Modeling a Flow-Cell for Electrochemical Reduction of Carbon Dioxide to Formate

by

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in partial fulfillment of the requirements for the degree of

Master of Science
in Mechanical Engineering

at the Delft University of Technology,
to be defended publicly on Monday October 29, 2018 at 10:00.

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Project duration: February 2018 – October 2018
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An electronic version of this thesis is available at http://repository.tudelft.nl/.
Acknowledgements

My research is incomplete without thanking the people who have actively participated during its entire process. First of all, I would like to thank my supervisor Dr. ir. J.W. Haverkort for guiding me, motivating me, and consistently challenging me to push the boundaries of my research. The present work has its shape and depth because of his valuable inputs throughout my research. I will never forget his words – "Enjoy the process rather than just focusing on the end goal” – which helped me orient myself. I believe, working with him has helped me be a better researcher.

I would also like to thank TNO for providing me the opportunity to work during my thesis, and more importantly, to Dr. ir. A. Anastasopol who was my supervisor at TNO. I express my sincere gratitude towards her for encouraging me through her positive words. This encouragement from my both supervisors helped me tremendously to push through the difficult part of this work.

I would like to thank Dr. R. Kortlever for providing me valuable insights during my work. Extremely informative discussions with him helped me develop a better perspective.

Like every other research, this work also faced road-blocks, maybe several times. Crucial discussions with Guus De Koning, Andrea Mangel-Raventos and Aviral Rajora were very helpful. I thank them for devoting their time.

My stay in the Netherlands has been memorable because of my friends. I am extremely thankful to them for being there in time of need.

Last but definitely not the least, I express my deepest gratitude to my family, without their constant support and love, my dream of pursuing master's would have not been so easy. Their undying faith in me has been a constant source of motivation.

Nitish Vinay Gadgil
Delft, October 2018
Abstract

Increasing CO\textsubscript{2} levels in the atmosphere due to over-dependence on fossil fuels is a growing concern. Its alarming impact on global climate has prompted the United Nations (UN) to set up its sustainable goal of carbon-neutrality. Electrochemical reduction of CO\textsubscript{2} (ERC) is one of the solutions of carbon neutral cycle, which can be driven by renewable energy sources for utilizing CO\textsubscript{2} to produce high energy density fuels/feedstocks. In this way, CO\textsubscript{2} becomes a carbon source for the production of renewable fuels/feedstocks. However, ERC in aqueous solutions is a severely mass-transfer limited process, mainly due to low CO\textsubscript{2} solubility in such solutions. Flow-cells have been found to be promising in mitigating this problem as compared to H-cells, making them more suitable for the commercial realization of ERC. Moreover, high pressures and continuous flow of electrolyte have been shown to lower the mass-transfer limitations. However, their simultaneous influence on ERC in flow-cells has not been explicitly analyzed.

This work primarily focuses on ERC using tin (Sn) electrodes, in which formate is the main product of interest. During ERC in aqueous electrolytes, CO\textsubscript{2} is known to undergo an electrode reaction as well as a homogeneous reaction. This dual action increases the modeling complexity. In this study, a simplified analytical 1D model is developed to find the conditions under which the previously mentioned CO\textsubscript{2} homogeneous reaction can be safely neglected. It is found that CO\textsubscript{2} can be assumed to undergo only the electrode reaction at low current densities (lower than 7 mA/cm\textsuperscript{2}). However, the current densities for commercial realization are about 100-200 mA/cm\textsuperscript{2}, which therefore requires incorporating the CO\textsubscript{2} homogeneous reactions in the model.

Therefore, a multiphysics model of a flow-cell is developed. The model demonstrates how different pressures, velocities and cell potentials influence the current densities and the faradaic efficiencies of different products as well as pH near the cathode (surface pH). At atmospheric pressure, for a constant cell potential, increasing the velocity by an order of magnitude is observed not only to increase the faradaic efficiency of formate by about 20% but it is also found to lower the surface pH. In addition, at a fixed velocity, to maintain a constant faradaic efficiency of formate at high total current densities (for instance, 100 mA/cm\textsuperscript{2}) requires using higher pressures. The results from this work will help future modeling studies to simplify their models when investigating low current densities, and it will guide the experimental studies on flow-cells to select appropriate operating conditions.
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Nomenclature

Abbreviations

CCS Carbon Capture and Sequestration
ERC Electrochemical Reduction of CO₂
FE Faradaic Efficiency
FEM Finite Element Method
GDE Gas Diffusion Electrode
HER Hydrogen Evolution Reaction
IE Instant Equilibrium Case
NE NO Equilibrium Case
OER Oxygen Evolution Reaction
PDE Partial Differential Equation
RAM Random Access Memory
RHE Reversible Hydrogen Electrode
SHE Standard Hydrogen Electrode
TCD Tertiary Current Distribution

List of Common Symbols

A Geometric area of the electrode [m²]

\(a_0\) Activity of oxidizing species [mol/m³]

\(a_R\) Activity of reducing species [mol/m³]

\(c\) Concentration of species [mol/m³]

\(c_{\text{elec}}\) Electrolyte concentration [mol/m³]

\(c_O\) Concentration of oxidizing species [mol/m³]

\(c_R\) Concentration of reducing species [mol/m³]

\(c^*\) Concentration of species at the electrode surface [mol/m³]

\(c^*\) Bulk concentration of species [mol/m³]

\(D\) Diffusivity of species [m²/s]

\(E\) Applied voltage at the electrode [V]

\(E^a\) Standard electrode potential [V]

\(E_{eq}\) Equilibrium potential [V]

\(F\) Faraday’s constant [C/mol]
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>Body Force</td>
<td>[N/m$^3$]</td>
</tr>
<tr>
<td>$\Delta G^{0}_{\text{reaction}}$</td>
<td>Gibbs energy change for the complete reaction</td>
<td>[J/mol]</td>
</tr>
<tr>
<td>$\Delta G^{0}_{f}$</td>
<td>Standard Gibbs free energy of formation</td>
<td>[J/mol]</td>
</tr>
<tr>
<td>H</td>
<td>Henry’s constant</td>
<td>[M/bar]</td>
</tr>
<tr>
<td>$H_{\text{cell}}$</td>
<td>Cell height</td>
<td>[m]</td>
</tr>
<tr>
<td>h</td>
<td>Channel height</td>
<td>[m]</td>
</tr>
<tr>
<td>I</td>
<td>Ionic strength</td>
<td>[mol/m$^3$]</td>
</tr>
<tr>
<td>i</td>
<td>Net current</td>
<td>[A]</td>
</tr>
<tr>
<td>$i_a$</td>
<td>Anodic current</td>
<td>[A]</td>
</tr>
<tr>
<td>$i_c$</td>
<td>Cathodic current</td>
<td>[A]</td>
</tr>
<tr>
<td>j</td>
<td>Current density</td>
<td>[A/m$^2$]</td>
</tr>
<tr>
<td>$j_e$</td>
<td>Exchange current density</td>
<td>[A/m$^2$]</td>
</tr>
<tr>
<td>$j_l$</td>
<td>Electrolytic current density</td>
<td>[A/m$^2$]</td>
</tr>
<tr>
<td>$j_{\text{lim}}$</td>
<td>Limiting current density</td>
<td>[A/m$^2$]</td>
</tr>
<tr>
<td>K</td>
<td>Sechenov constant</td>
<td>[-]</td>
</tr>
<tr>
<td>$K_i$</td>
<td>Equilibrium reaction constant for reaction i</td>
<td>[dependent]</td>
</tr>
<tr>
<td>$k_f^i$</td>
<td>Forward rate constant of homogeneous reaction i</td>
<td>[dependent]</td>
</tr>
<tr>
<td>$k_r^i$</td>
<td>Backward rate constant of homogeneous reaction i</td>
<td>[dependent]</td>
</tr>
<tr>
<td>N</td>
<td>Total ionic flux</td>
<td>[mol/(m$^2$-s)]</td>
</tr>
<tr>
<td>O</td>
<td>Oxidizing species</td>
<td>[-]</td>
</tr>
<tr>
<td>P</td>
<td>Pressure</td>
<td>[bar]</td>
</tr>
<tr>
<td>p</td>
<td>Partial pressure</td>
<td>[bar]</td>
</tr>
<tr>
<td>R</td>
<td>Reducing species</td>
<td>[-]</td>
</tr>
<tr>
<td>$R$</td>
<td>Universal gas constant</td>
<td>[J/(mol-K)]</td>
</tr>
<tr>
<td>S</td>
<td>Salinity</td>
<td>[-]</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>[K]</td>
</tr>
<tr>
<td>$U_0$</td>
<td>Inlet velocity</td>
<td>[m/s]</td>
</tr>
<tr>
<td>$\textbf{u}$</td>
<td>velocity vector form</td>
<td>[m/s]</td>
</tr>
<tr>
<td>$u_{m,i}$</td>
<td>Mobility of species i</td>
<td>[m$^2$/(V-s)]</td>
</tr>
<tr>
<td>$V_{\text{cell}}$</td>
<td>Cell potential</td>
<td>[V]</td>
</tr>
<tr>
<td>$w_{\text{cell}}$</td>
<td>Width of anodic/cathodic gap</td>
<td>[m]</td>
</tr>
<tr>
<td>$w_m$</td>
<td>Membrane thickness</td>
<td>[m]</td>
</tr>
<tr>
<td>z</td>
<td>Stoichiometric number of electrons involved in an electrode reaction</td>
<td>[-]</td>
</tr>
<tr>
<td>$z_i$</td>
<td>charge on species $j$ in signed units of electronic charge</td>
<td>[-]</td>
</tr>
</tbody>
</table>
### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
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</thead>
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<tr>
<td>( \alpha_a )</td>
<td>Anodic charge transfer coefficient</td>
<td>[-]</td>
</tr>
<tr>
<td>( \alpha_c )</td>
<td>Cathodic charge transfer coefficient</td>
<td>[-]</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>Activity coefficient</td>
<td>[-]</td>
</tr>
<tr>
<td>( \eta )</td>
<td>Overpotential</td>
<td>[V]</td>
</tr>
<tr>
<td>( \kappa )</td>
<td>Electrolytic conductivity</td>
<td>[S/m]</td>
</tr>
<tr>
<td>( \delta )</td>
<td>Boundary layer thickness</td>
<td>[m]</td>
</tr>
<tr>
<td>( \rho )</td>
<td>Density</td>
<td>[mol/m³]</td>
</tr>
<tr>
<td>( \mu )</td>
<td>Dynamic viscosity</td>
<td>[(N·s)/m²]</td>
</tr>
<tr>
<td>( \sigma_m )</td>
<td>Membrane conductivity</td>
<td>[S/m]</td>
</tr>
<tr>
<td>( \phi_l )</td>
<td>Electrolytic potential</td>
<td>[V]</td>
</tr>
<tr>
<td>( \phi_s )</td>
<td>Electrode potential</td>
<td>[V]</td>
</tr>
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Introduction

1.1. Background
We have spent over 100 years in developing efficient industrial practices that are responsible for extracting carbon from the ground and emitting the oxidized carbon back into the atmosphere. It is now time for us to figure out what to do about all of that carbon dioxide (CO$_2$) [66]. The alarming increase in atmospheric CO$_2$ level, currently amounting to more than 400 ppm [2], can no longer be ignored – the rising sea level, shifting weather patterns are some of its testimonies. More importantly, the time span of around several hundred years required to re-balance this climate change [94] presents a new challenge of reducing CO$_2$ emissions and artificially closing the atmospheric carbon cycle.

Currently, there are several technologically advanced alternatives to tackle CO$_2$ emissions: Carbon Capture and Sequestration (CCS), increasing the renewable energy share, process efficiency improvement, among others. [4]. Apart from these, Electrochemical Reduction of CO$_2$ (ERC) to value-added products is gaining increasing attention, despite being in its technological infancy [77]. This is primarily because it can efficiently integrate CO$_2$ utilization with energy storage. This is demonstrated in Figure 1.1, it schematically shows how the fluctuating renewable energy sources can provide energy for the electrochemical reduction of the industrially emitted or captured CO$_2$ to fuels/feedstocks. This technology provides a promising path for its re-utilization, and also aids in artificially closing the carbon cycle. This undoubtedly provides a sustainable

![Figure 1.1: A general system level overview of electrochemical CO$_2$ reduction, and its role as carbon neutral cycle](image-url)
pathway for storing the excess renewable energy into high-energy density chemical energy [110]. Notably, Pletcher [79] strongly points out that, the current technological status and advancements, ERC has potential only to reduce the CO$_2$ emissions and that reducing atmospheric CO$_2$ levels remains wishful thinking. Nevertheless, being a promising technology in reducing CO$_2$ emissions, it has attracted industries and academics alike, in great numbers since early 90s.

1. Introduction

1.2. Electrochemical Reduction of CO$_2$

An electrochemical cell consists of an anode, a cathode and an electrolyte: electrochemical conversion takes place at the cathode/anode, and the transport of ions occurs through the electrolyte. One such cell configuration is shown in Figure 1.2. Under the influence of applied electric potential, CO$_2$ molecules are reduced at the cathode. Simultaneously, H$_2$O molecules are oxidized at the anode forming oxygen and H$^+$ ions. These H$^+$ ions are transported through electrolyte to the cathode to ensure charge conservation. As indicated in Figure 1.2, oxidation at the anode produces electrons, whereas reduction at the cathode consumes them. The electron flow shown below clarifies this.

![Figure 1.2: A schematic representation of a typical electrochemical cell showing ERC [117]](image)

As shown in Figure 1.2, different products are possible when one considers ERC. However, the required number of electrons, and therefore the energy input, vary considerably between these products. Table 1.1 lists CO$_2$ reduction reactions assuming alkaline as well as in acidic media. The listed $E^0$, standard electrode potentials, are measured against Standard Hydrogen Electrode (SHE) at pH=7. $E^0$ is the theoretically minimum amount of voltage required to carry-out certain electrochemical reaction. However, in practice, these reactions require an excess voltage (or energy input) than indicated by their respective $E^0$. This can be understood by considering the stable nature of CO$_2$ molecule – carbon atoms in CO$_2$ are already in their highest oxidation state. The nature of CO$_2$ molecule makes ERC an energy intensive process.

<table>
<thead>
<tr>
<th>Product</th>
<th>Half-cell reaction</th>
<th>$E^0$ (vs SHE at pH=7) [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formic Acid/Formate</td>
<td>CO$_2$(aq) + 2(H$^+$ + e$^-$) ----&gt; HCOOH(l)</td>
<td>-0.61</td>
</tr>
<tr>
<td>HCOOH/HCOO$^-$</td>
<td>CO$_2$(aq) + H$_2$O + 2e$^-$ ----&gt; HCOO$^-$ (aq) + OH$^-$</td>
<td>-0.43</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>CO$_2$(aq) + 2(H$^+$ + e$^-$) ----&gt; CO(g) + H$_2$O(l)</td>
<td>-0.53</td>
</tr>
<tr>
<td>CO</td>
<td>CO$_2$(aq) + H$_2$O + 2e$^-$ ----&gt; CO(g) + 2OH$^-$</td>
<td>-0.52</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>CO$_2$(aq) + 4(H$^+$ + e$^-$) ----&gt; HCHO(l) + H$_2$O(l)</td>
<td>-0.48</td>
</tr>
<tr>
<td>HCHO</td>
<td>CO$_2$(aq) + 3H$_2$O + 4e$^-$ ----&gt; HCHO(l) + 4OH$^-$</td>
<td>-0.89</td>
</tr>
<tr>
<td>Methanol</td>
<td>CO$_2$(aq) + 6(H$^+$ + e$^-$) ----&gt; CH$_3$OH(l) + H$_2$O(l)</td>
<td>-0.38</td>
</tr>
<tr>
<td>CH$_3$OH</td>
<td>CO$_2$(aq) + 5H$_2$O + 6e$^-$ ----&gt; CH$_3$OH(l) + 6OH$^-$</td>
<td>-0.81</td>
</tr>
<tr>
<td>Methane</td>
<td>CO$_2$(aq) + 8(H$^+$ + e$^-$) ----&gt; CH$_4$(l) + 2H$_2$O(l)</td>
<td>-0.24</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>CO$_2$(aq) + 6H$_2$O + 8e$^-$ ----&gt; CH$_4$(g) + 8OH$^-$</td>
<td>-0.25</td>
</tr>
</tbody>
</table>
1.3. Problem Description

The energy input for ERC scales linearly with the number electrons required to form a certain product [42]. Due to the energy consumption, and based on current technology, carbon products requiring 2 electrons are more realizable on a commercial scale: formate is one of them [96, 101]. Formate/formate salts can be converted to formic acid through acidification treatment. Given the wider industrial usage of formic acid—particularly in leather, agriculture and rubber industry—producing formate/formic acid using ERC has become an attractive alternative [15]. Additionally, it is one of the highest value-added products of ERC (1300$/ton as compared to 400$/ton for CH$_3$OH). Apart from its direct industrial usage, its high volumetric capacity (53 g H$_2$/L), low toxicity and flammability at ambient conditions make formic acid/formate a promising hydrogen carrier [21]. Although the current size of the formic acid/formate market is comparatively small [79], it is estimated to reach 620 million dollars by 2019 [52].

Conventionally, p-block elements (Pb, Sn, In, Hg) [12], and some d-block elements (Cd, Ru and Pd) [60] are the effective catalysts for ERC to formate. Out of which, Sn has emerged as a highly selective catalyst [22, 62] having a potential for the large-scale production of formic acid/formate [4]. However, formate is not the only product of this conversion: carbon monoxide (CO) and hydrogen (H$_2$) are the main competing products. Under certain operating conditions, hydrogen evolution reaction (HER) does not only compete with ERC but often surpass it [43]. Therefore, choosing correct operating conditions, and improving the selectivity of Sn catalyst are unavoidable challenges. There are several other difficulties in using Sn electrodes:

1. The loss of activity due to its surface oxidation in aqueous electrolytes [91]
2. Surface degradation caused by the formation of alkali-metal complexes [23]
3. The electrode pulverization, attributed to hydrogen diffusion-induced stress, leading to performance degradation [113]

To the author’s best knowledge, no solution to these challenges has yet been reported. Despite these challenges, the abundance of Sn makes it a promising catalyst material for the large-scale production of formic acid/formate [102].

This large-scale production of formate is not feasible using conventional H-cells, which cover a vast majority of ERC literature. The commercial realization of ERC requires current densities of around 100-200 mA/cm$^2$, which is beyond the capability of conventional H-cells [63]. Instead, flow-cells are promising for the commercial realization because those can produce current densities typically 2-3 orders of magnitude higher than H-cells [4].

However, to optimize ERC to formate in flow-cells, it is essential to understand how the operating conditions (for instance, pressure, velocity, cell potential) influence the current density and selectivity towards formate production. Another equally important parameter of interest is the near-surface pH. Often, during ERC the pH near the cathode surface increases because CO$_2$ reduction in alkaline media produces OH$^-$ (Ref. Table 1.1). Notably, the local pH influences the rate of hydrogen evolution reaction (HER), and also the cathode (Sn) stability: HER can become a competing reaction below pH around 8, and Sn is prone to get oxidized between pH 6.5 - 10.5 [53]. The main issue is that the near-cathode pH is difficult to estimate experimentally. Therefore, one must rely on the numerical modeling approach for its estimation. Additionally, what makes modeling ERC challenging is that CO$_2$ can undergo an electrode reaction as well as a homogeneous reaction [26], thus increasing the modeling complexity.

Recently, Hashiba et al. [29] have indicated through a 1D modeling study that flow-velocity has a positive influence on current density. Moreover, the experiments on H-cell setups by Hara et al. [28] and Todoroki et al. [99] have shown the positive impact of pressure on the current density of formate. However, its simultaneous influence on ERC to formate has not been explicitly analyzed. As mentioned above, such analysis is crucial in designing and optimizing ERC to formate in flow-cells.

1.4. Research Questions

Based on the above problem description, the following research questions are formulated:

1. Under what conditions can the CO$_2$ homogeneous reactions be safely neglected in modeling ERC?
2. How does pressure, velocity and cell potential influence the near-cathode pH, current density and selectivity of formate production in a flow-cell?
1.5. Thesis Outline

Figure 1.3: A representation of thesis outline: dashed lines indicate the chapters that are frequently referred back and forth

Figure 1.3 presents the thesis outline. Chapter 2 includes a short overview of ERC and a literature review. A few theoretical concepts are presented in Chapter 3 which are necessary to grasp the nuances of the report. Chapter 4 focuses on the model development. Chapter 5 shows the results and discusses the modeling assumptions in detail. The report concludes with Chapter 6 which also highlights the future outlook relevant to experimental as well as modeling studies.
Literature Review

The multi-disciplinary nature of ERC has led to contributions from wider research communities. The following section summarizes its current status. This is done by grouping the ERC research into three categories: catalysts, electrolytes and electrochemical cell designs. The second section of this chapter reviews some specific experimental studies that are based on ERC to formate. Lastly, the final section highlights the ERC modeling studies that are relevant for the present work.

2.1. An Overview

2.1.1. Catalysts

Ever since the discovery by Hori et al. [34] which highlighted that ERC produces different products depending on different metal catalysts, the catalyst research has advanced significantly. In addition to mono-metallic catalysts, more recently, bimetallic [44, 47], ion-modified metallics [13, 61, 64], nano-structured [59, 82, 83], molecular [85] and non-metallic catalysts [51, 116] have been shown to be promising for ERC. The quest for a suitable catalyst has been motivated by the three catalyst related pressing challenges in ERC [43]– low selectivity, low activity and low durability/stability. The importance of selectivity is briefly explained with the help of Figure 2.1.

![Figure 2.1: Standard reduction potential (vs SHE at pH=7) for different ERC products](image)

As indicated in Chapter 1, ERC produces different products. However, an important issue is selectively producing the desired product [43]. Central to the issue of selectivity are the closely spaced standard reduction potentials ($E^0$) of different ERC products (Figure 2.1). This clearly indicates why different products can compete with one another. Even more important, although not shown in Figure 2.1, $H_2$ evolution reaction
has a standard reduction potential of -0.41 V vs. SHE (at pH=7), overlapping closely with other C-products. Therefore, for ERC in aqueous electrolyte, H₂ evolution easily becomes a problematic competing reaction. Indeed, improving and tuning the catalyst selectivity is therefore essential. A recent review by Wang et al. [105] summarizes the advancements in tuning the catalyst selectivity.

Next, apart from improving the selectivity, nano-structures on catalyst surface have been shown to influence the catalyst activity [73] – targeting the second challenge in ERC. A higher activity is directly related to lower energy input. In other words, a catalyst with higher activity better stabilizes the reaction intermediate of CO₂ reduction (for instance, *CO₂⁻*), consequently reducing the overpotential [48]. Overpotential is the excess amount of voltage above standard reduction potential required to carry out the reaction.

An extremely essential and relatively less researched challenge of ERC is improving the catalyst durability [69]. Low durability causes a faster degradation of catalyst, consequently increasing the overpotential, and therefore the energy input. Notably, some contributions to this have been made through understanding the degradation of copper-based catalysts [32, 38] and tin-based catalysts [23] during short tests. Long pre-electrolysis and anodic periodic pulses have been suggested for improving the durability. Furthermore, in case of Sn electrodes, the faster degradation was associated to the formation of inter-metallic compound; a technique to avoid such degradation is still unknown.

### 2.1.2. Electrolytes

Aqueous electrolytes containing K⁺, Na⁺ cations and HCO₃⁻, OH⁻ anions cover a vast majority of the literature. The presence of electrolyte lowers the CO₂ solubility in water due to "salting-out" effect [89],[107] – the effect of cation and anion solvation which leaves lesser water molecules for dissolving CO₂. On the other hand, more recently, ionic liquids have been found not only to have higher CO₂ solubility and electrical conductivity [65] but also to reduce the reaction overpotentials [81]. However, their production cost limits their widespread usage [65]. Alvarez et al. [5] extensively reviewed the usage of ionic liquids in electrochemical processes.

Apart from improving the conductivity, electrolytes have been shown to act as a co-catalyst, consequently altering the product selectivity. Electrolytes modulate the selectivity through their composition, concentration [29]. In addition to this, it was Murata et al. [74] who have shown that the choice of cation between Li⁺, Na⁺, K⁺, Cs⁺ remarkably alters the product selectivity on Cu electrodes. Similar results have been reported on Ag electrode showing higher selectivity towards CO with heavier cations [98]. Interestingly, Singh et al. [93] used a modeling approach to highlight another aspect of cations: increasing the size of cations leads to reduced near electrode pH, and naturally higher CO₂ availability, and therefore, higher selectivity towards the carbon based products. Conversely, reduced selectivity with increasing cation size was reported in the experimental work on Sn electrodes by Wu et al. [112]. Quite similar to cations, Hori et al. [35] have shown that anions also play a significant part in influencing the product distribution on Cu electrodes: C₂H₄ is a preferred product with Cl⁻, SO₄²⁻ and ClO₃⁻, whereas CH₄ is preferentially produced in presence of concentrated HCO₃⁻. Later on, Wu et al. [112] discovered a similar influence of anions on Sn electrode. Apart from product selectivity, electrolytes have been shown to influence catalyst activity: a study on Ag electrodes has shown the effect of anions (OH⁻, HCO₃⁻ and Cl⁻) on the onset potential of CO₂ reduction [101].

A recent review by Sharma [90] covers some important aspects governing the role of aqueous electrolytes and ionic liquids in ERC. The authors have indicated that aqueous electrolytes is the most economical alternative.

### 2.1.3. Electrochemical cell designs

As shown in Figure 2.2, electrochemical cells can be broadly classified in two categories: H-cells and Flow-cells. H-cells (Figure 2.2a), as mentioned in Chapter 1, cover the vast majority of the literature, mainly due to their simplicity in testing newly developed catalysts. However, they suffer from poor cell performance due to large inter-electrode distance and limited surface area [60]. In addition to this, the low solubility of CO₂ in aqueous electrolytes leads to mass-transport limitations in H-cells; consequently restricting the testing of industrially relevant conditions [106]. Therefore, a noteworthy insight is that the conclusions drawn from such static H-cell experiments need not be relevant to the industrial electrolysers [20].

Generally, flow-cells are found to be promising in providing higher current densities relevant for the industrial electrolysers. They do so by maximizing the surface-to-volume ratio or (and) by overcoming the CO₂ solubility limitations. The flow-cell configuration dictates which one (or a combination) of these techniques would be used. In general, flow-cells are classified in two configurations [106]: membrane reactors and microfluidic reactors (often membraneless). In literature, different configurations of membrane reactors...
2.2. Experimental Studies

The reviews by Du et al. [15] and Lu et al. [60] specifically discuss the studies related to ERC to formate. These studies mainly cover the role of pH [9, 53, 111], electrolyte [112], catalyst morphology [53, 115, 119] and electrochemical cell designs [45, 50, 110], in formate production. Table 2.1 provides some representative studies. Please note: the above mentioned categories (see section 2.1) are used for the comparison.

Interestingly, majority of such studies have used ambient conditions for their analysis, in fact at which CO₂ solubility in aqueous electrolyte is low. One obvious way to overcome this solubility limitation is using higher pressures. Hara et al. [28] were one of the first to report the use of high pressures (upto 30 Bar) for ERC in aqueous KHCO₃. They observed 92.3% faradaic efficiency towards formate production on Sn electrodes, and the partial current densities upto 163 mA/cm². In the same year, Todoroki et al. [99] investigated the effects of pressure on ERC using Pb, Hg and In cathodes in 0.5 M aqueous KHCO₃ at pressures upto 60 bar. They observed a linear increase in the maximum partial current density for formate with increasing pressure. However, the faradaic efficiency towards formate was found to reach a plateau beyond 20 bar. This was attributed to the change of rate limiting step – from typical mass-transport limitations to electron transfer limitations at the cathode surface. Later on, in their study on reaction mechanisms of ERC to formate, Chaplin [12], stressed that high pressures enhance formate/formic acid production.

Although these studies highlighted the promising effects of using high pressures, none of them used the flow-cell configuration, which is promising for large-scale production through continuous operation. This fact is evidently represented in Table 2.1, in which flow-cell configurations have shown to outperform the H-cell configurations. Li [55] were among the first to report the use of flow-cell at higher pressures (3.5-6 bar). A successful scale-up of ERC to potassium formate was achieved in their experiments on a continuous "trickle-bed" reactor with granulated 3D tin cathode. 100% CO₂ gas with catholyte (0.5 M KHCO₃ + 2M KCl) and anolyte 2 M KOH were used. A superficial current density of 0.6-3.1 kA m⁻² corresponding to 91-63% faradaic efficiency, respectively, for reactor voltage of 2.7-4.3 V. In the same work, a simplified model was also developed, assuming Tafel kinetics for electrode reaction. A rather noticeable discrepancy between model predictions and experimental results pointed out a need for more work in ERC modeling.

Recently, Proietto et al. [80] successfully tested a membraneless filter-press flow-cell upto 30 bar. They highlighted the influence of pressure and flow-rate on production and faradaic efficiency of formic acid. The
formic acid production was observed to increase almost linearly with pressure and, on the other hand, the faradaic efficiency was found to remain constant after 20 bar. This confirmed the earlier observations of Todoroki et al. [99]. In addition to this, it was discovered that, faradaic efficiency and formic acid production decreased with increasing flow-rate. In fact, this is contrary to a previous study [95] which observed an increase in the formic acid production with increasing flow-rates. They attributed this contrary result to the anodic oxidation of formic acid.

Table 2.1: A few selected experimental studies focusing on ERC to formate highlight the effect of high pressure

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Catalyst</th>
<th>Electrochemical Cell</th>
<th>Electrolyte</th>
<th>Current Density (mA/cm²)</th>
<th>Faradaic Efficiency/ formate/formic acid</th>
<th>Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hori et al. [34]</td>
<td>Sn foil</td>
<td>H-cell</td>
<td>0.5 M KHCO₃</td>
<td>5.5</td>
<td>63.5-79.5</td>
<td>-0.75 V vs RHE</td>
</tr>
<tr>
<td>Hara et al. [28]</td>
<td>Sn foil</td>
<td>High pressure cell (P:30 bar)</td>
<td>0.1 M KHCO₃</td>
<td>163</td>
<td>92.3</td>
<td>-0.78 V vs RHE</td>
</tr>
<tr>
<td>Li [55]</td>
<td>Sn granules</td>
<td>Flow-cell (P: 3.5-6 bar)</td>
<td>0.5 M KHCO₃ + 2M KCl</td>
<td>60-310</td>
<td>91-63</td>
<td>(2.7 - 4.3) V (cell voltage)</td>
</tr>
<tr>
<td>Whipple et al. [111]</td>
<td>Sn GDE</td>
<td>Micro-fluidic cell</td>
<td>0.5 M KCl</td>
<td>100</td>
<td>90</td>
<td>3 V (cell voltage)</td>
</tr>
<tr>
<td>Feaster et al. [22]</td>
<td>Sn foil</td>
<td>Flow-cell</td>
<td>0.1 M KHCO₃</td>
<td>10</td>
<td>70</td>
<td>-1 V vs RHE</td>
</tr>
<tr>
<td>Proietto et al. [80]</td>
<td>Sn foil</td>
<td>Flow-cell (P: 1-30 bar)</td>
<td>0.1 M Na₂SO₄</td>
<td>50</td>
<td>9-65</td>
<td>-</td>
</tr>
</tbody>
</table>

2.3. Modeling Studies

Generally, modeling complements the experimental efforts. A rigorously validated model can aid in gaining valuable insights on important quantities (for instance, surface pH) which are difficult to measure experimentally. To accurately replicate the experimental conditions, any model should ideally include all the process-relevant physics: in case of ERC, this means incorporating the migration, the diffusion and the convection, the adsorption/desorption of species, the homogeneous chemical reactions, the electrode kinetics and the gas bubbles for correctly estimating the current distribution. Not surprisingly, this approach may increase the model complexity. Therefore, to reduce this complexity, several researchers have developed simplified models. Table 2.2 summarizes a few modeling studies, highlighting details of their model.

A 1D model depicting ERC was developed by Gupta et al. [26]. It was greatly simplified to include a well-mixed bulk region, and a diffusion layer region. In particular, the diffusion layer incorporated CO₂ homogeneous reactions as well as species diffusion. The diffusion layer thickness was used as a free parameter in the model. The model was solved using MATLAB, and it was discovered that electrolyte concentration as well as stirring rate influenced the surface concentration of species. Moreover, it was shown that surface pH differs significantly from bulk pH, and even more so at higher current densities. Recently [100], this model has been extended, although for a different process: ERC to formate, to incorporate the effect of high pressures. In that study, the Tafel kinetics were assumed for the cathodic reaction (ERC to formate), the kinetic parameters for which were fitted to the experimental data of Todoroki et al. [99]. Again, it was concluded that higher pressures essentially improve the overall formate production. Further, contrary to the constant diffusion layer thickness (concentration boundary layer thickness) assumed by Gupta et al. [26], Burdyny et al. [10] developed a 1D model in MATLAB, to incorporate variable boundary layer thickness. This was achieved by linking the boundary layer thickness to the total mass-transport. The mass-transport was calculated by combining the effect of convection and gas evolution. In this model, the bubble departure diameter was treated as a free parameter. It was reconfirmed, as previously observed by Vogt [104], that low bubble diameters essentially lowered the boundary layer thickness by enhancing the micro-convection of electrolyte due to wake flow generated after bubble detachment. This mechanism, in fact, enhanced the mass-transport, which provided high current densities and low surface pH. This relatively straightforward model extended the previous models to incorporate the presence of gas-bubbles.

Recently, Hashiba et al. [29] have suggested that velocity and gas bubbles can positively influence the ERC. In that study, 1D steady-state model was developed using COMSOL 5.2a, for ERC to CH₄ on Cu electrode. The developed model was used to study the effect of pressure, different electrolytes, electrolyte strength and diffusion layer thickness on the limiting current. The model qualitatively re-produced the experimental trends of limiting current. The limiting current was found to increase with lower concentration boundary layer thickness.

Kotb et al. [49] developed a 2D model of microfluidic electrolytic cell in COMSOL for modelling ERC to CH₃OH. The electrode kinetics were modeled using the concentration dependent Butler-Volmer equation.
Species migration, diffusion and also convection was taken into account through the Nernst-Planck equation. However, the effect of pressure and gas bubbles was neglected. In their analysis, the faradaic efficiency towards CH$_3$OH was observed to increase with the flow rate, whereas current density was predicted to remain unaffected – a result which was contrary to the experimental findings.

In a completely different study by Anders et al [76], a 2D model was developed in COMSOL for incorporating the two-phase flow effects (free convection and gas bubbles). However, the main focus of the study was modeling electrochlorination cell, and not ERC. In their analysis, the presence of gas bubbles have been shown to alter the species concentration distribution, and consequently the current distribution. Notably, the model incorporated a two-phase flow behaviour, but it neglected the homogeneous reactions (including water dissociation). This assumption made their results pH independent.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Diffusion</th>
<th>Migration</th>
<th>Convection</th>
<th>Gas Bubbles</th>
<th>Homogeneous Reactions</th>
<th>Membrane</th>
<th>Package</th>
<th>1D/2D Model</th>
<th>Major Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gupta et al. [26]</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>MATLAB</td>
<td>1D</td>
<td>CH$ _4 $</td>
<td></td>
</tr>
<tr>
<td>Van Beusekem [100]</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>MATLAB</td>
<td>1D</td>
<td>HCOO$ ^-$</td>
<td></td>
</tr>
<tr>
<td>Burdyny et al. [10]</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>MATLAB</td>
<td>1D</td>
<td>Cl$ _2 $</td>
<td></td>
</tr>
<tr>
<td>Hashiba et al. [29]</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>MATLAB</td>
<td>1D</td>
<td>CH$ _4 $</td>
<td></td>
</tr>
<tr>
<td>Kotb et al. [49]</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>COMSOL</td>
<td>2D</td>
<td>CH$_3$OH</td>
<td></td>
</tr>
<tr>
<td>Anders et al. [76]</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>COMSOL</td>
<td>2D</td>
<td>H$_2$ and Cl$_2$</td>
<td></td>
</tr>
</tbody>
</table>
Some concepts from electrochemistry, homogeneous chemical reactions and fluid dynamics are essential in understanding the nuances of any electrochemical flow-cell. This chapter highlights a few of such concepts and the underlying equations, which serve as a foundation for the further model set-up and its analysis.

This chapter should by no means be treated as the only reference: a thorough treatment of the electrochemistry concepts can be found in the textbooks by Bard and Faulkner [7], West [109], Newman [75]; for further reading on CO₂ equilibria, the books by Zeebe [114] and Pilson [78] are recommended; for fluid dynamics the book by Batchelor [8] is recommended.

### 3.1. Electrochemistry
#### 3.1.1. Thermodynamics

Thermodynamics aids in describing the properties of any electrode reaction at equilibrium. For instance, consider an electrode reaction shown in equation 3.1, in which O is the oxidizing species and R is the reducing species. In particular, standard Gibbs free energy change of such reaction is an important parameter, which is often expressed using equation 3.2. This can be conveniently related, using Faraday’s constant $F$, to the standard electrode potential ($E^0$), as shown in equation 3.3. This signifies the minimum theoretical potential required to initiate the electrode reaction; its positive value is associated with spontaneous processes ($\Delta G^0_{\text{reaction}} < 0$), and a negative value with non-spontaneous processes ($\Delta G^0_{\text{reaction}} > 0$).

$$
\begin{align*}
O + z \text{ e}^- & \longrightarrow R \\
\Delta G^0_{\text{reaction}} &= \sum \Delta G^0_{\text{f, R}} - \sum \Delta G^0_{\text{f, O}} \\
\Delta G^0_{\text{reaction}} &= - zF E^0
\end{align*}
$$

Here,

- $\Delta G^0$ is Standard Gibbs Free Energy Change [J/mol]
- $z$ is Ionic Charge [-]
- $F$ is Farady’s Constant [C/mol]
- $E^0$ is Standard Potential [V]
- O is Oxidizing Species [-]
- R is Reducing Species [-]

Away from standard conditions ($c_O = c_R = 1 \text{ M}$), $E^0$ is modified using the Nernst Equation (equation 3.4) [7],

$$
E_{eq} = E^0 + \frac{RT}{zF} \ln \frac{a_O}{a_R} = E^0 + \frac{RT}{zF} \ln \frac{Y_O c_O}{Y_R c_R}
$$

Here,

- $E_{eq}$ is Equilibrium Potential [V]
- $a$ is Species Activity [mol/m$^3$]
- $R$ is Gas Constant [J/(mol-K)]
- $T$ is Temperature [K]
- $c$ is Species Concentration [mol/m$^3$]

| $\Delta G^0$ | Standard Gibbs Free Energy Change [J/mol] |
| $z$ | Ionic Charge [-] |
| $F$ | Farady’s Constant [C/mol] |
| $E^0$ | Standard Potential [V] |
| O | Oxidizing Species [-] |
| R | Reducing Species [-] |
| $E_{eq}$ | Equilibrium Potential [V] |
| $a$ | Species Activity [mol/m$^3$] |
| $R$ | Gas Constant [J/(mol-K)] |
| $T$ | Temperature [K] |
| $c$ | Species Concentration [mol/m$^3$] |
Often, an excess amount of voltage \((E - E_{eq})\), also known as overpotential \((\eta)\), is required to drive ERC. The overpotential is usually expressed as follows,

\[
\eta = E - E_{eq} = \eta_{act} + \eta_{conc}
\]

(3.5)

\[
\eta_{conc} = \frac{RT}{zF} \ln \frac{c^*}{c^s}
\]

(3.6)

Here,

- \(E\) is Applied Voltage \([\text{V}]\)
- \(\eta\) is Overpotential \([\text{V}]\)
- \(\eta_{act}\) is Activation Overpotential \([\text{V}]\)
- \(\eta_{conc}\) is Concentration Overpotential \([\text{V}]\)
- \(c^s\) is Species Concentration near the electrode \([\text{mol/m}^3]\)
- \(c^*\) is Species Concentration in the bulk \([\text{mol/m}^3]\)

Notably, the overpotential consists of the activation overpotential \(\eta_{act}\), which is the activation energy required to initiate the electrode reaction, whereas the concentration overpotential \(\eta_{conc}\) is the activation energy required to drive the mass transfer at rate needed to support the current [7]. Notably, high \(\eta_{act}\) corresponds to charge-transfer limitations, whereas high \(\eta_{conc}\) corresponds to mass-transfer limitations. Ideally one wishes to lower the required overpotential because it is directly related to the energy input, and therefore to the overall efficiency.

### 3.1.2. Kinetics

**Butler-Volmer Equation**

As explained above, quite often, applying overpotential is necessary for ERC, and the reaction rate of such electrochemical process is a strong function of the applied potential [7]. Fundamentally, under the applied potential every non-spontaneous electrode reaction, say equation 3.1, can proceed in forward (reduction) or backward (oxidation) direction, often producing a net current [7]:

\[
i = i_c - i_a = zFA[k_o c^s_O - k_b c^s_R]
\]

(3.7)

Here,

- \(i\) is Net Current \([\text{A}]\)
- \(k_o\) is Heterogeneous Rate Constant (forward reaction) \([\text{m/s}]\)
- \(k_b\) is Heterogeneous Rate Constant (backward reaction) \([\text{m/s}]\)
- \(i_a\) is Anodic Current \([\text{A}]\)
- \(i_c\) is Cathodic Current \([\text{A}]\)

The electrode kinetics primarily quantifies the dependence of this resulting net current on the applied potential and the involved species concentration. The forward \(k_o\) and backward \(k_b\) rate constants from equation 3.7 incorporate the effect of applied potential/overpotential. After following a thoroughly explained procedure in the textbook of Bard and Faulkner [7] involving transition-state theory, one can arrive to the following result, which is conventionally called the Butler-Volmer equation:

\[
 j = j_0 \left[ \exp \left( -\frac{\alpha_c F}{RT} \eta \right) - \exp \left( \frac{\alpha_a F}{RT} \eta \right) \right]
\]

(3.8)

Here,

- \(j\) is Current Density \([\text{A/m}^2]\)
- \(j_0\) is Exchange Current Density \([\text{A/m}^2]\)
- \(\alpha_c\) is Cathodic Charge Transfer Coefficient \([-]\)
- \(\alpha_a\) is Anodic Charge Transfer Coefficient \([-]\)

Equation 3.8 relates current density \(j\) to overpotential, in which current density is current per geometric surface area. Generally in this equation, \(\alpha_c + \alpha_a = 1\) [7]. As a matter of fact, this equation neglects the transport-limitations, and therefore the concentration dependence. When those are incorporated, which are mostly unavoidable in ERC, equation 3.8 is converted to concentration dependent Butler-Volmer equation:
3.1. Electrochemistry

\[ j = j_0 \left[ \frac{c^e}{c^o} \exp \left( -\frac{a_e F}{RT} \eta \right) - \frac{c^e_R}{c^o_R} \exp \left( \frac{a_R F}{RT} \eta \right) \right] \]  \hspace{1cm} (3.9)

There are two notable variables in the above equations. First, \( j_0 \), it is the current density corresponding to zero overpotential \( (E = E_{eq}) \). Since this is defined at equilibrium condition, the net current (for instance, given by equation 3.8) is zero. At these conditions, this balanced faradaic activity is quantified by the exchange current density. Second, \( \alpha \), it is the parameter responsible for assessing the relative distribution of the applied potential between the cathodic (forward) and anodic (backward) processes. Therefore, in this respect, it modifies the forward/backward reaction rates. Its minimum and maximum value is 0 and 1, respectively [7].

Tafel Equation

Another equation worth mentioning here is the Tafel equation. In case of sluggish electrode kinetics (for instance, low \( j_0 \)), high overpotentials are necessary to extract net current, it results in an irreversible electron transfer. This irreversible electron transfer is quantified by Tafel equation; one can easily derive it using the Butler-Volmer equation (equation 3.8):

\[ \eta = \frac{RT}{aF} \ln j_0 - \frac{RT}{aF} \ln j \]  \hspace{1cm} (3.10)

Although somewhat ambiguous as reported by some [67], the Tafel equation is often used for fitting the experimental data for estimating \( j_0 \) and \( \alpha \). Following a similar approach, the kinetic parameters used in this report, which are documented in Chapter 4, are obtained by fitting to the experimental data reported by Feaster et al. [22].

Cell Potential

Generally, in flow-cells, the applied voltage, unlike in the above explanation, corresponds to the voltage applied between the cathode and the anode. Here, it is termed as cell potential \( (V_{cell}) \). Over the entire flow-cell the cell-potential is typically divided as follows:

\[ V_{cell} = (E^0_a - E^0_c) + (\eta_a + \eta_c) + \eta_{ohm} \]  \hspace{1cm} (3.11)

Here,

- \( V_{cell} \) is Cell Potential \([V]\)
- \( \eta_{ohm} \) is Ohmic Drop \([V]\)
- \( \eta_a \) is Anodic Overpotential \([V]\)
- \( \eta_c \) is Cathodic Overpotential \([V]\)

3.1.3. Current Distribution

The primary goal in modeling an electrochemical cell is obtaining the current distribution. It is one of the important parameters used for characterizing any electrochemical cell. What makes it interesting is its direct relation to the total ionic flux \( (N) \). This has contributions mainly from three sources: diffusion, migration and convection of species. Now, in case of ERC in aqueous electrolyte, assuming dilute species transport, the ionic flux \( (N_i) \) of species \( i \), is given by the Nernst-Planck equation:

\[ N_i = \frac{-D_i \nabla c_i}{\text{Diffusion}} - \frac{z_i u_{m,i} F c_i \nabla \phi_l}{\text{Migration}} + \frac{c_i u}{\text{Convection}} \]  \hspace{1cm} (3.12)

Here,

- \( N \) is Total Ionic Flux \([\text{mol/m}^2\cdot\text{s}]\)
- \( D \) is Species Diffusivity \([\text{m}^2/\text{s}]\)
- \( u \) is Velocity \([\text{m/s}]\)
- \( u_{m,i} \) is Species Mobility \([\text{m}^2/\text{V}\cdot\text{s}]\)
- \( \phi_l \) is Electrolytic Potential \([\text{V}]\)

In this equation, mobility \( (u_{m,i}) \) is given by the Nernst-Einstein relation:

\[ u_{m,i} = \frac{D_i}{RT} \]  \hspace{1cm} (3.13)
The total electrolytic current density is related to the summation of individual ionic flux:

\[ j_l = F \sum \nabla \cdot (\mathbf{N}_i) \]  

(3.14)

Here, \( j_l \) is Electrolytic Current Density expressed in [A/m²].

It is assumed that the solution is electrolytically neutral everywhere, except near the electrode due to the presence of the double layer. The electroneutrality condition reads,

\[ \sum z_i c_i = 0 \]  

(3.15)

Using equation 3.15 and the Nernst Planck equation 3.12, the electrolytic current density, given by equation 3.14 reduces to,

\[ j_l = -F \sum z_i D_i \nabla c_i - \kappa \nabla \phi_l \]  

(3.16)

Here, \( \kappa \) is Electrolytic Conductivity expressed in [S/m].

Lastly, charge conservation has to be ensured,

\[ \nabla \cdot j_l = 0 \]  

(3.17)

Equation 3.17 is solved to obtain the electrolyte potential. The current density expressions given in the kinetics section 3.1.2 becomes the boundary conditions. Therefore, it is not surprising that, the electrode kinetics can, and definitely does, influence the current distribution. It should be noted that, although due to electroneutrality (equation 3.15), the velocity does not appear in the equation 3.16, it still affects the current distribution through species transport.

The species transport, with diffusion, migration and convection, is given by

\[ \frac{\partial c_i}{\partial t} = -\nabla \cdot (\mathbf{N}_i) + R_i \]  

(3.18)

in which \( R_i \) corresponds to homogeneous source/sink of species i. In case of ERC, it is safe to assume \( R_i = 0 \) as long as the homogeneous reactions (those shown in Table 3.1) are not considered as rate-dependent.

Substituting Flux \( \mathbf{N}_i \) from equation 3.12 we get,

\[ \frac{\partial c_i}{\partial t} + (\mathbf{u} \cdot \nabla) c_i = D_i \nabla \cdot (\nabla c_i) + F z_i u_i c_i \nabla \cdot (\nabla \phi_l) \]  

(3.19)

The total number of unknowns are \( i+2 \) (i number of \( c, \phi_l \), and \( u \)). Therefore, the above equation together with the electroneutrality (equation 3.15) and the momentum equation (equation 3.29) described in section 3.3 would complete the system of equations. After solving this system one can obtain the current distribution.

The current distribution is mainly divided in three types: Primary, Secondary and Tertiary. To put it simply, the primary current distribution assumes facile electrode kinetics (for instance, very high \( j_0 \)) and negligible concentration variations; on the other hand, the secondary current distribution considers finite rate of electrode kinetics, but the concentration variations, similar to the primary current distribution, are assumed to be negligible; in the tertiary current distribution, however, electrode kinetics as well as concentration variations are finite. For further details on current distributions it is recommended to refer the electrochemistry book by West [109].

It should be noted that, under very high overpotentials ERC becomes mass-transfer limited. At these conditions any further increase in overpotential has no effect on the current density, and the system is said to have reached its limiting current density (\( j_{lim} \)). The limiting current density is given by:

\[ j_{lim} = \frac{zF D_{CO_2} c_{CO_2}^*}{\delta_{conc}} \]  

(3.20)

Here, \( \delta_{conc} \) is the concentration boundary layer thickness in [m] as will be explained in section 3.3.
3.2. Chemical Reactions

The homogeneous reactions of CO\textsubscript{2} constitute an extensively studied carbonic acid (H\textsubscript{2}CO\textsubscript{3}) buffer system – one of the major contributions to which are the studies assessing the impact of rising CO\textsubscript{2} levels in seawater. ERC in aqueous electrolytes shares a similarity with studies concerning CO\textsubscript{2} dissolution in seawater: both fields require estimating the CO\textsubscript{2} solubility in saline water (pure water + dissolved ions). Therefore, some of the relevant concepts from these studies are briefly mentioned here, mainly highlighting the CO\textsubscript{2} dissociation reactions (CO\textsubscript{2} homogeneous reactions) which will be later used for model development in Chapter 4.

The primary focus of this section is to highlight the influence of temperature and electrolyte concentration (or salinity) on CO\textsubscript{2} equilibrium reactions. This understanding is crucial in further implementation of these reactions.

When CO\textsubscript{2} is bubbled in water, it undergoes the following set of reactions:

\[
\text{CO}_2(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \quad (3.21)
\]

\[
\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \quad (3.22)
\]

\[
\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} \quad (3.23)
\]

Reaction (3.21) is usually referred to as hydration reaction [40], and \(K_h\) as hydration constant. It is known that the hydration reaction is much slower than its subsequent dissociation (reactions (3.22) and (3.23)). Therefore, at equilibrium H\textsubscript{2}CO\textsubscript{3} concentration is around 3 orders of magnitude lower than that of CO\textsubscript{2} [11]. Moreover, H\textsubscript{2}CO\textsubscript{3} is an uncharged species, and has no particular significance in acid-base equilibria because it can safely be treated as an intermediate species between reaction 3.21 and 3.22. Therefore, it is grouped with more concentrated dissolved CO\textsubscript{2}(aq). For simplicity, cCO\textsubscript{2}(aq) + ch\textsubscript{2}CO\textsubscript{3} will be hereafter denoted as cCO\textsubscript{2}, where c denotes the species concentration. Therefore, reaction (3.21) and (3.22) can be combined as follows:

\[
\text{CO}_2(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \quad (3.24)
\]

The equilibrium constants \(K_{a1}\) and \(K_{a2}\), corresponding to reactions (3.24) and (3.23), are given by:

\[
K_{a1} = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{CO}_2]} \quad \text{and} \quad K_{a2} = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]} \quad (3.25)
\]

These equilibrium constants of CO\textsubscript{2} dissociation reactions (\(K_{a1}\) and \(K_{a2}\)) are well-known for the dissolution of CO\textsubscript{2} in pure water. However, as mentioned in Chapter 2, ERC is rarely carried out in pure water. Moreover, \(K_{a1}\) and \(K_{a2}\) are influenced by the presence of electrolyte as well as temperature. Millero et al. [72] have provided explicit parametric expressions for calculating \(K_{a1}\) and \(K_{a2}\) for CO\textsubscript{2} dissolution in sea water at different temperatures. To use these expressions in this study, two terminologies need to be introduced. First, the ionic strength (I), it is given by [114]:

\[
I = \frac{1}{2} \sum c_{\text{ion},j} z_j^2 \quad (3.26)
\]

Here,

\[
I \quad \text{is Ionic Strength [mol/m}^3\text{]} \quad c_{\text{ion}} \quad \text{is Concentration of ion [mol/m}^3\text{]}
\]

In case of ERC, \(c_{\text{ion}}\) would represent the concentration of cation/anion present in the electrolyte. The second terminology is salinity (S) which is related to ionic strength as follows:

\[
I = \frac{19.924 S}{1000 - 1.005 S} \quad (3.27)
\]

With the knowledge of salinity, \(K_{a1}\) and \(K_{a2}\) can be conveniently calculated. Table 3.1 shows p\(K_i(= \log K_i)\) values calculated from expressions given in Millero et al. [72], along with forward and reverse reaction rates of different CO\textsubscript{2} dissociation reactions in pure water at room temperature (298.15 K). The predominant dissociation pathways in acidic environment are denoted by ‘a’ and those in basic environment by ‘b’. In addition, water dissociation reaction is represented by w.
### Table 3.1: Reaction rates and equilibrium constants for the dissociation of CO$_2$ in water at 25°C

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k_f$</th>
<th>$k_r$</th>
<th>$pK_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a1</td>
<td>$k_{a1}^{f}$</td>
<td>$k_{a1}^{r}$</td>
<td>3.71 × 10$^{-2}$ s$^{-1}$</td>
</tr>
<tr>
<td>a2</td>
<td>$k_{a2}^{f}$</td>
<td>$k_{a2}^{r}$</td>
<td>2.34 s$^{-1}$</td>
</tr>
<tr>
<td>b1</td>
<td>$k_{b1}^{f}$</td>
<td>$k_{b1}^{r}$</td>
<td>2.23 × 10$^3$M$^{-1}$s$^{-1}$</td>
</tr>
<tr>
<td>b2</td>
<td>$k_{b2}^{f}$</td>
<td>$k_{b2}^{r}$</td>
<td>6 × 10$^9$M$^{-1}$s$^{-1}$</td>
</tr>
<tr>
<td>w</td>
<td>$k_{w}^{f}$</td>
<td>$k_{w}^{r}$</td>
<td>-</td>
</tr>
</tbody>
</table>

* The pK values are calculated from parametric relations provided in Millero et al. [72]; please note: these values are accurate for temperature 273.15 K - 313.15 K and salinity 0 - 50
** Values adapted from Schulz et al. [88]

Apart from temperature and ionic strength, the solution pH also affects the relative amounts of CO$_2$, HCO$_3^-$ and CO$_3^{2-}$ at equilibrium. This influence is represented in Figure 3.1. A similar graph can be also found in [114]. Increasing the electrolyte concentration (or salinity) or temperature, increases the equilibrium constants of CO$_2$ dissociation, or in other words it reduces the corresponding pK values (see dashed/dotted lines).

![Figure 3.1: The influence of temperature, ionic strength and pH on CO$_2$ dissociation reactions in (solid lines) pure water 298.15 K, (dashed lines) aqueous solution of 0.5 M KHCO$_3$ at 298.15 K and (dotted lines) aqueous solution of 0.5 M KHCO$_3$ at 313.15 K](image)

### 3.3. Single Phase Laminar Flow

This section provides a brief theory on single phase laminar flow required for modeling a flow-cell. Single phase flow can be conveniently modeled using the Navier-Stokes equations. There are several books which deal with the derivation of the Navier-Stokes equation, for instance, the classical text by Batchelor [8].

For incompressible flow the Navier-Stokes equations read:

\[
\nabla \cdot \mathbf{u} = 0 \tag{3.28}
\]

\[
\rho \frac{\partial \mathbf{u}}{\partial t} + \rho (\mathbf{u} \cdot \nabla) \mathbf{u} = -\nabla P + \mu \nabla^2 \mathbf{u} + \mathbf{F} \tag{3.29}
\]
3.3.1. Graetz Problem

To illustrate the relevance of these equations in flow-cells, consider a simplified 2D flow-cell shown in Figure 3.2. Flow enters the channel with a uniform velocity and a concentration profile. The outlet is assumed to have a constant pressure, and the rest of the boundary conditions are shown in the figure.

\[ \begin{align*}
  u &= U_0 \\
  c &= C_0
\end{align*} \]

Figure 3.2: The interplay between concentration boundary layer and velocity boundary layer in relation to flow-cells

It can be seen from Figure 3.2 that there are two distinct flow regimes – developing flow and fully developed flow. The developing flow corresponds to a part of channel in which the velocity boundary layer thickness (\( \delta_{\text{vel}} \)) is increasing (black dashed line). At a certain point downstream, it remains constant. The flow thereafter is called fully developed flow. The fully developed flow profile has a distinct parabolic shape (solid black curve) which remains unchanged along the x-direction. The parabolic flow profile can be obtained by solving equation 3.29 with above-mentioned boundary conditions. This derivation can be found in Batchelor [8], here, only the final result is provided. The fully developed velocity profile is given by:

\[ u(y) = \frac{6U_0}{h^2} (yh - y^2) \]  

Similarly to \( \delta_{\text{vel}} \), the concentration boundary layer can be seen in the same figure (red dotted line), which results from the current density equal to \( j_{\text{lim}} \) at the bottom wall. At this current density, species \( c \) is consumed, therefore its value falls as one approaches the bottom wall (solid red line), and it is zero at the wall. Here, \( \delta_{\text{conc}} \) is shown to be significantly smaller than \( \delta_{\text{vel}} \). Indicating that the concentration profile, in contrast to the velocity profile, is still in the developing regime. This assumption holds as long as the following condition is satisfied:

\[ Pe = \frac{U_0 h}{D} \gg 1 \]  

where \( Pe \) is a well-known parameter, Peclet number.

This situation is, in fact, similar to the classical Graetz problem [25], which assumes a developing concentration profile and a fully developed velocity profile. The main idea behind this problem is to estimate \( \delta_{\text{conc}} \), which actually varies along the channel length. In a 2D channel, at steady-state the species transport can be simplified to (see equation 3.19):

\[ u_x \frac{\partial c}{\partial x} + u_y \frac{\partial c}{\partial y} = D \left( \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} \right) \]  

The velocity profile varies only in y direction, therefore \( u_x = u(y) \) (Eq. 3.30) and \( u_y = 0 \). Furthermore, at high Peclet number convection is the dominant mode of transport. Therefore, the axial diffusion can be neglected. These substitutions simplifies the equation 3.32.

\[ \left( \frac{6U_0}{h^2} (yh - y^2) \right) \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial y^2} \]  

Now, if \( \delta_{\text{conc}}(X) \ll h \), the velocity profile can be assumed to be linear. This assumption is known as the Lévêque approximation [54]. Using this approximation the above equation reduces to:

\[ \left( \frac{6U_0 y}{h} \right) \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial y^2} \]
This equation is solved for the concentration boundary conditions mentioned in Figure 3.2. After using a similarity transformation, the derivation of which is provided in West [109], the concentration boundary layer thickness $\delta_{\text{conc}}$ comes out to be:

$$\delta_{\text{conc}}(x) = 1.022 \left( \frac{hDx}{U_0} \right)^{3/2}$$  \hspace{1cm} (3.35)

### 3.4. Finite Element Method

In this study, COMSOL is used to develop a 2D flow-cell model. COMSOL uses FEM to solve the system of equations. This section provides a short description and introduction to FEM, mainly introducing the terms which are frequently used in the report.

In mathematics, finite element method derives its strength from the minimization principle—minimizing the overall energy of the system. To explain its central idea, consider the partial differential equation (PDE) given by equation 3.29. This momentum equation is obtained by integrating the forces acting on an infinitesimally small volume of fluid [8]. The equation thus obtained has volume integral terms and surface integral terms. Volume integral terms describe what is stored inside the domain and surface integral terms describe the interaction with the neighbouring domains or external environment. The Gauss divergence theorem can transform the surface integrals into volume integrals, thereby converting the integral form of momentum equation (eq.3.29) into differential form (PDE). In FEM, essentially this differential form (strong form) is converted to 'weak form' with the help of shape functions.

In FEM, the domain of interest is first divided (by meshing operation) into smaller domains—elements. Then, the weak equations, mentioned above, are solved on these elements. In fact, each element has a certain number of nodes depending on its order. For example, consider Figure 3.3 which shows linear and quadratic elements. For simplicity, 1D elements are considered, but the same philosophy is applicable for higher dimensions.

![Figure 3.3: A schematic showing a 1D linear and a quadratic element and their shape functions](image)

A striking difference between the linear and the quadratic element is the number of these nodes—quadratic element has an extra node at the centre of element. The weak equations are actually solved on the nodes of each element. After finding a solution on each node, the solution is interpolated between these nodes to obtain the final solution. The dashed lines shown in figure indicate the way in which the solution is interpolated for the respective element order: for linear elements linear interpolation function is used, and similarly for quadratic elements, quadratic interpolation function is used. Usually, Lagrange polynomials are used as interpolation functions [3]. In FEM, these are also known as shape functions. Clearly, increasing the number of nodes (mesh refinement) increases the number of shape functions, which, on one hand, improves the solution accuracy, and on the other, increases the computational time.
This chapter presents three models relevant to the scope of this work with their respective application and underlying assumptions. First, a few selected CO\textsubscript{2} solubility models are compared to select one for further analysis. Secondly, an analytical 1D model is developed, simplifying the previously developed 1D model [100]. Lastly, a more complex 2D model is created to analyze ERC in flow-cells. Given the multidisciplinary nature of ERC, COMSOL Multiphysics is selected for modeling a 2D flow-cell. In COMSOL, the electrochemistry interface is directly available for modeling purposes, whereas in other softwares, for instance, Fluent, this functionality is yet to be made available.

In this chapter, it is assumed that the reader is acquainted with relevant equations from Chapter 3. Therefore, for brevity and wherever necessary, these equations are directly referred to.

4.1. CO\textsubscript{2} Solubility

The operating conditions – pressure, temperature and electrolyte concentration (or salinity)– significantly affect the CO\textsubscript{2} solubility in aqueous electrolytes [19]. Estimating its approximate value is essential for an effective system modeling and its performance prediction.

There are several solubility models available in the literature, each one with its own advantages and limitations [19]. In this section a few selected models are briefly explained, and a simple modification is proposed in one of the models. These models were selected after considering a trade-off between their implementation complexity, computational requirements and accuracy.

Conventionally, there are two fundamental, and relatively simple CO\textsubscript{2} solubility models: First is Henry’s law, which takes into account the pressure and temperature effects, and second is Sechenov equation, which extends Henry’s law to account for the salinity effects, also known as salting-out effects, encountered in the presence of electrolyte. Henry’s law assumes a linear relationship between the partial pressure of CO\textsubscript{2} (\(p_{\text{CO}_2}\)) and its solubility (\(c_{\text{CO}_2,\text{Henry}}\)),

\[
    c_{\text{CO}_2,\text{Henry}} = H_{\text{CO}_2} p_{\text{CO}_2} \tag{4.1}
\]

Here, 

\(H\) is Henry’s Constant [M/bar], \(p\) is Partial Pressure [bar]

\(H_{\text{CO}_2}\) is about 0.0169 Mbar\textsuperscript{-1} at 333.15 K. This value is, of course, higher at 298.15 K, but the above-mentioned temperature (333.15 K) is selected due to the unavailability of experimental data (for the validation purpose) at 298.15 K. Conventionally, Henry’s law, mentioned above, provides the CO\textsubscript{2} solubility in pure water (notably, Henry’s constant can be made salinity dependent as will be explained below). The Sechenov equation was the first model to incorporate the salinity effects on CO\textsubscript{2} solubility [89]. It assumes an exponential reduction in CO\textsubscript{2} solubility (\(c^*_{\text{CO}_2}\)) with increasing salinity (or electrolyte concentration):

\[
    \ln \left( \frac{c_{\text{CO}_2,\text{Henry}}}{c_{\text{CO}_2}} \right) = K_{\text{elec}} \tag{4.2}
\]

where, \(c_{\text{elec}}\) denotes the electrolyte concentration [mol/m\textsuperscript{3}], and \(K\) signifies the Sechenov constant, which depends on the type of cation/anion of the salt, temperature and the type of gas being dissolved (in this case,
it is CO$_2$ [107]. Apart from the Sechenov equation, several other studies modified the Henry’s constant (H) to incorporate the salinity effects, one such empirical model was proposed by Weiss [108]:

$$\ln(H_{CO_2}(T,S)) = \frac{9345.17}{T} - 167.8108 + 23.3585 \ln(T) + (0.023517 - 2.3656 \times 10^{-4}T + 4.7036 \times T^2)S$$  (4.3)

(4.4)

Notably, all the above mentioned models consider CO$_2$ solubility estimated by Henry’s law as the reference. However, the predictability of Henry’s law is known to deteriorate at high pressures (above 5 bar) [58]. Therefore, Duan et al. [16, 17] proposed a CO$_2$ solubility model which was successfully validated upto 2000 bar. However, the incorporated salinity effects are restricted to salts with cations Na$^+$, Mg$^{2+}$, Ca$^{2+}$ and anions Cl$^-$ and SO$_4^{2-}$. In case of ERC, notably, majority of the experiments in the literature are conducted using KHCO$_3$, which of course contains HCO$_3^-$ anion. Clearly, as shown above, its effect was not accounted for in the model by Duan et al. [16, 17]. Therefore, a modification is proposed in this report, to make a more general model that is applicable for ERC studies. The modification is termed as modified Sechenov equation. It is given as follows,

$$\ln\left(\frac{c_{CO_2,Duan}}{c_{CO_2}}\right) = K_{elec}$$  (4.5)

It is essentially same as the Sechenov equation (equation 4.2) except for the reference CO$_2$ solubility. In the original Sechenov equation (eq. 4.2) it is predicted by Henry’s law, whereas in the modified form it is replaced by the CO$_2$ solubility calculated using explicit empirical correlations proposed by Duan et al. [16, 17]. The motivation behind this modification is to have a better predictability of CO$_2$ solubility at higher pressures as well as at different electrolyte concentrations.

Figure 4.1a shows the CO$_2$ solubility at different pressures obtained using the above-mentioned methods. For validation purpose, the experimental data from Han et al. [27] and Tang et al. [97] is also provided. It should be noted that, the reported experimental conditions are temperature 333.15 K and the electrolyte (NaHCO$_3$) concentration is 0.5 M. It can be seen that, Henry’s law clearly overestimates the solubility at higher pressures, and so do the other methods which use Henry’s law as the reference (Sechenov [89], Weiss [108]). In a striking contrast, the solubility model by Duan et al. [16, 17], and the modified Sechenov model, perform better at higher pressure. Unfortunately, this contrast is not much evident at different electrolyte concentrations, Figure 4.1b. Again, the experimental results from Han et al. [27] are used for the validation. The models are tested for lower (3.5 bar) and higher (20 bar) pressure, and notably at slightly lower temperature (313.15 K) than above. Surprisingly, none of the models accurately estimate the solubility at different electrolyte concentrations. Therefore, it is suspected that the experimental data by Han et al. [27] may have errors (see the outlier for P = 3.5 bar at 0.1 M electrolyte concentration in Figure 4.1b)

In view of the above observations, it can be said that the modified Sechenov equation better estimates CO$_2$ solubility at higher pressures and it will be used hereafter for estimating the CO$_2$ solubility.

### 4.2. Analytical 1D Model

Electrochemical reduction, in general, is a complex process involving mass-transfer, chemical reactions, adsorption/desorption and electron transfer [7]. Moreover, CO$_2$ can undergo electrode reaction as well as homogeneous reaction (CO$_2$ dissociation reaction). It is often necessary to develop a simplified model for quick but accurate estimates of current densities. Moreover, from a modeling perspective it is interesting to know when can one neglect these homogeneous reactions to simplify the model. Therefore, one such simplified model of ERC to formate is developed as shown in Figure 4.2, which incorporates only the mass-transfer and the electron-transfer. It is a 1D model based on the following assumptions:

1. Anodic reaction (for instance, the water oxidation in Figure 1.2) does not influence the cathodic reduction process (CO$_2$ to formate in this case), thus eliminating a need to model the anodic reaction
4.2. Analytical 1D Model

Figure 4.1: The comparison between different CO\textsubscript{2} solubility models (a) at different pressures; T: 333.15 K (b) at different electrolyte (NaHCO\textsubscript{3}) concentrations; P: 3.5, 20 bar, T: 313.15 K

2. The bulk is well-mixed, indicating a uniform CO\textsubscript{2} concentration outside the boundary layer.

3. High cathodic overpotentials are assumed, thereby preferentially favouring CO\textsubscript{2} reduction over formate oxidation.

4. The faradaic efficiency of formate is assumed to be 100%.

Figure 4.2: A schematic of a 1D model representing ERC to formate.
This 1D analytical model is inspired by a previous work of Van Buesekom [100]. However, there is one crucial difference: in the proposed model, CO$_2$ mass-transport through boundary layer is approximated by Fick's law, which essentially means CO$_2$ is assumed to undergo only the reduction reaction and not any homogeneous reactions. In fact, this is a choice motivated from the results of Van Buesekom [100], which reported a similar to fickian behaviour of CO$_2$ in boundary layer despite incorporating the homogeneous chemical reactions. One reason for this behaviour is CO$_2$ to HCO$_3^-$ homogeneous reaction is around 3 orders of magnitude slower than HCO$_3^-$ to CO$_3^{2-}$ (see Table 3.1). It is already shown that CO$_2$ reduction in alkaline media produces OH$^-$ along with C-products. Therefore, based on the homogeneous reaction rate mentioned above, HCO$_3^-$ to CO$_3^{2-}$ reaction is preferred over CO$_2$ to HCO$_3^-$. One of the aim behind developing this model, as mentioned above, is to check under what conditions does this argument hold, because, as it will be discussed later in section 4.3.2 and in Appendix C, the rate of CO$_2$ to HCO$_3^-$ depends on pH. Indeed, this assumption of using Fick's law greatly simplifies the analysis.

Now, following the assumption (3), the concentration dependent Butler-Volmer equation (eq. 3.9) is reduced to,

$$j = j_0 \left[ \frac{c^*_c}{c_{CO_2}} \exp \left( \frac{-\alpha_c F \eta}{RT} \right) \right]$$

(4.6)

which can then be modified using following substitutions,

$$\frac{c^*_c}{c_{CO_2}} = 1 - \frac{j}{j_{lim}}$$

(4.7)

to a compact expression,

$$j = j_0 \exp \left( \frac{-\alpha_c F \eta}{RT} \right)$$

$$\frac{1}{1 + \frac{j_0}{j_{lim}} \exp \left( \frac{-\alpha_c F \eta}{RT} \right)}$$

(4.8)

Equation 4.8 can estimate the formate current density based on the given kinetic parameters, activation overpotential and limiting current density.

Notably, pressure and velocity will influence the formate current density through $j_{lim}$ (eq. 3.20), mainly by changing $c^*_c$ (See section 4.1) and $\delta_{conc}$ (eq. 3.35), respectively. Therefore, the proposed 1D model can effectively predict formate current density at a particular location along the cathode. But for the complete current distribution along the cathode one needs to consider a 2D model.

### 4.3. 2D Model

Figure 4.3 schematically represents a flow-cell geometry with the necessary dimensions. One essential difference between Figure 4.3 and Figure 1.2 is that it allows the flow of electrolyte. The flow (consisting of electrolyte and the dissolved species) enters at bottom (inlet), as indicated by the flow distribution, and leaves the compartment from top (outlet). Moreover, the sides of the rectangular geometry represent the cathode (right) and the anode (left). Furthermore, the anodic and cathodic compartments are separated by a thin membrane.

Under the action of applied potential ($V_{cell}$) electrochemical reduction of CO$_2$ on Sn cathode produces three products, HCOO$^-$, CO and H$_2$, as shown, whereas water oxidation at the anode produces O$_2$. These electrochemical reactions consume certain species (for instance, CO$_2$ at the cathode), thereby developing a concentration boundary layer as shown. Although not shown in the figure, a similar concentration boundary layer development is seen along the membrane, due to the transport of H$^+$ ions from anodic to cathodic compartment (see Appendix D).

Notably, apart from the mass-transport effects, as studied in the 1D model above, the 2D model shown in Figure 4.3 is extended to incorporate convection and migration effects; anodic reaction; membrane effects. The primary aim behind developing this 2D flow-cell model is to understand the influence of high-pressure, velocity and cell potential on the overall cell performance.

### 4.3.1. Model Input Parameters

**Geometry Details and Process Conditions**

The 2D model is developed based on the geometric details listed in Table 4.1. Additionally, among the process conditions listed in Table 4.1, all except for pressure, velocity and cell potential are kept constant.
According to the above description, the dissolved CO$_2$ enters the cathodic chamber. CO$_2$ solubility at given operating conditions is calculated using the method elaborated in Section 4.1. With KHCO$_3$ as the electrolyte, the equilibrium concentrations of different species are calculated as follows:

\begin{align*}
    K_{b1} &= \frac{k_{f1}}{k_{r1}} = \frac{[CO_2][OH^-]}{[HCO_3^-]} \quad (4.9) \\
    K_{b2} &= \frac{k_{f2}}{k_{r2}} = \frac{[HCO_3^-][OH^-]}{[CO_2]} \quad (4.10) \\
    [K^+] + [H^+] &= [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] \quad (4.11) \\
    [K^+] + \frac{K_w}{[OH^-]} &= [OH^-] + K_{b1}[CO_2][OH^-]^2 + 2K_{b1}K_{b2}[CO_2][OH^-] \quad (4.12)
\end{align*}

In equations 4.9 and 4.10, $k_f$ and $k_r$ are calculated from Table 3.1. As ERC is assumed to occur in neutral to alkaline medium, the reaction rates corresponding to b1 and b2 are used. This is further elaborated below in section 4.3.2. Further, equation 4.11 ensures the charge conservation (or electroneutrality). Lastly, equation 4.12 can be solved iteratively to get OH$^-$ concentration, and subsequently that of the remaining species.

Contrary to the cathodic compartment, only dilute H$_2$SO$_4$ flows through the anodic compartment. H$_2$SO$_4$ being a strong acid, it dissociates in water. Table 4.2 lists these dissociation reactions, which are assumed to be in equilibrium [24]. The inlet concentration is calculated assuming complete dissociation of H$_2$SO$_4$. 

---

**Table 4.1: Model input parameters**

<table>
<thead>
<tr>
<th>Input Type</th>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Geometry Details</strong></td>
<td>Cell Height (H$_{cell}$)</td>
<td>0.05</td>
<td>m</td>
</tr>
<tr>
<td></td>
<td>Cell Width (w$_{cell}$)</td>
<td>0.001</td>
<td>m</td>
</tr>
<tr>
<td></td>
<td>Membrane Width (w$_m$)</td>
<td>$7.5 \times 10^{-5}$</td>
<td>m</td>
</tr>
<tr>
<td><strong>Process Conditions</strong></td>
<td>Pressure (P)</td>
<td>1 - 50</td>
<td>bar</td>
</tr>
<tr>
<td></td>
<td>Velocity ($U_0$)</td>
<td>0.025 - 0.5</td>
<td>m/s</td>
</tr>
<tr>
<td></td>
<td>Cell potential (V$_{cell}$)</td>
<td>1.8 - 3.2</td>
<td>V</td>
</tr>
<tr>
<td></td>
<td>Temperature (T)</td>
<td>298.15</td>
<td>K</td>
</tr>
<tr>
<td></td>
<td>Catholyte (KHCO$_3$) concentration</td>
<td>0.5</td>
<td>M</td>
</tr>
<tr>
<td></td>
<td>Anolyte (H$_2$SO$_4$) concentration</td>
<td>0.3</td>
<td>M</td>
</tr>
<tr>
<td></td>
<td>Membrane conductivity ($\sigma_m$)</td>
<td>$10^8$</td>
<td>S/m</td>
</tr>
</tbody>
</table>
Another important input parameter is the species diffusivity. The diffusivity directly alters the diffusive flux, and indirectly the migrational flux, through the Nernst-Einstein relation (equation 3.13). Table 4.3 lists the diffusivities of different species involved in the model. These tabulated values are taken from various sources [24, 26, 75]. Although, these values are temperature dependent, viscosity dependent [26], and vary slightly between different sources, in the present work these are kept constant.

Table 4.3: Species diffusivities

<table>
<thead>
<tr>
<th>Species</th>
<th>CO₂</th>
<th>COO⁻</th>
<th>HCOO⁻</th>
<th>H⁺</th>
<th>OH⁻</th>
<th>HCOO⁺</th>
<th>CO⁻</th>
<th>H₂</th>
<th>H₂SO₄⁴⁻</th>
<th>HSO₄⁻</th>
<th>SO₄²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusivity [m²/s] × 10⁻⁹</td>
<td>1.91</td>
<td>0.923</td>
<td>1.19</td>
<td>9.3</td>
<td>5.3</td>
<td>1.5</td>
<td>2.03</td>
<td>4.5</td>
<td>1</td>
<td>1.33</td>
<td>1.065</td>
</tr>
</tbody>
</table>

Electrode Kinetics
ERC in aqueous electrolyte using Sn electrodes produces mainly three products, as shown in Figure 4.3: HCOO⁻, CO, and H₂. Researchers proposed different plausible reaction mechanisms for HCOO⁻ and CO production, its precise mechanism still remains debatable. For this research, however, a recently proposed mechanism is adapted [22] that involves following steps: the formation of radical anion *CO₂⁻, its subsequent protonation to form an intermediate (*COOH or *OCHO), which is further reduced to form either HCOO⁻ or CO. The intermediate *OCHO yields HCOO⁻, and the intermediate *COOH produces CO. Notably, the formation of *CO₂⁻ is assumed to be the rate-limiting step [31]. The subsequent protonation of *CO₂⁻ can take place via the transfer of H⁺ from the aqueous electrolyte. However, in this model, CO₂ reduction reactions are modelled assuming that the protonation of CO₂⁻ proceeds via its insertion into adsorbed hydrogen atom (H⁺) [48]. Implying, CO₂ reduction reactions are treated to be pH independent. Similarly, hydrogen evolution reaction is considered only in alkaline media (H₂O being the proton donor). The first step in H₂ evolution is the Volmer step, in which Hydrogen atom from H₂O gets adsorbed on to the electrode surface. The second step can proceed in two ways, either it can combine with H⁺ from water (Heyrovsky step) or it can combine with another adsorbed Hydrogen atom (Tafel step) [92].

Table 4.4 lists the electrochemical reactions used in this study. The kinetic parameters (α and j₀) for cathodic reactions are fitted using Tafel equation 3.10 on the experimental data by Feaster et al. [22].

Table 4.4: The kinetic parameters for the electrode reactions

<table>
<thead>
<tr>
<th>Electrode Reaction</th>
<th>α</th>
<th>E°(vs SHE at pH=7)/[V]</th>
<th>j₀ [mA/cm²]</th>
<th>c⁰/c⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cathode</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂ + H₂O + 2e⁻ → HCOO⁻ + OH⁻</td>
<td>0.472</td>
<td>-0.43</td>
<td>4.33e-7</td>
<td>c_hcoo/c_co2</td>
</tr>
<tr>
<td>CO₂ + H₂O + 2e⁻ → CO + 2OH⁻</td>
<td>0.1946</td>
<td>-0.53</td>
<td>1.4e-3</td>
<td>c_co2/c_co2</td>
</tr>
<tr>
<td>2H₂O + 2e⁻ → H₂ + 2OH⁻</td>
<td>0.3182</td>
<td>-0.41</td>
<td>6.91e-7</td>
<td>1</td>
</tr>
<tr>
<td><strong>Anode</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O → O₂ + 2H⁺ + 2e⁻</td>
<td>0.5</td>
<td>0.82</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

On the other hand, for the anodic reaction the kinetic parameters are chosen such that it would not influence the cathodic reaction (that is by ensuring small anodic overpotential). A relevant discussion concerning the effect of anode kinetics can be found in Section 5.3.2. All these parameters are used in the concentration dependent Butler-Volmer equation (see chapter 3) to estimate the current density of each product. Therefore, for the sake of completeness, the concentration dependence of each electrode reaction is also provided in Table 4.4. There are two notable remarks: First, for the cell potential range considered the the rate of backward electrochemical reactions (for instance, oxidation of formate to CO₂) is negligible. Second, α values shown in Table 4.4 are for forward reactions, α for backward reaction can be calculated as 1-α.

4.3.2. Model Assumptions
Cathode/Anode compartment:
1. In COMSOL, both compartments are modelled using tertiary current distribution (TCD) with a built-in dilute-species transport. This is justified as concentration overpotential (η_conc), activation overpo-
tential ($\eta_{act}$) and ohmic drop are equally important, and neither can be always neglected. The dilute species assumption assumes infinitely diluted aqueous electrolyte, and therefore no interaction among the dissolved species.

2. In this model catholyte is KHCO$_3$, mainly because it was found to be an optimal electrolyte for higher formate production [112].

3. The temperature is fixed at 298.15 K. Although, in reality, the overpotential losses can be dissipated as heat (for instance, ohmic heating).

4. The ERC is assumed to occur at neutral to alkaline pH. Therefore, CO$_2$ homogeneous reactions b1 and b2 from Table 3.1 are dominant reactions. Moreover, for electrode reaction this means H$_2$O is the proton donor, as mentioned in Table 4.4. The current model therefore does not allow operation in acidic conditions.

5. All CO$_2$ chemical (homogeneous) reactions (reaction b1 and b2 from Table 3.1) are assumed to be in instant equilibrium—the equilibrium is established instantaneously. In reality, this assumption may not be valid for b1 (see Appendix C), as its reaction rate depends on pH [88]. However, implementing the rate-dependent reaction is found to be numerically challenging—it is difficult to achieve solution convergence. This is further explained in chapter 5.

6. The flow is assumed to be fully-developed at the inlet of the flow-cell. This assumption is reasonable for the given geometry, because the entrance length is found to be less than 10% of the channel height for the velocities considered. Therefore, its effect on the average current densities will not be significant.

7. The electroneutrality (equation 3.15) is valid throughout the domain, because the double-layer is not explicitly modelled in this work. As double-layer is not modelled, the influence of electrolyte on product selectivity (see Chapter 2) is also neglected.

8. All the reaction products (HCOO$^-$, CO, H$_2$ and O$_2$) are assumed to remain in liquid phase. However, it is worth mentioning that, in reality CO, H$_2$ and O$_2$ bubbles out immediately due to their low solubility in water at atmospheric pressure.

**Membrane:**

1. The membrane is modelled using secondary current distribution, because the concentration variation is irrelevant in the case of membrane.

2. The potential drop across the electrolyte-membrane junction is assumed to be zero. Usually, it is expressed using Donnan potential [7].

3. The exchange of only H$^+$ ions is assumed through the cation exchange membrane (Nafion), because Na$^+$ allows to conduct only H$^+$.

**Cathode/Anode:**

1. At the cathode, only CO$_2$ and H$_2$O are assumed to get reduced. Implying, other carbon containing species, for instance, HCO$_3^-$ and CO$_3^{2-}$ do not participate in the electrode reactions. Notably, it has been already proved that CO$_3^{2-}$ does not get reduced [53]. On the other hand, the role of HCO$_3^-$ remains debatable: some researchers have observed that HCO$_3^-$ can be directly reduced [46, 53], some others disagree [14, 22], and there are others, who claim that HCO$_3^-$ is decomposed to CO$_2$ first, before it is reduced [18, 33, 112]. Therefore, due to this ambiguity over the role of HCO$_3^-$, in the present work it is assumed that it does not undergo electrochemical reduction.

2. As mentioned above, the anodic reaction (water oxidation) is assumed to be non-limiting. Practically, this means using a catalyst which has extremely facile kinetics of water oxidation. However, in practice, oxygen evolution, in fact, has sluggish kinetics, and it is an energy intensive process [57]. Nevertheless, the assumption facile kinetics of anodic reaction allows for studying the ERC independent of the anodic reaction.
4.3.3. Boundary Conditions and Simulation Settings

This section presents what boundary conditions should be set to solve the underlying equations presented in Chapter 3. Figure 4.4 shows these equations and their respective boundary conditions. These equations shown in the anodic compartment, and the boundary conditions shown on cathodic compartment are applicable to the other compartment as well. There are three remarks worth noting: First, Danckwerts’ flux is the inlet boundary condition selected for species transport. According to COMSOL knowledge base [1], any reaction – here cathodic reaction – which starts right from the inlet, causes unwanted negative concentrations in the domain. By choosing Danckwerts’ flux condition this can be avoided. Second, applied cell potential is assigned to anode, while the cathode is grounded, because it is required to ground one electrode when using COMSOL [2]. All other boundary conditions are self-explanatory.

\[-n \cdot j = 0\]
\[\nabla u = 0\]
\[\nabla_c = 0\]

The underlying equations are grouped in three parts (dashed rectangles) as shown in the anodic compartment of Figure 4.4. The main purpose here is to explain how COMSOL treats these equations while solving the problem. The first rectangle shows the equations for obtaining the velocity field, the second represents the species transport and the third rectangle shows the equations for obtaining electrolytic potential. As it can be noticed, each rectangle contains a set of equations related to what COMSOL refers to as ‘physics’. Moreover, given the non-linear nature of these underlying equations, the solution is found iteratively using the Newton method (see appendix B). This procedure requires finding a jacobian matrix (similar to the derivative of the functional shown in appendix B). In COMSOL this Jacobian matrix can be formed in two ways: fully coupled approach and segregated approach. In the fully coupled approach one jacobian matrix is created covering all the problem relevant ‘physics’. Conversely, in the segregated approach the jacobian matrix corresponding to each ‘physics’ is created separately. In the fully coupled approach one jacobian matrix is created covering all the problem relevant ‘physics’. Conversely, in the segregated approach the jacobian matrix corresponding to each ‘physics’ is created separately. In other words, each ‘physics’ is solved separately. This means, for example, first solving for the velocity field, then for the species transport and lastly for the electrolytic potential, until the solution is converged.

Please note: primarily, the flow-cell model is studied using steady state simulations, and only a few time-dependent (transient) simulations are performed, mainly for the comparison purpose. The steady state and the transient simulations have essentially similar settings. Both use fully coupled approach. Notably, fully
4.3. 2D Model

Coupled approach requires less iterations albeit at a higher memory requirements. Moreover, direct solver is used over iterative solver, mainly because in COMSOL different ‘physics’ require different settings which unnecessarily increases the implementation complexity. The solution is said to be converged when the relative tolerance is below $10^{-3}$. Relative tolerance is essentially the relative difference between previous and current solution. In addition, linear elements with linear shape functions are used for solving the problem. The motivation behind this choice is discussed in section 5.3 by comparing the solution accuracy and computational time when using the first and the second order elements, respectively. An additional solver setting worth noting: during the model set-up, crosswind diffusion in TCD interface should be unticked for achieving a smoother convergence [3].

4.3.4. Meshing

It is mentioned above that COMSOL uses FEM for solving the given equations. To achieve this, a bigger domain (for instance, Figure 4.3) is divided into smaller domains by meshing operation. Given the simple rectangular geometry (Figure 4.3), a structured mesh with quadrilateral elements is an obvious choice. Generally, the meshing philosophy is, generating a finer mesh where higher concentration/velocity gradients are expected. However, creating a finer mesh improves the accuracy albeit at a higher computational cost. In a flow-cell, higher concentration gradients are expected in the wall normal direction of the cathode/anode and membrane; also near the inlet where the flow enters, and immediately undergoes an electrochemical reaction at the cathode/anode. High aspect-ratio quadrilateral mesh elements can meticulously capture these concentration/velocity gradients close to electrode surface and membrane. In addition to this, making the mesh finer at the inlet, and progressively coarser towards the outlet – for instance, as shown in Figure 4.5– can help in accurately resolving the desired physics.

Choosing a mesh size involves balancing the solution accuracy and its computational cost. The mesh size is selected through the mesh independence study, further details on which will be provided in Chapter 5.
Results and Discussion

5.1. 1D Model Validation

The idea behind the 1D model discussed in section 4.2 is inspired by a recent work of Van Beusekom [100]. As explained in Chapter 2, in that work, CO$_2$ homogeneous chemical reactions were not assumed to be in instant equilibrium (Table 5.2), instead they were treated rate-dependent. At the end of the analysis, Van Beusekom [100] reported that CO$_2$ concentration in the boundary layer followed a close to fickian behaviour. Implying, CO$_2$ does not undergo any chemical reaction in the boundary layer. This behaviour is hereafter referred as No Equilibrium case, one in which CO$_2$ undergoes only the electrode reaction and it does not simultaneously undergo any homogeneous reaction (See, Table 5.2). Interestingly, this fickian behaviour of CO$_2$ has aided not only in simplifying the model (Equation 4.8) but also in avoiding its rigorous implementation in MATLAB [100].

To validate the analytical 1D model, it is decided to compare the I-V curves reported in Van Beusekom [100] with that created using the analytical 1D model (Equation 4.8). The results are presented in Figure 5.1. Clearly, both curves are fairly in agreement over the range of voltages tested, thereb successfully validating the analytical 1D model. Please note: in Van Beusekom [100], the limiting current density was incorrectly calculated without considering the stoichiometric number of electrons ($z$) required to reduce CO$_2$ to formate, which is 2 (see equation 3.20). Therefore, to match the results, CO$_2$ diffusivity ($D_{CO_2}$) is reduced by half.

![Figure 5.1: The validation of the analytical 1D model by comparing it with the model by Van Beusekom [100]; P: 5 bar, 0.5 M KHCO$_3$](image)

The analytical 1D model, as mentioned in Chapter 4, can incorporate the effect of pressure, and that of velocity. Essentially, the pressure influences CO$_2$ solubility, and the velocity influences $\delta_{conc}$, and thereby altering the limiting current in Equation 4.8. It can predict the current density at a particular point on the cathode, but to obtain the complete current distribution along the cathode a 2D flow-cell model is essential. Such model is developed in COMSOL, based on the assumptions listed in Section 4.3. The following section presents its analysis.
5.2. 2D Model Analysis

The results of 2D flow-cell model are divided in three sections: first section presents the mesh independence study for validating the 2D model. Second section discusses the two limiting cases regarding the treatment of \( \text{CO}_2 \) homogeneous reactions. Third and the final section elaborates the results of the parametric analysis. The input parameters for this parametric analysis include pressure, velocity and cell potential. The key performance monitoring parameters are formate current density, the faradaic efficiency of formate and surface pH. Furthermore, the results of parametric analysis are divided into three sub-sections: First, the velocity is fixed to analyze the effect of pressure and cell potential. Secondly, the cell potential is fixed to discuss the effect of pressure and velocity. Lastly, the effect on surface pH is analyzed for the above mentioned input parameters. The reader is reminded that, unless otherwise stated, catholyte is 0.5 M KHCO\(_3\), and anolyte is 0.3 M H\(_2\)SO\(_4\).

5.2.1. Model Validation

Before diving into the analysis, confirming the mesh independence is crucial. The 2D model used for this analysis assumes Instant Equilibrium case, contrary to the No Equilibrium case, \( \text{CO}_2 \) undergoes electrode reactions as well as homogeneous reactions. Furthermore, for verifying the mesh independence, four different mesh sizes are selected. Table 5.1 lists their relevant details. Essentially, the goal is to choose a performance monitoring parameter and find the mesh size that balances the trade-off between the solution accuracy and its computational time. To achieve this, \( \text{CO}_2 \) concentration ratio \( \left( \frac{c_{\text{CO}_2}}{c_{\text{CO}_2}^*} \right) \) along the cathode is monitored during the simulation. The results are shown in Figure 5.2 along with the corresponding computational time.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Coarse</th>
<th>Fine</th>
<th>Finer</th>
<th>Finest</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of cells along cathodic/anodic compartment</td>
<td>50</td>
<td>140</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>Number of cells in Membrane</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Number of cells along channel height</td>
<td>60</td>
<td>200</td>
<td>500</td>
<td>600</td>
</tr>
<tr>
<td>Number of cells in boundary layer (6 walls)</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Total number of cells in the entire domain</td>
<td>9060</td>
<td>59800</td>
<td>105500</td>
<td>126600</td>
</tr>
</tbody>
</table>

Figure 5.2: The mesh independence study for validating the 2D model with Instant Equilibrium case; \( U_0: 0.025 \text{ m/s; } P: 1 \text{ bar; } V_{cell}: 3V \)

In Figure 5.2, x-axis is represented in semi-log for the sake of clarity. It can be seen that the coarse and fine mesh poorly resolve the channel entrance, but perform fairly accurate in the rest of the domain. On the other hand, finer and finest mesh correctly resolve not only the entrance region but also the rest of the channel. Notably, the finer mesh provided a converged solution even for the highest velocity (0.5 m/s) and the highest cell potential (3.2 V) tested, whereas the coarse and the fine mesh failed to converge at these conditions. Therefore, finer mesh is selected for the further analysis. Please note: all simulations are performed on a computer with Intel i7 processor; 2.81GHz processor speed; and 16 GB RAM.
5.2.2. The Treatment of CO₂ Homogeneous Reactions

At this point, a pragmatic reader may ask: why are there two cases of treating CO₂ homogeneous reactions—No Equilibrium and Instant Equilibrium? The present study, as mentioned in Chapter 4, assumes Instant Equilibrium case. But, what is the consequence of this assumption? This question is discussed here, highlighting one of the limitations of COMSOL. As mentioned above, CO₂ can undergo electrode reactions as well as homogeneous reactions. All previously developed 1D models ([10, 26, 29, 100]) consider rate-dependent kinetics of CO₂ homogeneous reactions, and Hashiba et al. [29] have explicitly pointed out the importance of using rate-dependent reactions. All homogeneous reactions relevant for this study are re-listed in Table 5.2. Although, it is safe to assume reaction b2 in instant equilibrium, this assumption may not be that evident for reaction b1 [88]. Time required to achieve equilibrium for b1 depends strongly on pH: higher the pH (typically, pH>10) faster it reaches equilibrium (See Appendix D). This clearly justifies why one must use the rate-dependent homogeneous reactions.

However, in COMSOL, obtaining a converged solution for the rate-dependent reactions is found to be numerically challenging. Specifically, the hydroxide ion concentration near the membrane drops to extremely low value which COMSOL can not handle properly, resulting in negative concentrations—a non-physical result. One solution to avoid negative concentrations in COMSOL is defining the species in the rate-dependent homogeneous reactions, for example, as max(eps, cOH⁻) [1]. Where, eps is an extremely small number, around 10⁻¹⁵. This, in principle, avoids zero concentrations to be used in the simulation. However, after this modification, a converged but inaccurate solution is obtained—the concentration of OH⁻ is found to abruptly increase along its concentration boundary layer developed near the membrane. Therefore, in the scope of current study these reactions are considered to be in instant equilibrium.

But Before proceeding with the analysis it is worth comparing how the Instant Equilibrium case performs the No Equilibrium case. For more perspective on this, consider Table 5.2, where two limiting cases are considered: No Equilibrium (NE) and Instant Equilibrium (IE). In other words, NE represents infinitely slow kinetics of CO₂ homogeneous reactions. Conversely, IE assumes infinitely fast kinetics. The reality—finite-rate kinetics (rate-dependent reactions)—is expected to lie in between these two limiting cases.

<table>
<thead>
<tr>
<th>Case</th>
<th>CO₂ + OH⁻ → HCO₃⁻</th>
<th>HCO₃⁻ + OH⁻ → CO₃²⁻ + H₂O</th>
<th>H₂O → H⁺ + OH⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Equilibrium case(NE)</td>
<td>✓</td>
<td>X</td>
<td>✓</td>
</tr>
<tr>
<td>Instant Equilibrium case (IE)</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

From the above discussion, it is hypothesized that NE provides higher formate current density for the given input parameters than IE. Mainly because, CO₂ reduction reaction generates OH⁻, therefore shifting the homogeneous reaction (b1) to HCO₃⁻. To verify the above hypothesis, let us consider Figure 5.3a, which shows the average current density (averaged along the cathode) of formate against cell potentials. At atmospheric pressure, the average current density in NE plateaus out after 2.6 V, while in IE it keeps increasing. Implying, at higher cell potentials, HCO₃⁻ is converted to CO₂ (reaction b1), thereby sustaining the cathodic reaction at higher potentials. But, does HCO₃⁻ really produce CO₂? A simple way to verify this is by replacing KHCO₃ by KCl in IE. The current density in that case plateaus-out after 2.6 V. Implying, indeed at higher potentials HCO₃⁻ produces CO₂. Notably, the average current density in KCl with IE is lower than NE, because OH⁻—generated in electrode reaction favours the formation of HCO₃⁻, thereby lowering the CO₂ availability for the reduction reaction. More interestingly, as compared IE with KHCO₃, the IE with KCl produces lower current density. This may be attributed to the lower conductivity of KCl (5.3 S/m) as compared to KHCO₃ (6 S/m), which results in higher ohmic losses.

Now consider Figure 5.3b, it shows the relative concentration of CO₂ in a narrow region of the cathodic gap, upto 135 μm from the cathode, at half cell height. For cell potential 2.6 V, CO₂ concentration for NE and IE with KCl drops down to zero, the latter dropping relatively faster. Whereas, for IE with KHCO₃, although the CO₂ concentration drops faster than the other two cases, it still remains non-zero at the cathode surface. Another important point to note in Figure 5.3b is, unlike at 2.6 V, IE at 2.4 V follows almost fickian behaviour, similar to that observed in the previous work of Van Beusekom [100]. Indicating that at lower current densities CO₂ can be assumed to undergo only the reduction reaction. This can be confirmed by the similarity between the No Equilibrium and the Instant Equilibrium case in predicting the average formate current density at low cell potentials (Figure 5.3a). This will be further discussed in section 5.3.
From the above explanation, it is clear that for IE at 1 bar and at high cell potentials the homogeneous reaction reaction (b1) is shifted backwards to form CO$_2$, mainly because CO$_2$ concentration falls down close to zero. Therefore, IE predicts a higher current density (upper limit) than NE (lower limit). Conversely, at high pressure in Figure 5.3a, NE shows higher current density (upper limit) than IE (lower limit), mainly because high-pressures improve the CO$_2$ solubility, and the homogeneous reaction (b1) can therefore shift in forward direction to produce HCO$_3^-$, resulting in lower CO$_2$ availability for the reduction reaction than NE. Please note: it is correct to assume that rate-dependent reactions will provide the formate current density between these two limits.

![Graph](image)

**Figure 5.3:** The performance of two limiting cases: No Equilibrium (NE) and Instant Equilibrium (IE); $U_0$: 0.25 m/s (a) The variation of average current density of formate with cell potential; $P$: 1, 20 bar; (b) The relative concentration of CO$_2$ in a part of cathodic gap at the half cell-height; $P$: 1 bar

However, given the difficulty of implementing the rate-dependent reactions in COMSOL, it is decided to analyze the flow-cell with Instant Equilibrium case (IE). Therefore, the results presented hereafter, unless otherwise specified, are for IE.

### 5.2.3. Parametric Analysis

#### Variation of cell potential and pressure

Initially, the velocity is kept constant (0.025 m/s) to study the effect of cell potential and pressure. Let us consider Figure 5.4a. It is noticed that, at atmospheric pressure, increasing the cell potential beyond 2.8 V reduces the average current density of formate. Primarily, for potentials beyond 2.8 V, CO$_2$ at the surface starts depleting faster, resulting in decline in the formate current densities (see equation 3.9), and increase in the hydrogen evolution. This behaviour is evident in Figure 5.4b, the faradaic efficiency of HER is close to 100%, at 1 bar, for the highest cell potential (3.2 V). Along the same argument, another interesting fact in Figure 5.4b is that the improved CO$_2$ solubility at higher pressures increases the CO$_2$ availability near the cathode, thereby favouring CO$_2$ reduction over hydrogen evolution. This leads to increased faradaic efficiency of formate with increasing pressure and reduced faradaic efficiency of hydrogen evolution, which eventually reaches below 7% at 50 bar. It is worth noting that, the improved CO$_2$ solubility with pressure not only increases the formate current density but it also shifts the cell potential beyond which HER starts dominating. For instance, at 20 bar it is 3 V instead of 2.8 V (see, Figure 5.4a). At even higher pressures (50 bar), the formate current density keeps increasing for the tested cell potentials.

Figure 5.4c is essentially an extension of Figure 5.4b, mainly showing the faradaic efficiency of formate corresponding to different cell potentials and pressures. At atmospheric pressure, the faradaic efficiency of formate reduces steadily with increasing cell potential, for the same reason (reduced CO$_2$ availability at near the cathode) elaborated above. However, increasing the pressure can aid in maintaining a high faradaic efficiency of formate at higher cell potentials. Important to note is, for the given cell potential, the faradaic efficiency of formate increases with pressure, but eventually it plateaus beyond certain pressure. This trend is in line with the observations from previous experiments by Todoroki et al. [99], and modeling study by Van Beusekom [100]. The main reason behind this plateauing out is that at higher pressures the pre-exponent ($c_1^{CO_2}/c_1^{CO_2}$) in equation 3.9 starts getting closer to 1, resulting in the trend shown in Figure 5.4a. At 2.6 V, there
5.2. 2D Model Analysis

is a considerable difference (30 mA/cm$^2$) between current density of formate at 1 bar and at 20 bar, whereas this difference is smaller (4.5 mA/cm$^2$) in between pressure 20 bar to 50 bar.

Interestingly, the pressure beyond which the formate faradaic efficiency plateaus depends on the total current density, as shown in 5.4d. The trend indicates that at constant velocity, using higher pressures is necessary to maintain the same faradaic efficiency of formate at higher current densities.

![Graphs showing the effect of pressure and cell potential on formate production](image)

Figure 5.4: The effect of cell potential and pressure on ERC to formate; $U_0$: 0.025 m/s. (a) The average current density of formate (b) The faradaic efficiency of HCOO$^-$, CO and H$_2$ at $V_{\text{cell}}$: 3.2 V (c) The faradaic efficiency of formate (d) Pressure required to maintain the highest faradaic efficiency of formate

**Variation of velocity and pressure**

As shown in the above section, the faradaic efficiency of formate is above 70% at 2.8 V. Therefore, let us discuss the influence of pressure and velocity at this cell potential. Consider Figure 5.5a, the average current density of formate increases with pressure significantly up to around 20 bar. However, further increasing the pressure has no remarkable influence. To confirm the qualitative nature of this trend, the results from 1D analytical model are also shown for velocity 0.025 m/s in the same figure. $\eta_{\text{act}}$ required for the 1D analytical model is taken at half cell-height from 2D model simulations, and the $j_{\text{lim}}$ at that location is calculated using equation 3.20. 1D analytical model qualitatively follows the same trend as obtained using 2D simulations. However, it overestimates the formate current density because, unlike the 2D model simulations, it assumes 100% faradaic efficiency of formate. This analysis indicates that at higher pressure the CO$_2$ reduction reaction is no longer mass-transfer limited. In fact, for the same cell potential CO$_2$ near the cathode surface keeps increasing with pressure, as shown in Figure 5.5a. This is evident in Figure 5.5b, in which unlike at atmospheric pressure, at 50 bar the total normal CO$_2$ flux along the cathode remains almost constant, mainly due to increased CO$_2$ solubility. Please note: this figure represents CO$_2$ flux for 3.2 V, instead of 2.8 V. This is done for highlighting the influence of velocity on CO$_2$ flux and the cathode usage (what length of cathode actively participate in CO$_2$ reduction). Moreover, at 3.2 V it is already shown above that the faradaic efficiency of formate is below 10%. Therefore, it is interesting to find out how the velocity and pressure influences the cathode usage. The sudden drop in CO$_2$ flux coincides the location where CO$_2$ concentration at the cathode drops very low (below $10^{-3}$ [mol/m$^3$]), and this point is shifted at higher cathode heights for higher velocities. This
is mainly because of the reduced boundary layer thickness that improves the mass-transfer (see eq. 3.35).

Moreover, the average current density of foramate increases also with increasing velocity, and very similar to the pressure influence, this increase is more evident at low-moderate pressures (see Figure 5.5a). This increase in current density results, primarily, from reducing the concentration boundary layer thickness, thereby improving the mass-transport. This increased mass-transport is evident in Figure 5.5b. These observations confirm the suggestion given by Hashiba et al. [29] and Schillings et al. [87] that increase in velocity positively influences the current density. Again, as done above, for a qualitative comparison, results from 1D analytical model are shown for pressure 1 bar. A qualitative agreement between the two models is evident. Notably, the analytical model underpredicts the formate current density than the 2D model (see section 5.2.2). At a constant cell potential, this advantage of higher velocity steadily reduces at higher pressures (for instance, beyond 20 bar for 2.8 V). This is attributed to the fact that, at higher pressures, ERC is no longer mass-transfer limited process, and therefore any increase in velocity has no significant influence.

Similar to the current density, the faradaic efficiency of foramate also improves by increasing the velocity, as shown in Figure 5.5d. For 2.8 V the plateauing pressure is 20 bar (see Figure 5.4d), therefore, this influence of velocity on faradaic efficiency is significant below 20 bar. Before interpreting the observed trend, the reader is reminded that, in the current model, CO₂ reduction reaction is concentration dependent while H₂ evolution is not. As discussed above, higher the velocity, higher is the mass-transport. The higher formate current density so obtained increases the total current density, thereby leading to a higher ohmic drop. Therefore, for a fixed cell potential, this higher ohmic drop lowers the available cathodic overpotential for hydrogen evolution. Thus, improving the faradaic efficiency of formate. Contrary to this, Proietto et al. [80] have reported a
decrease in the faradaic efficiency of formic acid with increasing flow-rate. However, they attributed it to the anodic oxidation of formic acid in their membraneless filter-press setup. In the current study, the flow-cell is divided. Therefore, a different trend of formate faradaic efficiency is observed.

**Effect on surface pH**

Up to this point, the effect of input parameters is studied, especially focusing only on the current density and the faradaic efficiency. Another important parameter is the surface pH. Investigating the simultaneous influence of input parameters on surface pH is crucial – between surface pH 6.5-10.5 Sn has a higher tendency to oxidize [53]. In addition, highly acidic or alkaline pH promotes hydrogen evolution reaction. As already mentioned in the Chapter 4, the current model does not allow operation in acidic media, therefore, hydrogen evolution reaction in acidic media will not be studied. Nevertheless, knowing the surface pH allows one to heuristically estimate the conditions at which hydrogen evolution is dominating, and at which Sn is stable.

Before beginning the analysis regarding the surface pH, consider Figure 5.6a. It shows the CO$_2$ solubility and the respective bulk pH at different pressures. The increased CO$_2$ solubility with pressure lowers the bulk pH. Central to the analysis of surface pH is the fact that, in most cases, it differs considerably from the bulk pH. Primarily, because OH$^-$ is produced during reduction reaction (see Chapter 1). For instance, Figure 5.6b provides the variation of surface pH along the cathode at atmospheric pressure.

![Figure 5.6: The influence of pressure, velocity and cell potential on surface pH](image)

(a) The variation of bulk pH with pressure (b) The surface pH variation along the cathode (c) The surface pH at half cell height (d) HCO$_3^-$ flux along the cathode $V_{cell}$: 3 V
The bulk pH at atmospheric pressure is 7.14, however, even for the lowest cell potential, the corresponding surface pH is above 8. Moreover, higher the cell potential higher the surface pH. This rather obvious behaviour is directly linked to the higher reduction reaction kinetics at higher cell potential which results in higher OH\textsuperscript{−} generation and therefore higher surface pH. Notably, at cell potential 3.2 pH is around 12. This rather extreme increase in pH is attributed to increased hydrogen evolution due to strong depletion of CO\textsubscript{2} (see Figure 5.4b which indicates the faradaic efficiency of hydrogen evolution is close to 100% at 1 bar), and the simultaneous decrease in HCO\textsubscript{3}\textsuperscript{−} availability at 3.2 V. Figure 5.7 shows this strong decrease in CO\textsubscript{2} and HCO\textsubscript{3}\textsuperscript{−} at 3.2 V along the cathodic gap at the channel exit. CO\textsubscript{2} and HCO\textsubscript{3}\textsuperscript{−} regulate the surface pH through their homogeneous reactions (see Table 5.2). Therefore, decrease in their concentration near the cathode surface results in higher surface pH.

Now, the question is how pressure and velocity can alter this surface pH. To understand this, consider Figure 5.6c, which shows the surface pH variation extracted at the half cell-height (0.025 m) for two pressures: 1 bar (see Figure 5.6b) and 50 bar. Clearly, increasing the velocity (green line) reduces the surface pH, and this effect is pronounced at higher cell potentials. Similar to the explanation given in section 5.2.3, increased velocity reduces the boundary layer thickness. This reduced boundary layer thickness increases the HCO\textsubscript{3}\textsuperscript{−} flux towards cathode, as shown in Figure 5.6d. In fact, HCO\textsubscript{3}\textsuperscript{−} reduces the surface pH through its homogeneous reaction. A similar trend in surface pH was reported by Burdyny et al. [10] – lower boundary layer thickness resulted in lower surface pH. Another way to reduce the surface pH is increasing the pressure. As shown in Figure 5.6c, increasing the pressure from 1 to 50 bar reduces the surface pH remarkably (pH < 7). Moreover, at higher pressures, surface pH remains almost constant with increasing cell potentials. This is attributed to the already mentioned higher CO\textsubscript{2} solubility at those conditions, and increased CO\textsubscript{2} flux towards the cathode, which reduces the surface pH through its homogeneous reaction. More importantly, in the same figure, Sn stability range is marked [53]. It can be seen that Sn remain unstable, even for the extreme operating conditions mentioned in Figure 5.6c. Except for very high pressure (50 bar) or very high cell potential (3.2 V). However, at 3.2 V hydrogen evolution becomes a dominating reaction (see Figure 5.4b), and although not predicted in this model, hydrogen evolution is known to dominate in acidic conditions which are prominent at 50 bar.

5.3. Discussion
In this section, it is elaborated how the 2D COMSOL model (No Equilibrium case) is actually an extension of the analytical 1D model. In addition to that, some of the modeling assumptions from Chapter 4 are discussed, mainly to highlight the motivation behind the modeling choices.
5.3.1. Comparison between 1D Model and 2D Model

Technically, in the 2D model the boundary layer thickness increases along the cathode length. However, at a particular point along cathode, the 2D model (No Equilibrium case) and 1D model should ideally estimate similar formate current density under the given input conditions and assuming 100% faradaic efficiency of formate.

To verify this, initially, the formate current density and the cathodic overpotential is extracted from the 2D model. A point on cathode at the half cell-height is chosen for testing the agreement between the 2D model and the analytical 1D model. The reader is reminded that: the 1D model presented in Chapter 4 can calculate the current density for the known kinetic parameters, activation overpotential and limiting current density. The only unknown is the limiting current density, which can be calculated analytically (see equations eq. 3.20 and 3.35). Now, with all the necessary values known, the formate current density is calculated by using the 1D model (see equation 4.8). Further, it is then compared with the formate current density extracted from the 2D model (No Equilibrium case). Figure 5.8a represents the results. The close agreement between these two models confirms that a 2D model is in fact 1D model extended in other dimension. Please note: this statement holds as long as the cathodic overpotentials are high enough to neglect the backward reaction (formate oxidation) (see section 4.2). In Figure 5.8a, the limiting current is slightly overestimated by the 1D model. The reason is, at velocity 0.025 m/s the Lévêque approximation does not hold, which is used to calculate \( \delta_{\text{conc}} \). The concentration boundary layer covers about 1/4th of the channel width \( W_{\text{cell}} \) (see Figure 5.8b), thereby violating the assumption behind the Lévêque approximation. This violation results in the under-estimated value of \( \delta_{\text{conc}} \) and therefore overestimated current densities. Moreover, 1D analytical model is in agreement with 2D model (Instant Equilibrium case) only for lower current densities of formate (around 7mA/cm\(^2\)). Beyond which the 2D model predicts higher current densities for the same reasons given in section 5.2.2.

![Figure 5.8: The comparison between the 2D model (data at half cell-height) and the 1D model](image)

Figure 5.8a shows the limiting current density of formate for velocity 0.025 m/s. What is the dependence of limiting current density on velocity? As a quick reminder: the limiting current density is calculated using the Lévêque approximation, which assumes developing concentration profile and fully developed velocity profile. Figure 5.8b shows the comparison between the limiting current density of formate extracted from 2D model and that predicted using the analytical expression. A close match between the two re-validates the 2D model, now analytically. Please note: at low velocities below 0.2 m/s, as \( \delta_{\text{conc}} \) covers more than 10% of the of the channel width: the Lévêque approximation does not hold at these thick boundary layers.

5.3.2. Discussion on Modeling Assumptions

Modeling Choices based on Computational Time

As already mentioned in Chapter 4, COMSOL is used to solve the system of algebraic equations, and it uses Finite Element Method. Moreover in FEM, as mentioned in Chapter 3, a judicious choice is unavoidable in selecting the element order, particularly for maintaining a balance between the computational cost and
the accuracy. In COMSOL, velocity and electrode potential is calculated using linear elements, by default. However, species concentration and electrolyte potential can use linear or quadratic (or even higher order) elements. Therefore, to choose an appropriate element order, it is decided to monitor the formate current density along the cathode for both the element orders. The results are presented in Figure 5.9a. Linear and quadratic elements both predict fairly similar formate current density along most of the cathode height. Strikingly, the linear elements reduce the computational time (in this case) by almost 6 times than the quadratic elements. Therefore, using the linear elements is an obvious choice. Please note: for the quadratic elements, the simulation became extremely computationally-expensive with the finer mesh, which is the mesh-size selected after mesh independence study. Therefore, fine mesh was selected instead. The fine mesh, as mentioned in section 5.2.1, does not resolve the entrance region effectively, but it does accurately resolve the rest of the channel. This explains the odd-behaviour of formate current density at the entrance region in Figure 5.9a.

Similarly, the type of solver is also selected based on the computational time. Figure 5.9b presents the variation of formate current density along the cathode for the steady state as well as the time-dependent solver. Here, the time-step of 0.1 seconds is used for the time-dependent solver. The formate current density thus obtained neatly overlaps the steady state solution. However, the computational time requirements are remarkably high for the time-dependent solver. Therefore, the steady state solver has been used in this study.

![Figure 5.9: Analyzing the trade-off between accuracy and computational time in 2D model (a) Linear vs quadratic elements, (b) Steady-state vs time-dependent (transient) solver; P: 1 bar, V_{cell}: 2.6 V, U_0: 0.025 m/s](image)

Membrane Conductivity Variation

The membrane is modelled using secondary current distribution, as mentioned in Chapter 4. In secondary current distribution, the conductivity is a free parameter. Typically, a higher conductivity is desired to reduce the ohmic losses across the membrane. A general question would be, what is the influence of this membrane conductivity on the flow-cell performance? To answer this question, consider Figure 5.10a, which shows the variation of formate current density along the cathode for different membrane conductivities. The formate current density is seen to be almost similar along most of the cathode height, except for the entrance region, at which it is seen to be slightly higher for higher conductivities. However, there is no substantial difference on the average formate current density. Implying minimal variation in the ohmic drop corresponding to the lowest and highest conductivities.

In fact, this can be clearly seen in Figure 5.10b, which shows the variation of electrolytic potential along the flow-cell width at half cell-height. The electrolytic potential is almost similar for two extreme conductivities. More importantly, the ohmic drop across the membrane is found to be considerably smaller than what is found across the cathodic and the anodic gap. Therefore, for a given cell potential, the cathodic potential, and hence the formate current density, is found to remain nearly unchanged even for the two extreme membrane conductivities considered. Notably, the ohmic drop across cathodic gap is more than the anodic gap, which is evident from the slope of the electrolytic potential, mainly because the higher conductivity of H_2SO_4 (11.5 S/m, anolyte) than KHCO_3 (6 S/m, catholyte).
5.3. Discussion

The Effect of Anode Reaction Kinetics

Oxygen evolution reaction (OER) is the anodic reaction in the current study. Not surprisingly, its reaction kinetics influence the overall flow-cell performance. The anodic overpotential is altered depending on the anodic reaction kinetics. Typically, the cell potential is divided into cathodic/anodic overpotentials and ohmic drop (see equation 3.11). Therefore, for the given cell potential, lowering the anodic overpotential allows one to apply higher overpotential to cathodic reactions, thereby improving the current densities (in this case, the formate current density).

Figure 5.11 presents the influence of anodic reaction kinetics on the average formate current density. As mentioned above, increasing the exchange current density of OER, results in increased formate current density. This observation indicates that improving the reaction kinetics of anodic reaction is equally important, and therefore should not be neglected. In the current study, the exchange current density of OER is assumed to be $1 \text{ mA/cm}^2$. Although, this value is higher than what is observed in practice ($10^{-3}$ (catalyst: Ir) - $10^{-6}$ (catalyst: Pt) [mA/cm$^2$] [86]), it is selected to reduce the influence of anodic overpotentials on cathodic reactions.

Most notably, in a recent experimental study, Jiang et al. [39] have indicated a similar improvement in ERC to formate, mainly due to the reduction in the anodic overpotentials resulted from changing the anode...
catalyst from Pt to IrO$_2$-Ta$_2$O$_5$/Ti. Moreover, they have also stressed that lowering OER overpotential is a cost-effective strategy for electrochemical CO$_2$ reduction [39].

**Optimum Electrolyte Concentration**

In this study, the catholyte (KHCO$_3$) concentration is assumed to be 0.5 M. But whether it is optimum or not is unknown. The increase in electrolyte concentration, on one hand, reduces the CO$_2$ solubility (section 4.1) and therefore increases $\eta_{\text{conc}}$, but on the other hand, it increases the conductivity and therefore reduces the ohmic drop $\eta_{\text{ohm}}$. Therefore, there exists an optimum electrolyte concentration. To find that optimum corresponding to a current density, $\eta_{\text{conc}}$ and $\eta_{\text{ohm}}$ is calculated using the following equations,

$$\eta_{\text{conc}} = \frac{RT}{zF} \ln \left(1 - \frac{j}{j_{\text{lim}}} \right)$$  \hspace{1cm} (5.1)

$$\eta_{\text{ohm}} = j \left( \frac{w_a}{\kappa_a} + \frac{w_m}{\kappa_m} + \frac{w_c}{\kappa_c} \right)$$  \hspace{1cm} (5.2)

Equation 5.1 is obtained by combining equation 3.6 and 4.7. Moreover, in equation 5.2, $\kappa$ is the conductivity [S/m], in this case of KHCO$_3$ (assumed to be same in the cathodic and the anodic compartment), which is calculated using the explicit parametric relations given by McCleskey [70]. Here, subscripts $a$, $m$ and $c$ represent anodic gap, membrane and cathodic gap, respectively. Above equations are used to estimate an optimum electrolyte concentration for the given gap thickness ($w_{\text{cell}}$) and membrane thickness ($w_m$). The optimum electrolyte concentration essentially minimizes the summation of $\eta_{\text{conc}}$ and $\eta_{\text{ohm}}$. For this purpose, the current density is assumed to be fixed at 7 mA/cm$^2$, and half-cell height is selected to calculate the limiting current density (equation 3.20). For different electrolyte concentrations, the results are presented in Figure 5.12.

![Figure 5.12: The influence of pressure and velocity on the optimum electrolyte concentration; P: 1, 10 bar and U$_0$: 0.25, 0.5 m/s](image)

Increasing the velocity by 2 times at 1 bar increases the optimum electrolyte concentration by 0.5 M. Mainly because the $\eta_{\text{conc}}$ is reduced by increasing the velocity. Similarly, increasing the pressure from 1 bar to 10 for 0.25 m/s velocity, shifts the optimum electrolyte concentration to a value greater than 3 M (which is out of the range of the electrolyte concentrations considered). At higher pressure $\eta_{\text{conc}}$ is reduced substantially, which allows using higher electrolyte concentrations. What is interesting is even for such lower current densities the optimum electrolyte concentration is higher than what is generally used in the literature (see Table 2.1).

Therefore, it is clear that the optimum electrolyte concentration is influenced by operating conditions, and of course by current density. The current density used for this analysis is considerably low (7 mA/cm$^2$),
at higher current densities which are reported in this study (around 50-100 mA/cm$^2$) the ohmic drop is expected to start dominating. Thereby, shifting the optimum electrolyte concentration corresponding to 1 bar to a lower value. With the knowledge of operating conditions, such analysis can be useful for estimating the optimum electrolyte concentration for the experimental purpose.
Conclusions and Future Outlook

6.1. Conclusions

This study focused on modeling the electrochemical reduction of CO₂ (ERC) to formate on a tin (Sn) electrode in a flow-cell, the major findings of which are summarized below.

One of the complexities of modeling ERC is that CO₂ can undergo a reduction reaction (in this case to CO or HCOO⁻) as well as a homogeneous reaction (to HCO₃⁻). In this study an analytical 1D model is developed for the operating conditions at which the homogeneous reaction can be neglected. It is found that this assumption is valid only for very low current densities (below 7 mA/cm² as found in the analysis). At higher current densities, the CO₂ homogeneous reaction can no longer be neglected. Therefore, the analytical 1D model applicability is restricted to only low current densities.

Building on the above finding, a 2D flow-cell model is developed in COMSOL incorporating the cathodic and anodic electrode reactions, the membrane effect, and the CO₂ homogeneous reactions to study the influence of operating conditions – mainly pressure, velocity and cell potential – on the cell performance. It is observed that, for a fixed velocity, maintaining a constant faradaic efficiency of formate requires using higher pressures for higher total current densities. Otherwise, at these conditions, the hydrogen evolution reaction starts dominating. At a fixed cell potential (2.8 V), increasing the velocity by an order of magnitude increases the faradaic efficiency of formate by 20% at atmospheric pressure. This increase is less evident at higher pressures, mainly because at these conditions ERC is no longer mass-transfer limited (greater than 20 bar for 75 mA/cm² total current density). For cell potential 3.2 V and atmospheric pressure, ERC is found to be mass-transfer limited. At these conditions, increasing the velocity increases the cathode usage for CO₂ reduction. This is attributed to the reduced concentration boundary layer at higher velocities, which increases CO₂ flux towards the cathode and distributes the CO₂ reduction reaction along the cathode height. Similar to the influence of velocity, increasing the pressure at a fixed cell potential has the maximum impact on the formate current density as long as the process is mass-transfer limited.

At atmospheric pressure and at fixed velocity, increasing the cell potential increases the surface pH (near the cathode). This variation with cell potential is substantially reduced at high pressures, because the resulting higher CO₂ solubility helps lowering the surface pH through the homogeneous reaction. More importantly, increasing the velocity at atmospheric pressure lowers the surface pH. The higher velocity helps reducing the boundary layer thickness, which improves the flux of bicarbonate towards the cathode. The improved bicarbonate flux lowers the surface pH through the homogeneous reaction.

In addition, there are two notable conclusions: First, the anodic process can influence ERC, and it should not be neglected. High anodic overpotentials lower the available potential for the cathodic reaction. Second, a simplified approach is presented for estimating the optimum electrolyte concentration. Increasing the pressure or the velocity lowers the concentration overpotential. Therefore, for a fixed current density it allows for using higher electrolyte concentration.
6.2. Future Outlook

The future outlook is divided into three sections as follows:

6.2.1. Modeling

1. **Incorporating the effect of bubbles:** As mentioned in this study, CO and H\(_2\) are also produced during ERC to formate on Sn cathodes. The presence of these gases certainly alters the current distribution, and even more so at higher current densities. The presence of bubbles alters the cell performance notably in 3 ways [103]: 1) bubbles attached to surface reduce the effective electrode area which is otherwise used for the electrochemical reaction. 2) Bubbles, once detached from the surface, act as flowing insulators, thereby increasing the ohmic drop. 3) Lastly, bubble growth and its detachment, in fact, causes micro-convection of electrolyte around it. This in fact increases the reactant supply to the electrode. In this study, it was attempted to incorporate the bubble effects, but it was not entirely successful. The key insights on incorporating bubbles, gained during this work, are provided in Appendix A. These insights should be helpful in its further implementation.

2. **Rate-dependent CO\(_2\) homogeneous reactions:** As mentioned in Chapter 5, two limiting cases are studied: No Equilibrium and Instant Equilibrium. However, the rate-dependent kinetics should provide a better estimation of formate current density. Therefore, extending the current model to incorporate the rate-dependent CO\(_2\) homogeneous reactions should be beneficial. However, its implementation in COMSOL is difficult for the reasons mentioned in section 5.2.2

3. **Extending the operation of 2D model in acidic media:** At higher pressures (above 20 bar), for example, at 2.8 V cell potential, the surface pH can reach lower than 7. In such acidic conditions the hydrogen evolution reaction (HER) may start competing with ERC. This competition will lead to current densities lower than what it has been predicted by the current model. However, it is recommended to test this experimentally at such higher pressures.

4. **Experimentally validating the 2D flow-cell model:** As already recommended above, experimental validation of 2D flow-cell model is crucial. However, the experimental validation using Sn electrodes has been found extremely difficult due to its fast surface degradation (Sn surface is found to degrade within 1 hour). Nevertheless, it is reminded that, the kinetic parameters of anodic and cathodic reactions are free parameters in this model, which can be tuned to match experimental results. For instance, the exchange current density of OER is lower in practice (as mentioned in section 5.3.2), than the one assumed in this model (1 mA/cm\(^2\)). This means, catalyst activity is in practice is lower than what is assumed in the modeling work. Therefore, it can be changed to more appropriate values when comparing the results between the model and experiments.

5. **Extending the 1D model to incorporate the homogeneous reactions of CO\(_2\):** The proposed 1D model, as mentioned in chapter 4, assumes CO\(_2\) to undergo only a reduction reaction. As mentioned above, this limits its application to low current densities. Therefore, it is suggested to include the effects of CO\(_2\) homogeneous reaction in this model. This modification will certainly increase its application range to higher current densities. Such 1D models are useful for obtaining a quick estimation of current density.

6.2.2. Experimental

1. **Alternatives to Sn catalyst:** Sn is prone to oxidize between surface pH 6.5-10.5 [53]. It is found in this study that, maintaining the surface pH outside the above mentioned pH range favours hydrogen evolution reaction. Therefore, it is recommended to explore other alternative catalysts for formate production. For instance, recently brass catalyst have been reported to produce equivalent current densities to Sn [30]. Moreover, it was reported to be stable for 04 hours, which in case of Sn is less than an hour [23].

6.2.3. General

1. **Using GDEs and porous electrodes:** For higher current densities (more than 150-200 mA/cm\(^2\)), as mentioned in Chapter 2, GDEs and porous electrodes are more promising than the conventional parallel plate electrochemical reactor which is studied in this work. Essentially, GDEs strongly reduce the CO\(_2\) solubility limitations by supplying it in gaseous form, and porous electrodes increase the reaction area per unit volume. However, there are a few technical roadblocks in their commercialization. In case of
GDE the main challenge is \cite{106}: gas diffusion layer and catalyst layer optimization. For example, the thickness of catalyst layer, or the gas diffusion layer, its porosity influences the current density. Similarly, in case of porous electrodes, enhancing the gas removal from the pores is crucial in improving its utilization \cite{41}.

2. **Using paired electrolysis**: Conventionally, the oxygen evolution reaction (OER) is the anodic reaction during ERC, because water is abundantly available. However, OER has higher overpotentials due to its sluggish reaction kinetics \cite{57}. Instead, waste water treatment or water purification have facile kinetics, which can therefore be combined with ERC to reduce the anodic overpotentials \cite{20, 84}. Similarly, as another alternative, chlorine production can be coupled at anode instead of OER \cite{56}. 

Implementing the effect of bubbles in COMSOL

COMSOL Two-Phase Flow Interfaces

Table A.1: The advantages and limitations of the two-phase flow interfaces in COMSOL for modeling gas evolving electrodes

<table>
<thead>
<tr>
<th>COMSOL Interface</th>
<th>Advantages</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bubbly Flow</td>
<td>Lower computational time than Euler-Euler interface because the dispersed phase (gas) is not solved explicitly.</td>
<td>No explicit control over the bubble coverage. It is essential because it varies with current density and velocity [6]. Dispersed phase (gas) fraction up to only 10 percent is allowed in the domain, above which the simulation crashes. Bubble accumulation near the wall can lead to negative liquid fraction values—a non-physical result.</td>
</tr>
<tr>
<td>Euler-Euler</td>
<td>Explicit control over bubble coverage and gas injection velocity, it solves both dispersed (gas) and continuous (electrolyte) phase equations.</td>
<td>High computational time. No restriction on the maximum dispersed phase (gas) fraction, unlike the bubbly flow interface. Allows only constant current densities or bubble coverage as input. To ensure convergence, artificial diffusion is must. According to COMSOL support this condition would no longer be necessary from COMSOL version 5.4.</td>
</tr>
</tbody>
</table>

Simulation Settings
In COMSOL, it is recommended to use the transient simulations to study the gas evolving electrodes. Mainly because the stationary solvers have convergence problems. Similarly, the coupling between multiple interfaces (Tertiary current distribution, species transport and two-phase flow) should be segregated [36, 76]. According to Anders et al. [76] and Ipek et al. [36], the segregated steps should be set as follows:

1. Calculate the continuous velocity field and pressure
2. Calculate dispersed phase (gas) fraction
3. Calculate species concentration and electrolyte potential

The reader is reminded that: segregated approach is just a way of constructing the jacobian matrix (see section 4.3.3).

Recommendation
For implementing the effect of bubbles, it is now recommended to try the third two-phase flow interface of COMSOL: Mixture model. Schillings et al. [87] have used this interface for modeling buoyancy and forced convection driven gas evolving electrode.
Newton method

In COMSOL, non-linear equations are solved mostly using the Newton method. The following simple example explains the way it works. Consider a 1D spring with nonlinear stiffness.

\[
F = 2 \text{ N}
\]

\[
k = \exp(u) \text{ N/m}
\]

Figure B.1: A 1D spring with nonlinear stiffness stretched by a constant load

The functional \( f(u) \) is calculated as,

\[
f(u) = F - \exp(u) u
\]

Essentially, Newton method finds a solution through iterative process. The solution \( u \) makes \( f(u) = 0 \). With the knowledge of initial condition \( u_0 \) and slope of the functional \( f'(u_0) \), \( u_1 \) can be calculated using the following formula,

\[
u_{i+1} = u_i - \left[ f'(u_i) \right]^{-1} f(u_i)
\]

Graphically, the iterative process can be shown as,

Figure B.2: A graphical representation of Newton Method showing the iterative process
Interplay between different timescales in a flow-cell

Please note: this analysis assumes that CO$_2$ diffuses through the boundary layer before undergoing a reduction reaction, and not that it is being produced from HCO$_3^-$ near the electrode surface as reported by Dunwell et al. [18].

What makes the dynamics of ERC in flow-cells rather interesting? It is definitely the interplay between different timescales associated with different physics. There are four major time-scales (the unit is [s]):

1. Flow timescale: $t_{flow} = \frac{H_{cell}}{U_0}$

2. Diffusion timescale: $t_{diff} = \frac{\delta^2_{conc}}{D_{CO_2}}$

3. CO$_2$ homogeneous reaction timescale $t_{homo}$

4. Electrode reaction timescale $t_{hetro}$

The last timescale is extremely small as electrode reactions are generally very fast. The third timescale is what makes the dynamics interesting. The CO$_2$ homogeneous reactions in acidic and alkaline media are given in Chapter 3. The time required for converting CO$_2$ to HCO$_3^-$ actually depends on pH [88]. Figure C.1 shows the variation of e-folding time of CO$_2$ to HCO$_3^-$ with respect to pH.

![Figure C.1: The variation of e-folding time of the CO$_2$ homogeneous reaction to HCO$_3^-$ with pH](image)

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The figure shown here is assuming the catholyte to be 0.5 M KHCO$_3$, for any other concentration the e-folding time will differ. The homogeneous reaction is slowest at neutral pH, which becomes increasingly fast while moving away towards alkaline or acidic conditions. The point to note: if $t_{\text{diff}}$ is lower than $t_{\text{homo}}$, then CO$_2$ can diffuse to the electrode surface without undergoing the homogeneous reaction (CO$_2$ concentration following Fick's law). This will help maximize the availability of CO$_2$ for the electrode reaction. Moreover, as shown in Chapter 5, surface pH can be influenced by pressure, velocity and cell potential. Therefore, controlling the surface pH will aid in controlling the CO$_2$ homogeneous reaction time-scale, and therefore the CO$_2$ availability.
Figure D.1: The influence of pressure and cell potential on (a) The faradaic efficiency of formate (b) The current density of formate (c) surface pH; velocity: 0.025 m/s
Figure D.2: CO$_2$ concentration profiles at P: 1 bar, $V_{cell}$: 2.8 V (a) $U_0$: 0.025 m/s (b) $U_0$: 0.25 m/s

Figure D.3: H$^+$ concentration profiles at P: 1 bar, $V_{cell}$: 2.8 V (a) $U_0$: 0.025 m/s (b) $U_0$: 0.25 m/s


[17] Zhenhao Duan, Rui Sun, Chen Zhu, and I-Ming Chou. An improved model for the calculation of CO\textsubscript{2} solubility in aqueous solutions containing Na\textsuperscript{+}, K\textsuperscript{+}, Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, Cl\textsuperscript{−}, and SO\textsubscript{4}\textsuperscript{2−}. Marine Chemistry, 98 (2-4):131–139, 2006.


