was explored under the influence of CTAB. The formation of formate and ethylene is promoted in the electrolyte containing large size alkali cations. After introducing CTAB to the Cs-containing electrolytes, the formation of formate was improved, but ethylene generation was inhibited. HER was significantly suppressed and CO production was enhanced by the presence of CTAB in all electrolytes, which suggested CTAB, compared to alkali cations, is efficient for HER suppression and CO production via interactions with interfacial water and adsorbed CO intermediates. By combining SEIRAS and EIS measurements on the electrode-electrolyte interface, we verified the coexistence of alkali cations and CTAB cations within the double layer. Therefore, the coexistence of alkali cations and CTAB shows a synergistic effect on the promotion of formate while inhibiting the promoted effect of Cs cations on ethylene formation. The disturbance of CTAB on the compact layer of Cs cations decreases hydrogen bonding between interfacial water and adsorbed CO intermediates which is not favorable for ethylene generation.

In conclusion, this work enriches the understanding of cations effect on the
performance of electrochemical reactions and provides a method to study reaction mechanisms at the electrified metal surface. Fundamental insights in this work are valuable for novel designs of efficient electrocatalysts and optimum reaction environments for CO$_2$RR and other electrocatalytic reactions.

5.2 Outlook

Cations effect on electrochemical CO$_2$ reduction in gas-diffusion-electrode systems

So far, the majority of research literature on electrochemical CO$_2$ reduction including the work of this thesis is carried out in aqueous-fed electrolyzers, or so-called H-cell electrolysis, where CO$_2$ is solved in the electrolyte and diffuse to the electrode for reactions. Even though this type of electrolyzer is convenient for operations and adaptable for various electrode materials and configurations, the low solubility of CO$_2$ in aqueous electrolytes (33 mM at 298 K) and the limited CO$_2$ mass transport restrain the current densities of less than 50 mA/cm$^2$ [1, 2], which is inconceivable to achieve a viable high reaction rate for industrial applications, i.e., current densities above 250 mA/cm$^2$. The solubility of CO$_2$ can be improved by increasing operation pressure and lowering the temperature, but it can’t guarantee a higher conversion rate and is not even commercially desirable. Therefore, gas-fed electrolyzers take place to solve this mass-transport limitation problem. In the gas-fed electrolyzer, one side of a gas diffusion electrode (GDE) deposited with the electrocatalyst faces the electrolyte, and the other side opens to CO$_2$ feed for diffusing to the catalyst via macro- and micro-pores in the GDE [1, 3–7]. An apparent high performance of CO$_2$ reduction is achieved in the gas-diffusion
electrode system, that current densities higher than 200 mA/cm² and Faradaic efficiencies of ethylene production over 70% have been reported [1, 8]. The role of phases involved in CO₂ reduction is key to understand the reaction mechanism and improve the electrolyzer design. A three-phase interface (CO₂/catalyst/aqueous electrolyte) is originally considered and referenced for CO₂ reduction processes [9–11]. However, this hypothesis can not explain why the CO₂ reduction can be maintained in flooded GDEs and the conversion rate can be affected by the thickness of catalysts. Hence, Burdyny et al. proposed another perspective that CO₂ reduction proceeds at a two-phase interface (catalyst/aqueous electrolyte), where a thin film of electrolyte surrounds the catalyst, this thin-film aqueous phase not only provides proton sources and ionic pathways but also avoids large resistance for CO₂ transport [1, 12]. Base on this two-phase reaction interface, electrolyte cations probably play a key role as we discussed in the aqueous-fed electrolysis of CO₂. The effect of cations is still lacking explicit investigations in GDE systems and is expected to explore systematically in the future since it is probably not the same case as in H-cell electrolysis considering different configurations involved in the electrolysis. In addition, a recent study on CO₂ reduction with GDE reported by Xing et al. [13] shows that a hydrophobic-treated catalyst greatly improves the activity and Faradaic efficiency for CO₂ conversion, and the conversion is doubled comparing to untreated catalysts. Similarly, the hydrophobic microenvironment can be created from electrolytes with hydrophobic molecular cations. Therefore, further evaluations of the effect of solution cations on GDE systems will open up a new way for promoting electrochemical CO₂ conversion.
References


