Electrochemical reduction of CO₂ to low-molecular-weight organic molecules

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Abstract

As global warming directly affects the ecosystem and humankind in the 21st century, solutions are continuously being sought to reduce the emissions of greenhouse gases. Of a particular interest is carbon dioxide (CO₂) due to its increasing levels in the atmosphere and contribution to global warming. In response to this challenge, the government of Canada signed onto the Copenhagen accord, and recently the Paris accord in concert with the joint international efforts to curb the mounting CO₂ emissions. To achieve this goal, several methods prove to be useful; among the available technologies, electrochemical reduction of CO₂ is an emerging field that aims not only to reduce the levels of CO₂ but also to convert this undesirable product into valueadded molecules. However, the process is complex and involves several factors, each of which has an influence on the efficiency, selectivity, and yield. It has been established that the cathode (CO₂-reducing electrode) is the main component in the process as it serves as a platform on which the reaction takes place. Each electrode material possesses unique properties that dictate the CO₂ reduction potential, faradaic and energy efficiency, the product distribution and the selectivity toward desired CO₂ electroreduction products. In addition, the electrolyte plays a significant role as the charge-transfer medium between the electrode and the electroactive species in the solution. Other parameters such as temperature and pressure are also important determinants in the process due to the influence that those factors have on the mass transfer in the medium.

This thesis is composed of two main parts. The first part presents a comprehensive review of the scientific literature on the electrochemical CO_2 reduction with the aim of producing value-added products. The second part presents selected experimental results obtained by the thesis author. Namely, electrochemical reduction of CO_2 to produce value-added products dissolved in an aqueous electrolyte was investigated using Ru and Ir/Ru mixed metal oxide coatings deposited on a titanium substrate, as function of electrode potential, pH and temperature. Although potentiodynamic electrochemical experiments indicated that the electrodes can reduce CO_2 , no products dissolved (remained) in the aqueous phase were detected under the investigated experimental conditions. Thus, it is suggested that the products of CO_2 reduction are in the gaseous phase (e.g. CO, CH_4 , C_2H_4), which was not analyzed due to the construction of the electrochemical cell used in the project.

Abrégé

Puisque le réchauffement climatique affecte directement l'écosystème et l'humanité durant le 21^e siècle, des solutions sont donc recherchées afin de réduire les émissions de gaz à effet de serre. Le dioxyde de carbone (CO₂) est d'un intérêt particulier dû à son augmentation de niveaux atmosphériques et à sa contribution au réchauffement climatique. En réponse à ce défi, le gouvernement canadien signe l'accord de Copenhag, pour ensuite signer récemment l'accord de Paris avec les efforts internationaux conjoints afin de restreindre la croissance des émissions du CO2. Pour atteindre cet objectif, plusieurs méthodes s'avèrent utiles; parmi les technologies disponibles, la réduction électrochimique de CO₂ est un domaine assez vaste dont son objectif n'étant pas uniquement la réduction des niveaux du CO2 mais aussi la conversion de ce produit indésirable dans des molécules à valeur ajoutée. Toutefois, le processus est complexe et implique plusieurs facteurs, chacun ayant une influence sur l'efficacité, la sélectivité et le rendement. Il a été établi que la cathode (la réduction de l'électrode du CO_2) est le composant principal du processus car il sert de plate-forme sur laquelle la réaction prend place. Chaque électrode matérielle possède des propriétés uniques qui s'imposent sur la réduction potentielle du CO₂, l'efficacité énergétique et faradique, la distribution du produit et la sélection désirée à l'égard des produits d'électroréduction. En plus, l'électrolyte joue un rôle significatif en tant que moyen de transfert de charge entre l'électrode et l'espèce électroactif dans la solution. D'autres paramètres comme la température et la pression sont également des déterminants importants dans le processus dû à l'influence que ces facteurs ont sur le transfert de masse dans l'électrolyte.

Cette thèse est composée de 2 parties principales. La première partie présente une critique compréhensive de la littérature scientifique sur la réduction électrochimique du CO_2 avec un objectif de produire des produits de valeur ajoutée. La deuxième partie présente les résultats expérimentaux sélectionnés obtenus par l'auteur de la thèse. Particulièrement, la réduction électrochimique du CO_2 pour produire des produits à valeur ajoutée en solution dans un électrolyte aqueux a été étudiée en utilisant du Ru et Ir / Ru revêtements d'oxyde métallique mixte déposé sur un substrat en titane, en tant que fonction du potentiel de l'électrode, de pH et de température. Bien que des expériences électrochimiques potentiodynamiques ont indiqué que les électrodes peuvent réduire le CO_2 , aucun produit dissous (restant) dans la phase aqueuse n'a été détecté dans les conditions expérimentales étudiées. Par conséquent, il est suggéré que les produits de réduction de CO_2 se trouvent en phase gazeuse (par exemple, CO, CH₄, C₂H₄), ce qui n'a pas été analysée en raison de la construction de la cellule électrochimique utilisée dans le projet.

List of Abbreviations and Symbols Used

AES	Auger Electron Spectroscopy
CD	Current Density, mA cm ⁻²
CE	Counter Electrode
CV	Cyclic Voltammetry
Ea	Anodic Bias, V
E _c	Cathodic Bias, V
ECRC	Electrochemical reduction of Carbon Dioxide
EE	Energy Efficiency, %
EQCM	Electrochemical quartz crystal microbalance
FE	Faradaic Efficiency, %
GDE	Gas Diffusion Electrode
HER	Hydrogen Evolution Reaction
IL	Ionic Liquid
М	Molar (mol L^{-1})
LV	Linear Voltammetry
RE	Reference Electrode
SCE	Standard Calomel Electrode
SEM	Scanning Electron Microscopy
t	Time, s
t _a	Anodic Bias Time, s
t _c	Cathodic Bias Time, s
WE	Working Electrode
XPS	X-ray photoelectron spectroscopy
XRD	X-ray Diffraction

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Chapter 1

1. Introduction

The concentration of CO_2 in the atmosphere has recently reached a historic high and has been increasing at a drastically exponential rate [1]. Recent reports have shown that global average level of atmospheric carbon is greater than 400 parts per million, about 40 percent higher than in pre-industrial times and higher than in any other period in at least 800,000 years. In fact, some scientists go further and claim that present CO₂ levels are higher than at any time during the last 6,500,000 years [1]. As bad as it sounds, those figures should come as no surprise since the rising population and the global economy growth have stimulated an unprecedented growth in energy consumption over the past century [2]. In fact, the growing demand of energy has been unavoidably coupled with a rising consumption of fossil resources including petroleum, natural gas, coal and wood that collectively make 90% of our current energy needs [2, 3]. Unfortunately, these resources are associated with environmental concerns due to the emanation of various toxic elements including nitrous oxides, sulfur oxides, heavy metals, volatile components and CO₂. Sulfur and nitrous oxides produced by the combustion of fossil fuels contribute to acid rain and therefore impact both natural areas and biological ecosystems [4]. However, those hazardous components constitute a smaller portion of the emissions that are generated by burning fossil fuels (20%). CO₂, on the other hand, is a major by-product that is formed upon combusting fossil fuels (80%). It is estimated that the burning of one ton of fossil fuels results in the production of more than 2.5 tonnes of CO_2 [3].

The concentration of CO_2 has been on the rise over the course of the last century. While there are both natural and human sources of CO_2 emissions, human-related emissions are largely responsible for the increase that has occurred in the atmosphere since the industrial revolution [5]. CO_2 emissions increased by over 16 times between 1900 and 2008 and by about 1.5 times between 1990 and 2008 [6]. In fact, this surge in CO_2 emission has been translated into an increase in the concentration of CO_2 in the atmosphere which has grown by 25%, from 280 parts per million (ppm) in preindustrial times to over 400 ppm in 2014 according to the National Oceanic and Atmospheric Administration (NOAA) [7]. These alarming facts have signaled the attention of many governments around the world and paved the way for plans in attempt to reduce the rising level in CO_2 emissions and mitigate any potential repercussions.

Canada took a prominent role to the curb the increase in CO_2 emissions due its high annual CO_2 emissions per capita that was estimated to be 20.4 tonnes per person (14th in the world) [6]. Canada's total greenhouse gas (GHG) emissions in 2012 were 699 megatonnes (Mt) of CO_2 equivalent, or 18% (108 Mt) above the 1990 emissions of 591 Mt. Steady increases in annual emissions characterized the first 15 years of this period, followed by fluctuating emission levels between 2005 and 2008, and a steep decline in 2009 mostly due to the economic down-turn (**Figure 1**).



Figure 1: National CO₂ gas emissions, Canada, 1990 to 2012 from [6].

Canada's emissions growth between 1990 and 2012 was driven primarily by increased emissions from the fossil fuel industries and transportation [6]. The drop from 2005 to 2012 was mainly due to the reduced emissions from electricity generation and manufacturing industries [6]. However, the emissions in 2012 (699 megatonnes) were still significantly greater than that of 1990 (600 megatonnes). In an attempt to reduce the mounting emissions, Canada, along with 144 other countries, joined the Copenhagen Accord to achieve a 2020 economy-wide target of a 17 percent reduction in greenhouse gases from 2005 levels as shown in the last point of **Figure 1** [6]. However, according to a recent report by Environment Canada, Canada will fail to meet its 2020 greenhouse gas targets under the Copenhagen Accord even with more regulation of the oil

and gas sector [8]. The report also notes that the emissions are now projected to be 734 megatonnes in 2020–122 megatonnes higher than Canada's target of 612 megatonnes under the Copenhagen international treaty signed in 2009 [8]. This is mainly attributed to the expected rise in unconventional oil production from oil sands which is projected to go up from 1.1 to 2.3 million barrels of bitumen per day in 2020 [6]. By 2020, oil sands products will add roughly 70 megatonnes to the 2005 CO₂ emissions levels [6]. Recently, at the Paris climate conference (COP21), 195 countries adopted the first-ever universal, legally binding global climate deal. Among others, Canada committed to a global action plan to put the world on track to avoid dangerous climate change by limiting global warming to well below 2°C above pre-industrial levels [9]. An important implication would include undertaking rapid reductions in accordance with the best available science. Hence, to address these challenges, it is crucial to pursue further developments in greenhouse emissions mitigation technologies to honor Canada's commitments in the global effort to mitigate with climate change.

The commitment that Canada and most of the world took to reduce the CO_2 emissions stems from the fact the growing CO_2 emissions are associated with deleterious consequences. Although on the surface, CO_2 appears, as a compound which occurs naturally and serves as the primary source of carbon for photosynthesis of plants and crops, harmless, it is also a potent greenhouse gas that has been found to be closely correlated with ocean acidification and global warming, which might entail catastrophic climate change [10]. That is because this gas absorbs infrared heat that is emitted off earth. The level of longwave radiation that escapes the atmosphere depends on the concentration of greenhouse gases. As more greenhouse gases are present in the atmosphere, less heat is radiated out from the planet [11]. Indeed, it has been established that the heat trapped in the atmosphere is linked to the rise in the average global temperature [11]. **Figure 2** shows the relation between the atmospheric CO_2 concentration and the temperature change in the past 400 thousand years [2]. It is clear that the rise in temperature directly follows the trend as the increase in the CO_2 atmospheric concentration.

The increase in the planet's temperature has many consequences which are already taking place such as the melt of the glaciers and ice sheets, the increase in the sea level, the shift in precipitation patterns (rain and snowfall) and the increase in the oceans' acidity. Recently, it was reported that the oceans' water pH have dropped from 8.25 in 1751 to 8.14 to 2004 [7]. This

presents an increased risk for marine life and aquatic ecosystems. Furthermore, as atmospheric CO_2 increases, the rate of evaporation will go up which will consequently increase the levels of water vapor in the atmosphere [12]. Water vapor is also a very effective greenhouse gas and this will increase the earth's temperature even further- a positive feedback [12].



Figure 2: The correlation between atmospheric CO₂ concentration and temperature change for the past 400 thousand years [2].

These alarming facts necessitate seeking to either curb the rising levels of emissions or reduce the concentration of CO_2 in the atmosphere. The primary solution that is usually proposed is to lower our dependency on fossil fuels and rely on clean technologies to supply the necessary energy needs. That is because the use of alternative energy sources such as solar, wind, nuclear or water power is associated with zero CO_2 emissions and hence these alternatives can reduce our carbon footprint. However, the energy supply that can be obtained from the abovementioned sources is limited to 30% due to their intermittent nature and therefore cannot replace fossil fuels in the near future [13].

Since our dependence on fossil fuel does not seem to be ending anytime soon, it is essential to address the high levels of CO_2 emissions and reverse climate change. Currently, there are two

major approaches to this problem. The first includes capturing and geologically sequestrating CO_2 in underground reservoirs. The applicability of this process is, however, constrained by safety, space and cost [14]. The second technology is based on converting CO_2 into useful low-molecular weight molecules. This technique involves capturing CO_2 from point sources such as industrial plants and converting it into usable organic molecules such as formate/formic acid, methanol, ethanol, methane and ethylene, to name a few. Among the thermochemical, electrochemical, photoelectrochemical and photocatalytic routes developed so far for reducing CO_2 into value added chemicals, only the electrochemical routes appear to possibly be commercially viable due to the following reasons

The electrochemical reduction of CO_2 can be carried out under mild conditions such as atmospheric pressure and temperature, thereby bringing higher feasibility of reducing atmospheric CO_2 . Also, this process can be integrated with electricity that is obtained from sunlight using any of the existing technologies such as photovoltaics [1]. Further, water, as an abundant source, can supply protons needed in the reaction pathway of CO_2 conversion. In addition, the process is highly controllable that can lead to higher conversion efficiencies and thereby better favorability with respect to practicality and industrial prospects [15]. Indeed, being able to efficiently turn CO_2 into value-added molecules would have the largest benefit and impact in the efforts to reduce CO_2 emissions [16].

The electrochemical reduction of CO_2 to useful products has been studied extensively in many previous studies. Although this process provides a promising route for the reduction of CO_2 , a number of challenges still prevent its practical applicability. These challenges include the high costs associated with the energy needed to induce the electrochemical reduction [13, 15-17]. Also, the low faradaic (current) efficiency of the reaction discourages up-scaling the process [2, 13, 17-19]. Another obstacle that hampers this process is the choice of the electrocatalyst which represents a significant challenge, as many of the electrode material previously investigated proved to be limited by rapid deactivation, low selectivity and high overpotential [20]. Indeed, researches have recognized that the largest limitation in the process of reducing CO_2 electrochemically is the poor performance of the electrocatalyst, i.e. the low catalytic activity and selectivity, along with the poor stability associated with it [16]. Therefore, the practical application or industrial-scale implementation of CO_2 reduction to produce usable low-carbon fuels seems to be far from adequate.

In order to enhance the applicability of the process and prompt its optimization, one of the important steps is to investigate the relation between the process conditions and the performance of CO_2 electroreduction. For this purpose, this research discusses the influence of the several process conditions (i.e. electrode selection, hydrogen evolution, pressure, pH, temperature) on the product distribution, selectivity and the efficiency of the electrochemical reduction of CO_2 . In addition, the current knowledge on the process is also considered in detail putting emphasis on the factors affecting the efficiency and the selectivity of CO_2 conversion. Also, current concepts on the mechanisms of the reaction are examined shedding light on the most recent and elaborate reaction pathways reported in literature. Besides the comprehensive nature of this report, the author also presents an attempt to reduce CO_2 electrochemically using conductive RuO₂ oxide due to its surface and electrochemical characteristics commonly seen in material active toward CO_2 electroreduction. The influence of the process parameters and experimental conditions is also discussed using common electrochemical methods.

1.1 Thesis Structure

Chapter 1 introduces the topic of the electrochemical reduction of CO_2 with a perspective on the adverse effect associated with the mounting CO_2 emissions and the commitment that Canada took toward the reduction of those emissions. The final part presents the possible pathways to address the CO_2 dilemma and suggests that CO_2 electroreduction is the most promising and cost-efficient method.

Chapter 2 states the objectives of the thesis.

Chapter 3 provides an in-depth review on the electrochemical reduction of CO_2 . In this chapter, the discussion covers the most influential process parameters that dictate the product distribution, faradaic efficiency and selectivity. In the outset of the chapter, the fundamentals of CO_2 electrolysis are covered to facilitate the understanding of the content for the reader. In addition, terminology and figures of merit used commonly in the area of CO_2 electroreduction are discussed. The later sections in the chapter are aimed to review the relevant studies that have

been done on selected metal catalysts that yield value added products such as CO, hydrocarbons and alcohols.

Chapter 4 discusses the main challenges encountering the process and preventing its commercialization and covers the most promising solutions that have been suggested in literature to tackle those challenges and optimize the process.

Chapter 5 covers the screening experiments that have been done in the McGill-Electrochemistry/Corrosion Laboratory on RuO_2 -Ti to test its catalytic activity toward CO_2 reduction. The chapter also includes a brief discussion on the effect of some process conditions on the performance of the system.

Chapter 6 concludes the thesis by summarizing major findings and concepts and outlying future opportunists toward the aim of enhancing the applicability of the process.

Chapter 2

2. Objectives

In spite of the considerable work aimed to electrochemically reduce CO_2 to value-added products, problems such as poor efficiency, product selectivity, high overpotentials and lack of fundamental understanding of the CO_2 reaction mechanism, vitiates the commercialization and any large scale industrial application of this process. The selectivity of reaction is also highly susceptible to changes in local pH, temperature and types of electrolytes used. Fast deactivation of the catalyst is another serious issue, and usually occurs after several hours of CO_2 reduction. In the light of the above considerations, recent studies performed in the field of CO_2 electroreduction have focused on the development of robust electrocatalytic systems that have high selectivity toward a certain product at a minimal overpotential.

The aim of the experimental part of this research work is to investigate the possibility of utilizing Ru and Ir/Ru mixed metal oxide as effective catalysts in the electrochemical reduction of CO_2 . In addition, the effect of process parameters such as the voltage, pH and temperature are examined to understand the individual effect of each on the faradaic efficiency and the reduction rate of CO_2 .

Consequently, the general objectives of this research were to develop bimetallic Ru and Ir/Ru oxide coatings on a titanium metal substrate through thermal decomposition and to investigate their catalytic activity toward ECRC reduction to value-added products. However, since there were no analytical evidence for the formation of products that remained in the liquid phase (in the electrolyte), the thesis will only provide an overview on the experimental methods used to conduct the experiments and some electrochemical results of choice to demonstrate the effect of experimental conditions and the stability of the electrode.

The larger section of this work, thus, will be devoted to providing a comprehensive review on the state of knowledge on CO_2 electroreduction, which could serve the reader as a starting point toward further research and development in this area.

Chapter 3

3. Background and Literature Review

The electrochemical reduction of CO_2 is the conversion of CO_2 to more reduced species by means of electricity. Pioneering studies on CO_2 reduction go as far back as the last century [19]. The electrochemical reduction of CO_2 is of great interest in the fields of theoretical and applied electrochemistry [21]. In fact, many research groups studied this process extensively and reported the production of many value-added molecules, including HCOOH, various hydrocarbons, CO and alcohols [13, 15-18, 20, 22]. However, practical applications of this process have been always discouraged due the low efficiency of energy conversion, i.e. faradaic efficiency (ratio of the charge used to produce desired products to the total charge put in the process) which is in the range of 30 to 40% [20].

The major reduction products commonly encountered in the electrochemical reduction of CO_2 are carbon monoxide (CO), formic acid (HCOOH) or formate (HCOO⁻) in basic solution, oxalic acid (H₂C₂O₄) or oxalate (C₂O₄²⁻ in basic solution), formaldehyde (CH₂O), methanol (CH₃OH), methane (CH₄), ethylene (CH₂CH₂), ethanol (CH₃CH₂OH) and others [16]. The standard potentials for some of the most common reactions that can take place upon the electrochemical reduction of CO₂ in aqueous media at 25°C and pH 7 are listed below [23]. A complete and more elaborate list of the standard potentials can be obtained from reference [21]. The standard potentials are reported vs a common reference electrode—SCE (Standard Calomel electrode). The role of the reference electrode in the system is explained in Section 3.1.

$$CO_2 + H_2O + 2e^- \rightarrow CO + 2OH^- (-0.764 \text{ V vs SCE})$$
(1)

$$CO_2 + H_2O + 2e^- \rightarrow HCOO^- + OH^- (-0.854 \text{ V vs SCE})$$
(2)

$$CO_2 + 6 H_2O + 8e^- \rightarrow CH_4 + 8OH^- (-0.494 \text{ V vs SCE})$$
(3)

$$2CO_2 + 8H_2O + 12e^- \rightarrow C_2H_4 + 12OH^-(-0.584 \text{ V vs SCE})$$
(4)

$$CO_2 + 5H_2O + 6e^- \rightarrow CH_3OH + 6OH^- (-0.624 \text{ V vs SCE})$$
(5)

Note that the reactions listed above only indicate each reaction's tendency and possibility but giving no indication of the reaction's mechanism [23]. In addition, the standard potentials listed

above refer to aqueous solutions only; the potential values in non-aqueous solutions are different [23].

In addition to the thermodynamic and kinetic obstacles related to the reduction of CO_2 (i.e. low efficiency, high overpotential and poor reaction rate) another difficulty lies in the occurrence of competing reactions [2, 13, 14, 18, 20]. Namely, an important feature of any electrochemical reduction in an aqueous electrolyte is the formation of hydrogen gas or what is referred to as the hydrogen evolution reaction (HER) [11]. This triggers a decrease in the faradaic efficiency of the process since some of the energy supplied to the system, which aims to reduce CO_2 , gets consumed by the HER (this reaction is discussed further in Section 3.1.2 & 3.1.3).

Since much of the defining work in electrochemical CO_2 reduction was performed in the last 30 years [18], it is the aim of this work to mix old work with new work to give the reader an idea of where the field has come to and where it is heading to. This approach is used, in part, because many of the highest performing systems were reported in early studies, therefore a review of only current electrochemical CO_2 reduction might miss these important milestones.

3.1 Fundamentals of CO₂ Electrolysis

As the conversion of CO_2 to value-added product is carried out in an electrochemical setup, it is instructive to provide a basic overview on the electrochemical principles behind the process to facilitate the understanding of such an important climate change mitigation method.

A typical electrochemical cell consists of three electrodes (a working electrode (WE), a counter electrode (CE), and a reference electrode (RE)), a conducting medium (electrolyte), and cell boundaries with optional supporting facilities for heating/cooling of the entire cell and stirring of electrolyte to achieve the desired experimental temperature and homogeneous distribution of reactants (**Figure 3**).

In aqueous media, the electrochemical reduction of CO_2 involves the oxidation of H_2O at the anode (Counter Electrode [CE]) and the released electrons are utilized in the reduction of CO_2 at the cathode (Working Electrode [WE]) to reduce either CO_2 or the abundant H⁺ ions (competing HER) in the electrolyte, depending on the employed experimental conditions.

 CO_2 , as an oxidizing reagent, is known to be much less active than molecular oxygen, even with hydrogen as a reduction reagent. Indeed, CO_2 is a very stable molecule (standard Gibbs free energy of formation is -394.01 kJ/mol) which does not undergo any changes under standard state. Therefore, some form of energy has to be supplied in order to activate this inert molecule and to overcome the kinetics barriers. The form of energy is dependent on the nature of the process. While most of the existing processes (chemical and photochemical) require light and high temperature, electrochemical reduction requires a supply of electricity. A potentiostat (power source that operates at constant potential) is often used since it provides the necessary current and controls the voltage difference between the working and reference electrodes.



Figure 3: Basic structure of CO₂ electroreduction electrolytic cell [24].

In order for an electrochemical cell to operate electrolytically, a potential difference must be applied to the cell that is greater in magnitude than the equilibrium/reversible potential $E_{cell,eq}$ which is obtained using the following equation:

$$\Delta G = -n * F * E_{\text{cell,eq}} \tag{6}$$

where ΔG is the Gibbs free energy (J/mol), n is the number of electrons and $E_{cell,eq}$ is the cell voltage at equilibrium conditions (V). The value of ΔG is available in literature for almost all components involved in CO₂ electroreduction and can be thus used in the above equation to determine $E_{cell,eq}$. Ideally, a value slightly higher than the reversible equilibrium potential is

required to drive the reaction, but due to the sluggish kinetics of the reaction, a significantly large value is needed [2, 19]. The exact value of the required potential depends on the choice of the electrode and the experimental conditions. The difference between the applied potential and $E_{cell,eq}$ is referred to as the overpotential and is an important criterion in ECRC (Electrochemical reduction of CO₂) to assess the performance of the process. In this respect, standard potentials for the reactions producing value-added products from CO₂ at 298 K are tabulated in literature. Those standard potentials can be corrected for temperature and pH using the Nernst equation which would yield the theoretical equilibrium potential. It is noteworthy that the energy to initiate the reaction is one of the bigger obstacles in the path of commercializing the process hence the overpotential is an important parameter to consider.

In an electrochemical process, a voltage shift takes place at the anode and the cathode since the concentration of the electroactive species in the vicinity of those electrode changes over the course of electrolysis. A reference electrode is used since it has a stable and a well-known electrode potential and therefore eliminates the possibility of a voltage shift in the process. Hence all potentials used in ECRC are measured vs a reference electrode and not between the working and the counter electrode (which would be the "cell potential").

The three-electrode cell setup is the most common electrochemical configuration used in electrochemistry. In this case, the current flows between the counter electrode and the working electrode, but the potential difference is controlled between the working electrode and the reference electrode (the counter electrode adopts any potential required to drive the oxidation reactions to produce enough electrons for the cathodic reactions). The standard hydrogen electrode (SHE) is the most widely used reference electrode in electrochemical theory to discuss electrochemical redox reactions. To form a basis for comparison with all other electrode reactions, hydrogen's standard electrode potential is assumed to be zero at all temperatures. Potentials of other electrodes are compared with that of the standard hydrogen electrode at the same temperature. Due to its lack of reliability and complexity, the use of SHE has been on the decline, and other reference electrodes such saturated calomel electrode (SCE) and silver/silver chloride (Ag/AgCl) has evolved since then. In the literature review section of this thesis, the saturated calomel electrode is used as a basis of comparison for the work discussed. For this

reason, all the voltages that were not reported vs SCE were converted to the SCE using the following expressions.

E _{SCE}: E _{SHE} - 0.241 V E _{SCE}: E _{Ag/AgCl} - 0.042 V

In providing the required energy to the system, two modes are usually used, galvanostatic and potentiostatic polarization. In galvanostatic polarization measurements, the current between the working and counter electrodes is controlled, and the potential between working and reference electrodes is automatically adjusted to the value required to maintain the current. Alternatively, potentiostatic polarization allows the selection of a specific potential difference (between the working electrode and the reference electrode) while the resulting current can be monitored. Potentiostatic polarization is the most common mode of electrolysis used in literature on CO₂ reduction and hence would be assumed to be the case in the literature review, unless otherwise stated. In addition, most of the studies on the ECRC have been conducted at ambient conditions (i.e. room temperature and atmospheric pressure) and hence those settings will be assumed for the studies discussed in the literature review section, unless otherwise stated.

3.1.1 Terminology and figures of merit

Before shedding light on the considerable literature on the ECRC, it is useful to elaborate on key figures of merit that are commonly discussed in literature to assess the performance of and thus assist in determining the economic feasibility of the process. This terminology will also prove useful in understanding several aspects of the process.

The key figures of merit that characterize the performance of the process are: (i) the faradaic efficiency (FE), (ii) the energy efficiency (EE), (iii) the current density (CD), and the overpotential (discussed in Section 3.2):

(i) The Faradaic efficiency (FE): it is a measure of the selectivity of the reaction for a given product and describes the number of electrons that are used to form this product. FE represents the ratio of the charge used in producing a desired product calculated from the Faraday's law to the real charge supplied by the potentiostat (charge passed through the cell). A reaction with high faradaic efficiency for the formation of a specific product means a high selectivity toward this product. The following equation is used to determined FE:

$$FE = \frac{N * n * F}{Q} \tag{7}$$

Q is the charge passed from the anode to cathode during electrolysis (C)

N is the number of moles of the target product (mol)

n is the number of electrons exchanged to obtain a specific product (e.g. n = 2

for reduction of CO₂ to CO)

F is the Faradaic constant (96500 C/mol)

(ii) The energy efficiency (EE): it is a measure of the overall energy utilization toward the desired product. This is the amount of energy invested to produce the desired products divided by the amount of electrical energy put into the system. The following equation is used to compute EE:

$$EE = \frac{E^{o} * FE}{E^{o} + OV}$$
(8)

 E^{o} is the equilibrium cell potential for a certain product (E_{cathode} – E_{anode})

FE is the faradaic efficiency calculated using equation (7).

OV is the cell overpotential (or the sum of overpotentials) on the cathode and anode.

Based on equation (8), it is apparent that an energetically efficient process must require a high selectivity for a target product in ECRC in addition to a small overpotential typically within few hundred millivolts from the equilibrium potential.

(iii) Overall current density (CD): CD refers to the current response to an applied voltage divided by the geometric surface area of the working electrode. This term also describes the electrochemical reaction rate for of a specific reaction. The reaction rate, as measured by the current density, is also an important parameter as it determines the reactor size and thus capital cost of the process [25]. However, a common pitfall in research work is the reference to CD as the rate of CO_2 conversion whereas it might also include the rate of the HER in addition to that of CO_2 reduction. The partial current densities for the individual products formed can be calculated by

multiplying overall current density by the corresponding FE (equation 7). The electrochemical reduction of CO_2 can become a viable commercial process only when one can obtain high energy efficiency and high reaction rates at a high FE.

3.1.2 Hydrogen evolution reaction (HER)

It is important to explore the principles of the HER since electrochemical CO_2 reduction conducted in aqueous media has to compete with the HER, which occurs in the same potential range as that of CO_2 reduction. However, in most cases, the HER predominates due to its favorable kinetics despite the thermodynamic favorability of CO_2 electroreduction [12]. This would entail a lower selectivity and efficiency for the formation of valuable products from CO_2 conversion. The concern of the HER has been irking the workers on ECRC to the extent that many CO_2 reduction catalysts are often chosen not for their ability to catalyze CO_2 reduction itself, but rather because of their high hydrogen overpotential (poor HER electrocatalysts).

The reaction kinetics of the production of hydrogen depends on the pH of the medium, and it is enhanced in the acidic solution [20]. The abundance of hydrogen ions compared to CO_2 represents a major obstacle toward reducing CO_2 . This is because the solution of CO_2 in aqueous electrolytes under ambient conditions is as low as 30 mM (millimolar) and this means that this process is hindered by mass transport resistance [20]. The HER, on the other hand, is limited by electron transfer. Reactions 9 and 10 are the overall hydrogen evolution reactions that could take place in acidic or alkaline media respectively [26].

$$2\mathbf{H}^{+} + 2\mathbf{e}^{-} \rightarrow \mathbf{H}_{2} \tag{9}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{10}$$

Since CO_2 cannot exist in basic solution, as elaborated in Section 3.2.1.5 and **Figure 18**, only the HER occurring in acid solutions (reaction 9) will be further discussed. The standard potential for the HER is zero vs. SCE (or -0.241 V vs SCE) at standard conditions. Adsorption of the hydrogen atom on the electrode surface (M) takes place through the following reaction:

$$H^{+} + M + e^{-} \rightarrow M - H \tag{11}$$

where M represents the site on which adsorption occurs (electrode surface). It is noteworthy that the formation of the adsorbed species alters the free energy for the reduction of a proton by an amount equal to the free energy of adsorption of the hydrogen atom [26]. This means that the adsorbed hydrogen ions will be more stable than other bulk protons. The free energy of adsorption is specific to the nature of the electrode and hence the choice of the electrode material will govern the degree of adsorption of the hydrogen ion at the surface of the electrode [26]. Over the last decade, the nature and the parameters governing this process have been extensively investigated, and it was recognized that the overpotential required to trigger the HER varies to a high extent with the choice of the cathode material [26]. The further reaction of the adsorbed hydrogen atoms can take place through (12) or (13).

$$2M-H \rightarrow 2M+H_2 \tag{12}$$

$$M-H+H^{+}+e^{-} \rightarrow M+H_{2}$$
(13)

Thus, there are two pathways that could take place in the HER and those are governed mainly by the electrode surface these mechanisms are:

Mechanism 1:

$H^++M^+e^- \rightarrow M^-H$	(11	I)	ļ
	· · ·	- /	

$$2M-H \rightarrow 2M+H_2 \tag{12}$$

Mechanism 2:

$$H^{+}+M+e^{-} \rightarrow M-H \tag{11}$$

$$M-H+H^{+}+e^{-} \rightarrow M+H_{2}$$
(13)

For both mechanisms, there is a formation and cleavage of the M-H bond, and this process is controlled by the free energy of adsorption of the metal surface (M-H bond strength). An increase in the free energy of adsorption leads to the increase in the rate of reaction (11) in both mechanisms making reactions (12) and (13) the rate determining steps [26]. Hence, it can be concluded that the highest rate of hydrogen production will take place at metals where the M-H bond is of an intermediate strength [26]. This principle can be shown graphically by plotting the reaction rate against a property such as the heat of adsorption of the reactant by the catalyst (**Figure 4**).

Figure 4 emphasizes the influence of the metal surface on the product distribution in the electrochemical reduction of CO_2 . The plot (also referred to as Volcano plot because of its shape) exhibits a maximum which gives it a shape of a triangle or inverse parabola. The platinum group of metals exhibits intermediate bond strength while giving a high exchange CD. Metals on the lowest part of the plot, on the right side, are characterized with a very high M-H bond strength, while the metals on the opposite side have rather weak adsorption characteristics. As mentioned previously, the variation shown in **Figure 4** is actually desirable due to the fact that hydrogen evolution is sometimes a desired reaction in some process and in other processes like CO_2 reduction, there is need to suppress it [26]. The platinum metals prove to be an excellent electrocatalyst for hydrogen evolution. On the other hand, Hg, Cd and Pb exhibit high hydrogen overpotential and are suitable electrode materials when hydrogen evolution is an unwanted competing reaction [26,27]. As discussed in a later section, the classification of CO_2 metal electrodes will be closely related to their affinity for the HER and consequently their HER overpotential.



Figure 4: The variation of the exchange current density for the hydrogen evolution reaction at various metals as a function of the free energy of adsorption of hydrogen on metal [26].

3.2 Literature review

3.2.1 Factors governing the ECRC process

Extensive research conducted on the ECRC over the past 20 years provides a clear picture about the influence of process conditions in the process of CO_2 electroreduction. It has been reported that the product distribution, selectivity, and FE depend on factors such as electrode material, pressure, temperature, supporting electrolyte, pH and the interplay among these parameters [7, 14, 18, 20]. Hence, each of the aforementioned factors will receive a detailed treatment further in the text, specifying the role each one plays in the electrochemical conversion of CO_2 to useful products.

3.2.1.1 The nature of the electrode

Due to the varying characteristics of the metal electrodes, the product distribution resulting from CO_2 reduction differs greatly based on the nature of the metal as indicated in **Table 1**.

Metal electrodes are grouped into four broad classifications [20]. The 1st group exhibits high hydrogen overpotential and give HCOO⁻ / HCOOH as the major product. This group includes Pb, Hg, In, Sn, Cd, Ti, and Bi. The 2nd group, which contains Au, Ag, Zn, Pd, and Ga, is characterized with low hydrogen overpotential and form CO predominantly. Cu, in the 3rd group, has an intermediate hydrogen potential and produces considerable amounts of hydrocarbons and alcohol. The 4th metal group consists of Ni, Fe, Pt, and Ti and it does not entail any significant CO₂ reduction products [20]. The classification of these groups is based on the tendency of each metal to bind with one of the first intermediates of CO₂ reduction. It is generally agreed that 'CO₂⁻, the first intermediate in the reaction pathway, is unstable on most of the metals and requires high overpotential (-2.21 V vs. SCE) [18].

$$CO_2 + e^- \rightarrow CO_2^-$$
 (14)

The 'CO₂⁻ intermediate is very high in energy and readily reacts with either water and other electroactive molecules present in solution, including another CO₂ molecule. The generation of 'CO₂⁻, is critical because it is the rate limiting step and the coordination of this intermediate on the surface of the electrode determines if the second electron reduction product will be either CO or HCOO⁻ [14]. Group 1 of metals in **Table 1** consists of those that do not bind the 'CO₂⁻ intermediate and cannot reduce CO. Group 2 metals bind the 'CO₂⁻ intermediate, but cannot

reduce CO. Group 3 (Cu) binds CO_2^- moderately and can reduce CO to further products. Group 4 binds CO_2^- strongly, thereby promoting the HER over CO_2 reduction in aqueous media. CO is an intermediate that follows the formation of CO_2^- since it was proved that CO can be further reduced to other products such as alcohol and hydrocarbon while HCOO⁻ is the end product that cannot be further converted [20, 28].

Two important facts can be obtained from **Table 1**. It is clear that ECRC takes places at markedly more negative potentials than the values estimated from the thermodynamic data and as shown next to reactions (1) - (6). This is due mainly to the presence of intermediates in the CO_2 reduction pathway which require a high overpotential [20]. Also, **Table 1** indicates that the product distribution for each metal is related to the electrode potential that is applied. While the first group exhibits the higher potential varying between -1.48 V on Sn to -1.63 V on Pb and Cd, the second group requires less negative potentials ranging from -1.14 V on Au to -1.24 V on Ga. The reduction of CO_2 using Cu electrode takes place at an intermediate potential of -1.44 V. The fourth group that yields exclusively hydrogen has a wider variation in potentials and no clear pattern [20].

 Table 1: Faradaic Efficiencies of Products in CO2 Reduction at Various Metal Electrodes. Electrolyte: 0.1 M

 KHCO3, T = 18.5 ± 0.5°C: data [20].

Electrode	Potential vs. SHE V	Current density	Faradaic efficiency, %							
		de V m.	mA cm ⁻²	$\rm CH_4$	C_2H_4	EtOH	PrOH	CO	HCOO-	H_2
Pb	-1.63	5.0	0.0	0.0	0.0	0.0	0.0	97.4	5.0	102.4
Hg	-1.51	0.5	0.0	0.0	0.0	0.0	0.0	99.5	0.0	99.5
TI	-1.60	5.0	0.0	0.0	0.0	0.0	0.0	95.1	6.2	101.3
In	-1.55	5.0	0.0	0.0	0.0	0.0	2.1	94.9	3.3	100.3
Sn	-1.48	5.0	0.0	0.0	0.0	0.0	7.1	88.4	4.6	100.1
Cđ	-1.63	5.0	1.3	0.0	0.0	0.0	13.9	78.4	9.4	103.0
Bi ^c	-1.56	1.2	-	-	-	-	-	77	-	-
Au	-1.14	5.0	0.0	0.0	0.0	0.0	87.1	0.7	10.2	98.0
Ag	-1.37	5.0	0.0	0.0	0.0	0.0	81.5	0.8	12.4	94.6
Zn	-1.54	5.0	0.0	0.0	0.0	0.0	79.4	6.1	9.9	95.4
Pđ	-1.20	5.0	2.9	0.0	0.0	0.0	28.3	2.8	26.2	60.2
Ga	-1.24	5.0	0.0	0.0	0.0	0.0	23.2	0.0	79.0	102.0
Cu	-1.44	5.0	33.3	25.5	5.7	3.0	1.3	9.4	20.5	103.5 ^d
Ni	-1.48	5.0	1.8	0.1	0.0	0.0	0.0	1.4	88.9	92.4
Fe	-0.91	5.0	0.0	0.0	0.0	0.0	0.0	0.0	94.8	94.8
Pt	-1.07	5.0	0.0	0.0	0.0	0.0	0.0	0.1	95.7	95.8
Ti	-1.60	5.0	0.0	0.0	0.0	0.0	tr.	0.0	99.7	99.7

*tr.: Trace amount

A considerable amount of research has been performed with the aim of classifying a wide variety of catalyst materials under different experimental conditions (temperature, pressure, pH, electrolyte etc.). Each above-mentioned category will receive a detailed treatment by including a comprehensive literature review on the major studies that have been done under different conditions. In the following section, much of the prevailing research is broken down by the choice of the cathodic catalyst.

3.2.1.1.1 Category 1 (HCOOH/HCOO⁻)-producing metals

Well before Cu was established as an efficient catalyst in ECRC toward the formation of hydrocarbon and alcohol, HCOO⁻/ HCOOH producing electrocatalysts had been long discussed in the literature. HCOOH is formed in neutral or acidic solution, whereas HCOO⁻ is the main product in weak alkaline conditions. Both products have similar chemical characteristics and will be included within the scope of this comprehensive review [14].

The attempts to reduce CO_2 into HCOOH date back to the beginning of the 20th century when Coehn et al. [29] used amalgamated Cu and Zn based electrodes for the electroreduction of CO_2 in aqueous NaHCO₃ and K₂SO₄ solutions [30]. The results showed that the electroplated Cu with amalgamated Zn electrodes exhibited high efficiency for reducing pressurized CO₂. Since then, the investigation of HCOO^{-/} HCOOH producing metals has been a subject of many publications; most of which focused on the use of bare metals as electrocatalysts [14].

Unlike the complex kinetics for the formation of C_2H_4 , CH_4 and alcohol that involve multielectron transfer steps, the production of HCOOH or HCOO⁻ (depending on pH) requires the transfer of only two electrons (reaction 2). This proves advantageous to ease the challenging kinetic barriers. Secondly, HCOOH is a useful energy-storage medium, storing 4.35 wt% hydrogen [31]. Also, HCOO⁻, the anion derived from HCOOH, can be oxidized at similar potentials to hydrogen, making it a viable energy source. In addition, HCOOH can be used as source of energy in a direct fuel cell set-up [32, 33]. Utilizing HCOOH as oxidants in a fuel cell setup to produce electricity offers the possibility of closing the CO₂ loop while yielding useful products from CO₂ thus presenting promising commercial potential. Indeed, value analyses conducted by some industrial bodies have also concluded that this process is most likely to be profitable compared to its competitors that produce CH_3OH , CO, and long chain hydrocarbons [31]. Indeed, HCOOH is a fundamental chemical which is widely used in the textile, tanning, rubber processing and pharmaceutical industries [34]. Some of the most commonly used electrochemical CO_2 reduction catalysts for HCOO⁻ are: Sn, Pb, and Bi, all of which also happen to have significantly high HER overpotential.

3.2.1.1.1.1 Mercury (Hg)

To study their catalytic activity toward CO_2 conversion, Hg pool electrodes have been used as a catalyst in the ECRC in a variety of conditions [35-41]. Truman Teeter and Pierre Van Rysselberghe [38] carried out, in 1954, one of the first trials on the electroreduction of CO_2 using Hg. By investigation on three different lines, polarography, polarization curves and electrolysis, the group confirmed the possibility of reducing CO_2 to HCOOH in aqueous solutions and ambient conditions at a high FE. The authors, however, did not report the cathodic potential they used. The experiments showed that the ECRC on Hg is characterized by a high CO_2 overpotential - a fact that reduces the practical applicability of the process. In 1969, Paik et al. [39] investigated the formation of HCOOH in the potential range between -0.8 V and -1.9 V and discussed their reaction mechanism in different pH ranges.

In 1972, Eyring et al. [36] worked on the ECRC using a mercury pool cathode in a neutral, aqueous solution to establish the mechanism of CO_2 electroreduction on this electrode and to deduce kinetic parameters, which govern the process. The authors presumed that at a relatively high overpotential, the cathodic reduction of CO_2 on Hg proceeds with the charge transfer to CO_2 as the rate determining step. Hori et al. [40] confirmed the findings of Eryene et al. after conducting a similar study on Hg.

With a high overpotential of around 2 V, Russel et al. [37] achieved a FE of 82% using Hg pool electrode, toward the formation of HCOOH in aqueous 0.1 M sodium carbonate under ambient conditions.

Azuma et al. [42] reported that low-temperature electrolysis enhances the production HCOOH. The group studied the current-potential behavior of Hg in 0.05 M KHCO₃ at 0°C and reported an onset potential of -1.6 V for CO₂ reduction (**Figure 5**). The FE reaches its maximum in the region between -2.0 V and -3.0 V and then drops at more negative potentials. At potentials greater than -1.7 V, the FE of HCOOH decreases significantly, while that of H₂ increases up to

100%. This result indicates that CO_2 reduction to HCOOH on Hg requires a high overpotential (0.9 V).



Figure 5: HCOOH (black dot), CO (white dot) and H₂ (triangle) produced on a Hg electrode in a CO₂saturated 0.05 M KHCO₃ solution at 0°C as a function of the electrode potential [42].

Under high pressure, Kohijiro et al. [41] conducted the most recent work on Hg for ECRC in 0.5 M KHCO₃. The authors showed that the FE of HCOO⁻ at all electrodes substantially increases by raising the partial pressure CO₂ in the system, whereas that of H₂ formation drops. Indeed, at 60 atm, the FE toward HCOO⁻ reached 100% with a significant partial CD of 200 mA cm⁻².

In any case, the application of Hg for the electroreduction of CO_2 has been substituted by other materials, in part due to the significant pollution of the environment and adverse health effects that the release of this material may cause [30].

3.2.1.1.1.2 Tin (Sn)

Sn is another metal that was used for the ECRC due to its high hydrogen overpotential [34, 42-68]. Among all the metal electrodes used for electrochemical reduction of CO_2 to HCOO⁻/ HCOOH, Sn is the most commonly used electrode because of its low cost and relatively low toxicity [54].

In an early study, Kapusta et al. [44] discussed the mechanism behind the formation of HCOOH along with the identification of the rate limiting step. A high FE of 95% in aqueous 0.95 KCl +

0.05 NaHCO₃ was obtained but with a poor EE due to the large CO₂ overpotential that Sn exhibits.

Azuma et al. [42] studied ECRC on various metal electrodes in 0.5 M KHCO_3 aqueous solution. At -2.2 V, HCOOH was the main product for Sn with FE of 5.2% at room temperature and 28.5% at about 0°C. Trace amounts of hydrocarbons and CO were observed but not at the same levels as those of HCOOH.

In the same year, Noda et al. [53] reported the selectivity of Sn toward HCOO⁻ formation in 0.1 M KHCO₃ at -1.6 V. A FE of 63% was obtained for HCOO⁻ with a CD of 3.8 mA cm⁻². Under a galvanostatic system of 5 mA cm⁻², a higher FE of 89% was obtained in 0.1 KHCO₃ with a resulting potential of -1.7 V [57].

Mizuno et al. investigated the effect of both temperature and pressure at a potential of -1.8 V [63]. For Sn, 99.2% FE of HCOOH was obtained at 20°C in 0.5 M KHCO₃. Upon increasing the temperature, the FE of HCOOH decreased, and that of H_2 increased.

Most of the aforementioned studies were conducted in divided H-type cells with metal plate electrodes similar to that shown in **Figure 3**. In a recent study, Koleli et al. [47] attempted to reduce CO_2 at Pb and Sn granules in an undivided fixed-bed reactor. Their aim was to increase the surface area at the electrode/electrode interface and achieve a higher CD and a better selectivity. In an aqueous 0.5 M KHCO₃ and 0.1 M K₂CO₃, the highest FE obtained was 74% at - 1.50 V; however, this value dropped to 20% after 140 min. The largest CD of 0.76 mA cm⁻² was reported at -2.20 V. The use of a fixed bad reactor enhanced the performance of the process by lowering the overpotential of the reaction. However, compared to the results reported in literature, no significant improvement was observed as to the FE and CD.

In a novel approach, Li and Oloman [58, 59] developed a tricked-bed scale-up continuous reactor system for the ECRC in which a 3D cathode of tinned-copper mesh was used as a working electrode. Their work aimed to study major process parameters and the interaction between them in a continuous reactor. The results showed that the granulated tin cathode yielded good performance in terms of both FE and stability. The highest FE was 86% in 0.5 M KHCO₃ + 0.5 M KCl.

To alleviate mass transport limitations in the ECRC, Lee et al. [56] used a tin based gas diffusion electrode in a zero gap cell. At a potential of -1.6 V and a temperature of 40° C, the authors reported a FE of 12% and a CD of 2 mA cm⁻² after 2 h of electrolysis.

Recently, Lei et al. [34] used SnO₂ nanocrystals for the electroreduction of CO₂ in 0.1 M NaHCO₃ resulting in a high FE and production rate for HCOO⁻. The role of the oxide layer on Sn was evaluated. Experiments at different annealing temperature of SnO₂ were conducted; the higher the temperature the Sn plate was annealed at, the lower the FE the authors obtained. The Sn electrode with the native oxide layer formed in air had better catalytic performance. Electrolysis experiments were performed in 0.1 M KHCO₃ solutions applying a constant potential in the range from -1.6 to -2.0 V at 0.1 V intervals (**Figure 6**).

It is notable that the FEs on the bare Sn and OE-Sn (Sn oxidized in air for 24 h.) increase with higher voltages until reaching a maximum at -1.8 V. Beyond this point, the FE drops. The difference in the FE efficiencies between the Sn electrode and the OE-Sn electrode is small, whereas the HCOO⁻ production rate of the OE–Sn electrode is faster than that of the Sn electrode. Regarding the CD, OE-Sn achieved the highest overall CD with an average of 5.5 mA cm^{-2} compared to 4 mA cm⁻² on bare Sn.



Figure 6: Variations in the faradaic efficiency (a) and the production rate (b) for producing HCOO⁻ on the Sn electrode and the OE-Sn electrode with the electrolysis potential [34].

3.2.1.1.1.3 Lead (Pb)

Similar to Sn, the use of Pb in ECRC has been investigated in many literature accounts due to its high hydrogen overpotential [41, 42, 47, 53, 62-64, 69-74]. Among the high hydrogen

overpotential electrodes with negligible CO adsorption (Hg, Cd, Pb, Tl, In and Sn) that reduce CO_2 selectively to HCOOH/HCOO. in aqueous media, Pb appears to be the most suitable cathode material for an industrial application. Pb metal electrodes in aqueous electrolytes favored the formation of HCOOH, while in non-aqueous electrolytes, oxalic acid was the dominant product [23].

The earliest CO_2 electroreduction was conducted on Pb at -1.7 V to -2.4 V in quaternary ammonium salt aqueous solutions, with a carbonate/bicarbonate buffer to maintain the pH at 8.3 [69]. Glycolic acid was the only product formed with a FE in excess 100% - that was attributed to the combined effect of chemical and electrochemical reactions. When a Pb electrode was employed in a non-aqueous solution consisting of propylene carbonate, the main product at, -3.0 V, was oxalic acid at a FE of 80% [62]. Other products included CO, glyoxylic and glycolic acids in the potential range of -2.2 to -3.0 V at maximum FE of 15% for CO and 5% for the other products.

In 1987, Ikeda et al. [70] studied the ECRC on several metallic electrodes in aqueous and non-aqueous electrolytes. Using Pb in aqueous 0.1 M tetraethylammonium perchlorate (TEAP) and at -2.0 V and -2.4 V, the FE of HCOOH formation was 88% and 83% while that of CO was 7% and 4% respectively. In attempt to detect gaseous products, under galvanostatic electrolysis at a current of 5 mA cm⁻² and in 0.5 M KHCO₃, Hori et al. [57] reported that the major product at Pb was HCOO⁻ at a FE between 65.5% and 79.5% while that of CO was between 2.4% and 4.1%. Only a trace amount of CH₄ was detected [45].

The effect of low temperatures on the performance of Pb and 30 other metal electrodes was studied by Watanabe [42]. At -2.0 V in 0.05 M KHCO₃, the authors noted that the performance of Pb does not change significantly with lowering the temperature as the FE of HCOOH changes from 9% to 16% at 20°C and 0°C, respectively.

Similar to Watanabe [42], Noda et al. carried out CO_2 electroreduction in aqueous 0.1 M KHCO₃ at various metallic electrodes. Operating at a potential -1.5 V while keeping other experimental conditions constant, the FE was 50% for HCOOH and 3.4% for CO with a CD of 0.4 mA cm⁻².

Under elevated pressure, the effect of temperature was also investigated by Mizuno et al. [63] who reported a FE of 50% for HCOOH (same as Noda et al. [53] at -1.7 V in 0.5 M KHCO₃).

The FE vs temperature profile is characterized by a parabolic trend in which a maximum of 90% is observed at around 60° C (**Figure 7**). This is in stark contrast with what other workers concluded about the positive effect of lowering temperature on the FE of the ECRC [42].



Figure 7: Effect of temperature on the electrochemical reduction of CO₂ on Pb at -1.7 V [63].

In the same respect, Todoroki et al. [41] investigated CO_2 electroreduction, galvanostatically, under high pressure (< 60 atm) in an aqueous 0.5 M KHCO₃ solution using metal electrodes such as Pb, Hg and In. At a CD of 200 mA cm⁻², they reported that the FE for HCOOH formation on Pb increases with pressure and reaches a maximum at 60 atm (**Figure 8**).



Figure 8: Effect of CO₂ pressure on the faradaic efficiencies of HCOOH formation at Pb electrodes at a current density of 200 mA cm⁻², HCOOH : circles H₂: squares [41].

The partial CD of HCOOH formation also increased with the rise of pressure indicating a higher rate of reaction and better selectivity. Recently, ECRC to HCOO⁻ on Pb was carried out in a filter press electrochemical cell and for the first time in 0.5 M NaOH. Using cyclic voltammetry (CV), the authors suggested that the mechanism of HCOO⁻ production involves adsorption and mostly diffusion processes/mass transfer control and complicated kinetics involving parallel or successive reaction.

Koleli et al. [47] studied the ECRC on Pb granules in an undivided fixed-bed reactor with the advantages of relatively large geometric surface area and a small electrode gap. Using a range of potential between -1.5 V and -2.3 V and a different set of electrolysis time in 0.1 M K₂CO₃ and 0.5 M KHCO₃, the highest FE (90%) for HCOOH production was obtained in the bicarbonate solution after 30 min at 1.5 V producing current densities up to 4.36 mA cm⁻². Shifting the potential toward the negative direction caused a major decrease in the efficiency. Another interesting observation was the increase of FE with respect to electrolysis. This is surprising since metal electrodes are generally characterized by catalytic deactivation demonstrated by the rapid drop of FE (more information in Section 4.1.4). Additional electrolysis experiments were carried out by varying the temperature of the catholyte at a constant CD.

In a novel approach with lead oxide, Purkait et al. [74] utilized Pb₂O as electrocatalysts for CO₂ reduction in various electrolytes at different applied voltages with varying time. Carbonate-based electrolytes gave a higher CD compared with bicarbonates. However, larger FEs were obtained in bicarbonates than carbonate electrolyte solutions. For KHCO₃, at -1.5 V and -2 V, high FEs of 37% and 60% were observed. The authors also reported that the FE increased vs time in K₂CO₃. This claim is in contrast to the findings of Koleli et al. [47] who reported a FE of 90% that decays with time under the same experimental condition of Purkait et al.

Despite its good catalytic performance toward ECRC, some authors discourage the use of Pb since it presents a well-known toxicity, and thus they call for an efficient CO_2 electroreduction process based on other green catalysis materials [30].

3.2.1.1.1.4 Indium (In)

Indium (In) has been studied in various environments including both aqueous and CH₃OH solutions to test the effects of supporting electrolytes, pH and temperature on the selectivity and

kinetics of CO_2 reduction [75]. Normally, CO_2 electroreduction on In produces predominantly $HCOO^-$ in aqueous media and CO in non-aqueous solutions [41, 42, 44, 45, 53, 57, 62-64, 70, 76, 77].

Hori et al. [76] used In, for the first time, as an electrocatalyst in CO_2 reduction in 0.5 M NaHCO₃. At a constant current density of 5.5 mA cm⁻², the FE for In was 85% with a resulting voltage of -1.6 V. This suggests a high CO₂ overpotential at In since the equilibrium potential for HCOO⁻ production under similar experimental condition is -0.65 V. The energy efficiency was determined to be 40%. The authors attributed this low EE to the high overpotential for CO₂ reduction on In. These observations were consistent with those of Kapusta and Hackerman [44] who reported a low EE of CO₂ reduction to HCOO⁻ in 0.5 M HCOOH + 0.5 M HCOONa, although a high FE of 95% was achieved.

Hori et al. [57] attempted to identify the presence of gaseous products under galvanostatic electrolysis on In in 0.5 M KHCO₃ and at a constant CD of 5.5 mA cm⁻². The FE for HCOO⁻ ranged between 92.7% and 97.6% (highest among HCOO⁻/ HCOOH producing metal catalyst) and the resulting voltage was -1.70 V. Only trace amounts of gaseous products were detected.

In the same year, Ito et al. [62] tested the catalytic activity of In in non-aqueous solutions at a potential range of -2.1 V to -2.5 V; the main product was CO with FE varying between 95% (between -2.1 V and -2.3 V) and a 60% (at more negative potentials). In contrast with those results, Ikeda et al. [70] reported a FE of 90% at -2.7 V while the FE for HCOOH and oxalic acid was small. In an aqueous medium, the maximum FE was recorded in the potential range of -1.9 V and -2.0 V (close to what Hori et al. reported [76]).

Watanabe et al. [42] reported that at -2.0 V, the FE of HCOO⁻ on In at low temperatures (75%) is higher than that in room temperature (33%) [42]. The same trend was observed for the FE of CO, which dropped from 14% at room temperature to 3% at 0°C suggesting the CO₂ electroreduction on In is enhanced at low temperatures.

The effect of temperature was revisited by Mizuno et al. [63] who conducted experiments at elevated pressure and a series of temperatures in 0.5 M KHCO₃ on In (**Figure 9**). In accordance with the findings of Noda et al. [53] almost a 100% FE of HCOOH was selectively obtained at 20-60°C, whereas the FE drops to 44.5% at 100°C.


Figure 9 : Effect of temperature on electro-chemical reduction of high-pressure CO₂ for indium electrode. Solid circles, HCOOH; diamonds, hydrogen; double circles, CO; triangle, hydrocarbons [63].

Noda et al. [53] studied the effect of the potential on the performance of In in 0.1 M KHCO₃. There is proportional relationship between potential and FE for HCOO⁻ production while for CO and H₂ there is an inverse trend (**Figure 10**). In the studied range of potentials, the largest FE of 80% was obtained at the highest applied voltage. The authors reported a CD of 4.3 mA cm⁻² at - 1.60 V, which is the highest among HCOO⁻ producing metal electrocatalysts.



Figure 10: The faradaic efficiency curves for the formation of CO (0), HCOO⁻ (square) and H₂ (triangle) in 0.1 M KHCO₃ on In from [53].

Vassiliev et al. [78] used CV to investigate the effect of CO_2 pressure on the partial CD of CO_2 reduction at various metal electrodes, including In. They concluded that high pressure atmosphere enhances the performance of the ECRC without analyzing the products, using quantitative measurements, and by only relying on electrochemical measurements.

However, the quantitative analysis was part of the work done by Todoroki et al. [41] who carried out galvanostatic electrolysis of CO_2 on In in 0.5 M KHCO₃. Under a pressurized system, the authors noted an increase in the FE for HCOO⁻ formation reaching 100% at a pressure of 60 atm. This occurred in parallel to a decrease in FE of H₂ while that of CO remained unchanged. In addition, the rise in pressure was accompanied with an increase in the partial CD of CO_2 reduction. Therefore, the authors suggested that mass transfer/diffusion is the limiting step in the pathway of HCOO⁻ production. The authors also asserted that the formation of CO on In is independent of pressure and proceeds at a more positive potential to those required for HCOOH formation. This was attributed to the pH changes at the electrode proximity.

While the production of HCOOH / HCOO⁻ is advantageous for many reasons, a general problem related to the formation of those products is their large solubility in the reaction medium, and the high energy input that would be associated with their extraction. It is also to be mentioned, in this connection, that most of the published reports describe the formation of only highly diluted solutions of HCOOH by CO_2 electroreduction; therefore, the feasibility of a continuous process leading to the product concentrations in the range of mol L⁻¹ has not been conclusively demonstrated to date [79].

3.2.1.1.2 Group 3: CO forming group

Despite the public concern about CO due to its toxicity, the production of CO from CO_2 can be a promising pathway given the role it plays in downstream processing of syngas using Fischer–Tropsch (FT) chemistry. The Fischer–Tropsch process involves a set of chemical reactions that converts a mixture of CO and hydrogen into liquid hydrocarbons such as gasoline or kerosene [80]. It can, however, be advantageous to electrochemically generate CO and H₂ concurrently at the cathode in a H₂/CO ratio close to 2:1, and then to produce the synthesis gas. The synthesis gas can then, by further reaction, be transformed into CH₃OH [12]. Furthermore, the formation of CO electrochemically in the ECRC has the advantage of producing a pure gas that requires no

purification step that is otherwise necessary in commercial production of synthesis gas from natural gas.

The formation of CO takes place in the early steps of the ECRC reaction pathway. In addition, with caustic alkalis, CO forms alkali formates, which can be converted into either HCOOH or alkali oxalates for the production of oxalic acid. The applications of CO extend to many industries and hence its formation through green technologies without any downstream emissions is an advantageous route.

Although the production of CO requires just two electrons as seen in reaction (1), the potential difference that is to be applied is markedly higher than for most of the other products in CO_2 electroreduction, including HCOO⁻ that similarly requires the supply of two electrons. The reason behind that seems to be the high voltage needed to stabilize the first intermediate in ECRC ('CO₂⁻) on CO forming electrodes [18]. Unlike Cu which can produce higher order products, the metals that produce CO as an end product can bind the first intermediate ('CO₂⁻) but cannot further reduce CO (another intermediate) and are generally characterized by a medium hydrogen overpotential [18]. Typically, silver (Ag), gold (Au) and zinc (Zn) are the electrodes of choice for CO₂ reduction to CO due to their binding of CO₂ and inability to further reduce CO. In the following discussion, only the literature work on Au will be examined since both Au and Ag bare very similar features and under identical conditions, Au tend to require lower potentials than virtually any other metal [18]. On the other hand, Zn falls short of the good catalytic activity of Au toward ECRC.

3.2.1.1.2.1 Gold (Au)

The metallic Au surface is currently the most efficient electrocatalytic surface to convert CO_2 to CO selectively. Although the scarcity of Au may prevent its implementation in a large scale application, Au remains an ideal material for fundamental studies due to its high activity and stability [81]. In an early work, Hori et al [82] examined the activity of Au in aqueous 0.5 M KHCO₃. Unlike the HCOO⁻/HCOOH producing metals which require high CO₂ reduction overpotentials, this study concluded that CO is formed at markedly lower cathodic potentials, in the range of -1V and -1.4 V with partial CD between 3.7 mA cm⁻² and 10 mA cm⁻² and a maximum FE of 92% at -1.2 V. Thus this preliminary result pointed to the high catalytic activity of Au toward CO₂ reduction. However, this activity might drop if the potential is not within the

optimal range. This aspect was elucidated in the study of Sakata et al. [42, 83] who obtained, with Au, a FE as low as 17% at -2.2 V in 0.05 M KHCO₃ even though the experiment was carried out under a low temperature of 2° C. The CD was not reported in this study.

The importance of the potential was also highlighted by Noda et al. [53] who reported a high FE of 82% for CO at -1.2 V in 0.1 M KHCO₃ using Au (**Figure 11**). The reported CD was about 4 mA cm⁻². A slight increase in the potential to -1.5 V lowered the FE to 16% and led to the formation of HCOO⁻ with a FE of 6%, while the CD went up to a markedly high 41.3 mA cm⁻² (the highest among the other tested electrodes).

It is clear that the FE of CO at Au exhibits a parabolic trend in which a maximum is attained at around -1.30 V. The FE of H_2 seems to be following the inverse trend to that of CO, as a minimum FE is observed at the same potential that yields a maximum FE for CO formation.



Figure 11: The FE vs potential for formation of CO (circle), HCOO⁻ (square), and H₂ (triangle) in 0.1 M KHCO₃ aqueous solution on the Au electrode at 298 K [53].

Under galvanostatic electrolysis conditions of 5 mA cm⁻² and in 0.1 M KHCO₃, Hori and coworkers [57] reported the production of CO at a FE of 87% in addition to trace amount of HCOO⁻ at less than 1%.

Under high pressure (30 atm) in 0.1 M KHCO₃, Hara et al. [49] studied the effect of high pressure in the ECRC on Au at a constant current of 163 mA cm⁻². The authors reported a FE of 65% for CO formation, 12% for HCOO⁻ formation and 15% for H₂ at a resulting potential of

-1.3 V. These results showed that the product selectivity of CO formation on Au is not changed by increasing the CO_2 pressure. However, the formation of HCOOH on Au becomes more favorable under high CO_2 pressures.

The catalytic activity of Au was also tested in a CH₃OH-based electrolyte solution at a series of temperatures [84]. In contrast to the observations in aqueous media, the FE for CO formation increased with increasing voltages while that of HCOOH dropped within the tested range of temperatures. The maximum FE for CO formation (72.5%) was obtained at -2.4 V and 15°C, while that of HCOOH (14.7%) occurred at -1.6 V and -15°C. The FE of CO was higher than that of HCOOH under all the experimental conditions. In contrast with the conclusions of Azuma et al. [83] who indicated that low temperatures prompted the HER on Au, the authors suggested that the undesirable HER can be suppressed at low temperatures even at high voltages of -2.4 V. According to the authors, this effect may be attributed to the poor reactivity of the electrode surface with the hydrogen ions in the CH₃OH electrolyte at low temperatures. The authors also studied the effect of temperature on the partial current densities (PCD) of CO₂ reduction and the HER on Au, between -1.6 V and -2.4 V (Figure 12). The PCD curve of CO₂ reduction had a parabolic pattern in which a maximum is attained at around 0°C. However, the PCD for H₂ formation decreased markedly with lower temperatures. Therefore, the selectivities at less than 0°C were much larger than those at 15°C. The same trend was observed at potentials higher than -2.2 V. The best selectivity occurred at -1.6 V and 0°C. The Tafel plots that were constructed to study the reaction mechanisms revealed that CO and HCOOH form independently and their production is not limited by the diffusion of CO_2 in the tested potential range. The authors indicated that the sluggish mass transfer, often encountered in the ECRC, can be resolved by operating the process in CH₃OH-based electrolyte at low temperature.

Jaramillo and coworkers [85, 86] reported in 2011 that the surface modification of Au can enhance the activity and product selectivity of the ECRC through the change that occurs in the topology of the electrode's surface (**Figure 13**). The roughened Au exhibits a higher CD than the pristine surface at the entire voltage range. Despite their apparent catalytic activity, it is not clear whether this enhancement is due to the increase of the HER or the CO_2 reduction current.



Figure 12: Effect of temperature on partial current densities for CO₂ reduction and HER at Au electrode at -2.0 V. Total current density (triangle), PCD for HER (circle), PCD for ECRC (diamond). Catholyte and anolyte: 100 mM KOH+ methanol [84].



Figure 13: Current versus potential for pristine gold and mechanically roughened gold. Each data point is the average of potentiostatic CO₂ electrochemical reduction over the course of an hour [85].

Recently, Kanan and coworkers experimented with oxide-derived Au for the ECRC [87]. They resorted to a periodic symmetric square-wave potential routine by which amorphous, thick Au oxide layers were prepared on Au electrodes. The resulting electrodes were used directly in constant-potential-CO₂-electrolysis performed in 0.5 M NaHCO₃. Oxide derived Au was shown to reduce CO_2 more efficiently than polycrystalline Au at a greater FE and using a lower overpotential as low as 140 mV while retaining their catalytic activity for at least 8 h. In terms of stability, oxide-derived gold nanoparticles were more stable and were able to maintain activity

although sintering occurred within 15 min of reduction. Their stability was ascribed to the high stabilization of the CO_2^{\bullet} intermediate on the surfaces of the oxide-derived Au electrodes. The proposed mechanism is shown in **Figure 14**.

polycrystalline Au



Figure 14: Proposed mechanism for CO₂ reduction to CO on polycrystalline Au and oxide-derived Au from [87].

Zhu et al. [88] performed an interesting combined theoretical and experimental modeling study based on Au nanoparticles. The authors synthesized a series Au NPs with different particle sizes ranging from 4 to 10 nm. In an electrocatalytic study, the 8 nm Au NPs exhibited a better gravimetric activity than their larger or smaller counterparts. The study indicated that i) the edge sites on Au NP surfaces favored CO_2 reduction and, ii) the corner sites favored the HER. The authors examined the relationship between the density of the catalytically active surface sites and the Au cluster size. It was found that the 8 nm Au NPs with a 4 nm crystallite diameter are small enough to provide a near-optimum number of edge sites that are particularly active for CO_2

3.2.1.1.3 Hydrocarbon and alcohol producing electrodes

Research over the past several decades has shown that Cu is unique among the CO_2 electroreduction catalysts explored so far for its ability to convert CO_2 to hydrocarbons, CH_4 and C_2H_4 , with a high FE [13, 72, 83, 89]. However, Cu requires an overpotential of almost 1 V and the reaction does not proceed with high selectivity as a fairly broad mix of major and minor products are produced. Despite its low selectivity and high CO_2 electroreduction overpotential, Cu is the only known metal capable of catalyzing the formation of significant amounts of

hydrocarbons at high reaction rates over sustained periods of time [17, 28, 90]. Although Cu does not seem like the ideal catalyst that serves all purposes required in a process, understanding its unique ability to catalyze hydrocarbon formation would enable researchers to design new catalysts that have a higher stability and enhanced activity at low overpotentials [90]. Since Cu has been used extensively in due to its unique ability of reducing CO_2 to value-added products at significant amounts, the discussion below will shed light on the prominent studies on this electrode in the ECRC.

3.2.1.1.3.1 Copper (Cu)

Cu was the first metal catalyst that achieved promising results in the ECRC in terms of CD, FE and product distribution [91]. One of the first attempts using Cu was carried out by Hori et al. [45, 92]. They were able to prove the catalyst's activity toward the ECRC through the formation of CH₄ and C₂H₄, products that had not yet been observed with the ECRC at that time. Similar to the CO producing metals discussed previously, Cu is characterized by a medium hydrogen overvoltage and a weak CO adsorption; however, its strong catalytic performance to hydrocarbons lies in its ability to further reduce CO to higher order products in significant amounts [18]. The unique properties of Cu in the ECRC was studied by many authors and gave rise to many theories regarding the mechanistic pathway of CO₂ electroreduction on the surface of Cu. Aside from CH₄, C₂H₄, CO, HCOOH, alcohols (methanol, CH₃CH₂OH, and CH₃CH₂CH₂OH), and esters, some relatively higher order hydrocarbons, such as paraffins and olefins containing up to 6 carbon atoms, can also be formed using Cu [23].

In an early account, Hori et al. [45] studied the ECRC at several metal electrodes in aqueous hydrogen carbonate solution in which potential gaseous products were analyzed for the first time using Cu. In 0.5 M KHCO₃ and at a constant current of 0.5 mA cm⁻², the authors conducted electrolysis for 30 to 60 min and for the first time reported the production of CH₄ at Cu with a FE as high as 40%. HCOO⁻ and CO were also detected at a FE of 3.1% and 16.5% respectively. Since the total value of the FE for CO₂ reduction products fell in the range of 87-92% which is less than 100%, the authors suspected that some other unidentified products might have been produced.

In a subsequent study, Hori et al. [92] examined the possibility of the production of gaseous products on Cu other than CH₄, reported in their previous study. The process was conducted by

galvanostatic (constant 5 mA cm⁻²) electrolysis between 0°C and 40°C in 0.5 M KHCO₃. Along with the formation of CH₄ at a maximum FE of 65% at 0°C, which dropped with an increasing temperature, the production of C_2H_4 followed the opposite trend and attained a maximum of 20% at 40°C. The production of C_2H_4 observed in Hori et al.'s study was the first time this hydrocarbon was detected in any ECRC trial.

DeWulf et al. [93] were the first group to discuss, from a mechanistic standpoint, the formation of ECRC products and intermediates at a Cu foil electrode. The electrolysis was performed under potentiostatic conditions at -2.0 V and 0°C in 0.5 M KHCO₃. The formation of hydrocarbons was observed in which the major component was CH₄ with a small amount of C₂H₄. The authors suggested that the overall reaction path from CO₂ to CH₄ and C₂H₄ is complicated and involves many key steps and intermediate reactants. The authors also proposed the existence of surface carbene (Cu-CH) which was assumed to be a natural precursor of C₂H₄. In addition, the group suggested that atomic hydrogen formed *via* proton reduction is the active reductant in the production of CH₄ and probably in other steps of the ECRC on Cu.

The new findings about the strong electrocatalytic activity of Cu awakened interest in further evaluating Cu as a promising catalyst for the ECRC [28, 45, 90, 92-152]. Since then, the products observed using Cu have extended to more than just hydrocarbons, as initially reported by Hori et al. [45] in 1985. Alcohols (CH₃OH, CH₃CH₂OH), 1-propanol (C₃H₈), esters, as well as high hydrocarbons such as paraffins and olefins, have been reported in literature [23, 24, 80, 90, 111, 117, 124, 153-156].

In spite of the proven catalytic activity of Cu in the ECRC, its high overpotential, low EE and susceptibility to poisoning (rapid deactivation) are issues that limit the applicability of this electrode in possible large-scale applications. That is why many research groups attempted to enhance the performance of this electrode by employing different electrode designs.

3.2.1.1.3.2 Cu- Alloys

In CO_2 electroreduction, metal alloys such as Cu alloys can exhibit both high electrocatalytic activity and product selectivity in addition to generating products quite different from those obtained on a bare Cu, where the formation of CH_4 and C_2H_4 predominates [16].

Watanabe et al. [94, 95] studied the effect of adding ad-atoms to a Cu electrode to study the catalytic performance of the developed alloy on the selectivity, product distribution and FE of the process. The authors carried out their experiments in 0.05 M KHCO₃ at 2° C and they indicated that, by alloying Cu to other metals, the main products usually obtained in ECRC – HCOOH, CO and CH₃OH – are produced selectively very close to equilibrium potential (low overpotential and at less negative potentials compared to bare Cu. For example, the authors reported obtaining CH₃OH and HCOOH at a Cu-Ni alloy with FE of 10% in the potential region less negative than -0.4 V, whereas this product was not produced using the bare metal electrodes even in the potential range from -0.7 to -1.7 V. In addition to the newly formed products, alloying also proved an enhanced performance as in the case of Cu + Sn and Cu + Pb alloy which displayed a decrease in the overpotential for the production of HCOOH since it was produced at nearly reversible potential and at a maximum FE of 50%, (much higher than that of pure Cu, Sn or Pb electrodes). Cu-Au alloy electrodes showed that alloying the surface severely suppresses the formation of hydrocarbons and alcohols, leading to an increase in CO formation.

To further investigate the role of alloying in enhancing the performance of the bulk Cu, the same Watanabe et al. [110] studied the effect of the microcrystalline phases in the Cu-Sn and Cu-Zn alloys on the selectivity, reversibility and reactivity of the electroreduction of CO_2 . The authors proved that two electrodes made of the same gross alloy compositions but prepared using different baths can yield a different product distribution at different selectivities. For example, the major reduction product was HCOOH on the alloy electrode prepared in the phosphorous bath, while the main product was CO on the alloy prepared in a cyanide bath. Also, the onset potential of the ECRC was dictated by the method of preparation of the alloy and the atomic percentage of each component in the alloy.

Nakato and coworkers [140] studied the ECRC on electrodes made of Cu-Ag alloy in 0.1 M KHCO₃ aqueous solutions. The authors confirmed a higher FE for C_2H_4 on the alloyed Cu-Ag electrode relative to bulk Cu. For the alloy electrode, the FE of C_2H_4 was consistently higher than that of CH₄ over the tested potential region. The authors attributed the improvement in C_2H_4 selectivity to the synergetic effect that arise from the combination of Ag and Cu as Ag would produce predominantly CO which would be transferred to the neighboring Cu atoms and subsequently get reduced to CH₂- a precursor in the formation of C_2H_4 .

Flake et al. [137] conducted experiments using Cu nanoclusters on single crystal 1010 ZnO electrodes since the combination of Cu and ZnO has been used commercially for CH₃OH synthesis from syngas mixtures in the gas phase. The use of Cu/ZnO in the ECRC in aqueous 0.1 M KHCO₃ showed a CD of 12 mA cm⁻² at -1.4 V and a similar activity to metallic Cu (111) electrodes. Product analysis revealed that the main products of Cu/ZnO are similar to those of Cu (111), which included C₂H₅OH, C₂H₄, HCOO⁻, CO and CH₄. However, the authors observed that the relative selectivity of alcohols- measured by the estimated yield- increase by at least one order of magnitude when Cu/ZnO electrodes are used in place of Cu(111). One explanation is that ZnO supports stabilize Cu sites that are catalytically active toward alcohol formation. The ZnO possibly helps disperse Cu and enhances CH₃OH production *via* the "Cu-ZnO synergy" effect. Another possibility is the interaction between Cu nanoclusters and the semiconducting ZnO support.

3.2.1.1.3.3 Copper-oxide

In an attempt to enhance the electrochemical reduction of CO_2 , oxidized Cu surfaces have been applied since Frese et al. [122] reported in 1991 the electroreduction of CO_2 to CH₃OH at various oxidized Cu electrodes. The electrode types included anodized Cu foil, Cu foil thermally oxidized in air, and air-oxidized Cu electrodeposited on anodized or air-oxidized Ti foil. One of the major reasons for the selection of CuO₂ as a potential catalyst is its established ability in the commercial production of CH₃OH from CO and H₂ which are also intermediates in the electrochemical reduction pathway of CO₂. Exceptionally high FE for CH₃OH production, reaching up to 240%, was achieved using Cu plated on a Pt foil. It is important to note the FE of CH₃OH is calculated based on a six-electron (reaction (5)) and FEs greater than 100% indicate electrochemical–chemical mechanisms [104]. The authors reported the greatest CD and FE associated with the use of metallic catalyst under ambient conditions, reaching up to 33 mA cm⁻². The group suggested that the oxidation of Cu enhances the catalytic activity of the surface toward CH₃OH production through the enhancement of the heat of adsorption that occurs upon the oxidation of Cu.

In a study on the advantages of Cu oxide, Kaneco et al. [157] investigated the ECRC in a CH_3OH -based electrolyte with CuO/Zn and Cu₂O/Zn electrodes. The authors selected CH_3OH to enhance the solubility of CO_2 , which is by about four times that in water at ambient temperature.

Hydrocarbons such as CH₄, C₂H₄ and C₂H₆ were produced with both CuO/Zn and Cu₂O/Zn electrodes with a higher FE on the latter. Increasing the copper oxide content in the electrode, the FE of HCOOH and CO dropped gradually while that of C₂H₄, CH₄ and H₂ increased and levelled off at high copper oxide content. The authors suggested that copper oxides (CuO and Cu₂O) have more affinity to produce and chemically adsorb the reaction intermediate CO during the formation of hydrocarbons. The production of hydrocarbons proceeded via an interaction between adsorbed CO and atomic hydrogen at catalyst sites. The presence of Zn favored hydrocarbons *via* producing atomic hydrogens that bind to CO on the adjacent CuO/CuO₂ site. Regarding the relatively better performance of Cu₂O over CuO, the authors pointed to the possibility of efficiency loss due to the use of current in the reduction of CuO to copper metal.

In a recent work, Mul et al. [111] studied the effect of combining copper oxide and nanoparticles and discussed their catalytic activity and hydrocarbon selectivity in the ECRC. CO, CH₄, C_2H_4 and some C_2H_6 were gaseous products in 0.1 M KHCO₃, with a FE of around 25% for the three crystalline structures investigated, (110), (100) and (111). Surface characterization techniques such as SEM and OLEMS revealed that CO₂ reduction did not proceed on Cu₂O but rather on *insitu* formed metallic copper nanoparticles. Experiments at different oxide thicknesses showed that samples with a higher oxide thickness yielded CO at very low overpotentials. Hydrocarbons were formed at higher overpotentials in parallel with a drop in the FE of CO. C₂H₄ was the major product with minor amounts of CH₄ and CO at low initial oxide thickness while the product distribution consisted mainly of CH₄ rather than C₂H₄ at higher initial oxide thickness. The higher the thickness of the Cu₂O layer on the electrode was, the lower the FE of the products obtained at the investigated potential. No deactivation toward the hydrocarbon production was observed for the thinnest samples over the course of 5 h, as compared to polycrystalline Cu which was found to rapidly deactivate within 40 minutes.

A novel approach to study the influence of the catalytic structure on the performance of ECRC investigated the use of carbon-supported Cu nanoparticles in CO_2 electroreduction [152]. Activities of Cu nanoparticles supported on carbon black (VC), single wall carbon nanotubes (SWNTs), and Ketjen Black (Kb) were evaluated using a sealed rotating disk electrode (RDE) setup in 0.1 M KHCO₃ under atmospheric conditions. For all the catalysts studied, the only hydrocarbons detected were CH₄ and C₂H₄. The smaller the size of the Cu nanoparticles the

authors used, the larger the ratio of FEs for C_2H_4 to CH_4 obtained. Compared to smooth Cu, a significant difference in CO_2 reduction product distribution was observed. On supported Cu catalysts, CH_4 and C_2H_4 were generated at lower potentials compared to electrodeposited Cu. Also, it was notable that the onset potential for C_2H_4 was shifted by 0.2 V for the supported Cu nanoparticles versus smooth Cu films, implying that using Cu nanoparticles would be a more viable option in the ECRC. Another important observation was the difference in CH_4 to C_2H_4 ratios between the Cu nanoparticle supports. While Cu/VC and Cu/SWNT achieved a higher FE of C_2H_4 over CH_4 as the size of the nanoparticles became smaller, electroplated Cu exhibited a higher FE of CH_4 over C_2H_4 . The difference was attributed to the morphology of the electrode surface. Rough surfaces (containing corners, edges and defect) were found to be more active toward C_2H_4 production than smooth surfaces (e.g. electrodeposited Cu). The authors also pointed out to the role the support plays in promoting the formation of CH_4 through a mechanism referred to as "hydrogen spillover", in which hydrogen formed on the supports take part in the pathway of ECRC.

3.2.1.1.4 Methanol- Producing electrodes

Methanol (CH₃OH) is a green fuel with almost half of the energy density of the most commonly used fuel, gasoline (methanol: 15.6 MJ L^{-1} ; gasoline: 34.2 MJ L^{-1}) [1, 30]. CH₃OH has excellent combustion characteristics making it a suitable and proven fuel for internal combustion engine (ICE) driven vehicles. Furthermore, CH₃OH can also be employed directly in the fuel cells (direct methanol fuel cells, DMFCs) to produce energy. Today, CH₃OH is a primary raw material for the chemical industry. It is manufactured in large quantities as an intermediate for the production of a variety of chemicals including formaldehyde, methyl tert-butyl ether, and acetic acid [158]. In addition, CH₃OH is a viable liquid-fuel option due to its high energy density in comparison to many of the available energy storage methods (**Figure 15**).

The conversion of CO_2 into CH_3OH using energy that is not produced from fossil fuels has been is one of the best ways of storing energy and solving both global warming and energy crisis problems to a great extent [1, 30, 158]. At present, most of the commercial CH_3OH is produced from CH_4 through syngas (the mixture of CO and H_2) by steam reforming in large-scale industrial plants in several million tons per year capacity [158]. Production of CH_3OH through the ECRC is a better option because it can be carried out under mild conditions and subsequently at lower costs while achieving a better efficiency.



Energy density by weight (MJ/kg)



Thermodynamically, it is feasible to electrochemically reduce CO_2 to CH_3OH ; the reduction potential of CO_2 is only 20 mV positive with respect to the potential for water reduction. However, due to kinetic limitations, hydrogen gas is usually the main reduction product [30]. In order to achieve a high selectivity to CH_3OH , a very active and selective electrode material should be selected that is able to catalyze a complex CO_2 reaction involving the transfer of 6 electrons, while suppressing the competing HER [30]. For this purpose, many authors conducted studies over many metallic catalysts, only a few of which converted CO_2 to CH_3OH at varying extents. Among those, Ru and RuO₂ offered the highest FE at the lowest overpotential despite the drawback of a fairly low CD.

3.2.1.1.4.1 Ruthenium (Ru)

One reason for using Ru in the early studies of CO_2 electroreduction was its intermediate CO_2 reduction overpotential and its ability to adsorb a considerable amount of hydrogen at underpotentials [160]. Furthermore, the stability of the electrode surface under vigorous hydrogen evolution enables the investigation of the kinetics of CO_2 reduction under long-term potentiostatic conditions [21]. In addition, Ru has been an effective catalyst in the methanation of gaseous CO_2 on supported Ru catalysts from a $H_2 + CO_2$ mixture [161]. Ru is also an active catalyst for the hydrogenation of CO to hydrocarbons (Fisher-Tropsch synthesis) [160].

In light of the promising kinetic properties of Ru in the transformation of CO_2 to CH_4 and the existence of a mechanistic commonality between gas/solid and electrocatalytic approaches [162], Frese et al. [163] conducted CO_2 electrolysis using both electroplated and Teflon-supported Ru electrodes. They showed that the Ru surface is active in CO_2 reduction to CH_4 , CO and CH_3OH . In 0.2 M Na₂SO₄, the highest FE reported for CH_3OH was 42% at -0.54 V and 60°C in the pH range of 3.5-5.5, while the FE of CO and CH_4 reached 45% and 30%, respectively, at -0.57 V and $64^{\circ}C$ in the pH range of 4.3 to 5.9.

Arai et al. [164] used a Ru-modified glassy carbon electrode in 0.2 M Na₂SO₄. The group indicated that the FE of CH₃OH production can reach almost 100% on the Ru-modified electrode in the potential range of -0.6 to -0.8 V at a pH of 5.0. In view of the difference in the reported FEs by Arai et al. [164] and Frese et al. [163] despite using a similar electrolyte and pH range, it can be said that the preparation method and the fixation of Ru on the substrate can influence the selectivity of the process. Frese et al. [165] extended their work on Ru by providing a detailed report on the effect of pH, electrode potential, temperature, electrolysis time and electrolyte purity on the ECRC using Ru catalyst plated onto carbon rods. To confirm that the carbon substrate is not involved in the reduction of CO₂, the group used an electroplated Ru on a Ti solution in 0.3 M Na₂SO₄ and obtained a FE of 2.3% at -0.545 V. This result excluded any activity of the carbon substrate toward CO₂ electroreduction. Using CV, the group concluded that the HER is suppressed on Ru in a CO₂ saturated solution due to blocking of HER sites by CO₂ reduction intermediates or products. The group also studied the effect of CO and indicated that CO lowers the CD and the FE of CH_4 by blocking the sites for CO_2/H^+ reduction through a strong Ru-CO bond. The group also reported that an increasing level of hydrogen in the solution enhances the formation rate of CH₄ even though they noticed a slight increase in the FE. Moreover, the group conducted several trials to establish the influence of the electrode potential on the CH₄ formation rate. They observed that the onset standard potential for CH₄ formation is

by 120 mV more negative than the standard hydrogen potential. Further experiments on the effect of stirring rate proved that vigorous stirring lead to an increase in the overall current without changing the formation rate of CH₄. According to the authors, this indicates that the rate is not governed by mass transport to the surface but rather by a chemical rate determining step. The group proposed that the chemical combination of a surface H atom and a carbon containing intermediate is a rate determining step in CH₄ formation on Ru. They were able to achieve a FE as high as 27% in 0.2 M Na₂SO₄ at pH = 2.76 and 80°C and at a potential of -0.545 V.

Recently Shironita et al. [166] attempted CH₃OH generation by CO₂ reduction at carbon-supported Platinum-Ruthenium (Pt-Ru/C) using a membrane electrode assembly (MEA). At a reduction potential of -0.184 V and a temperature of 80° C, the team was able to establish, using CV, the generation of CO₂ reduction products mainly CH₃OH and some C₂H₅OH at an overall FE of 75% compared to 35% on Pt/C. Shironita et al. [166] also reported a drop in the CD with time due the accumulation of CH₃OH on the surface of the electrode which lowers the number of active site on the electrocatalysts.

3.2.1.1.4.2 Ruthenium Oxide (RuO₂)

 RuO_2 has also been used as a potential catalyst for the ECRC due to its promising catalytic properties [167]. That is due to its high electrical conductivity, electrochemical stability and compatibility with other oxides [167-170]. Also, RuO_2 possess a high capacity of adsorbing hydrogen reversibly- an important step in the pathway of CO_2 electroreduction [168, 170]. Metallic oxides such as RuO_2 are also less sensitive to impurities and contaminants than the pure metals [169].

Transition metal oxides in general and particularly RuO_2 have been used as effective catalysts for the oxygen evolution reaction (OER) and for the HER due to its large surface area and porous nature [172, 173]. The Ru-oxide electrode is believed to be more stable than bulk Ru since the former cannot be further oxidized. RuO_2 is also a dimensionally stable electrode (DSA) in the chloro-alkali industry due to its high catalytic activity for the anodic evolution of chlorine, compared to bare Ru that corrodes in the presence chloride ions [171].

One of the early studies on this material was carried out by Bandi [168] in which he studied the performance of RuO_2 among other conductive oxide mixtures for the ECRC. The

electrochemical measurements were made in 0.05 M H₂SO₄ at -0.5 V and pH 1.2. The CV carried out by this group in addition to Kuhn et al. [169] showed that a higher CD is obtained upon saturating the solution with CO₂. This is contrary to the observations with bulk Ru where the CD went down due to the hydrogen adsorption and surface blockage. Bandi indicated that the reduction of CO₂ starts at potentials more positive than that of water reduction, suggesting the need of a small CO₂ electroreduction overpotential [168, 169, 174]. The analysis of the liquid products revealed that the most promising electrode composition for the formation of CH₃OH was RuO₂+TiO₂ (35+65 mole percent). A FE of up to 76% was achieved by using a 0.2 M Na₂SO₄ (pH 4). The author indicated that the adsorbed intermediates include carbonate, bicarbonate, HCOO⁻ or methoxy adsorbate while the surface plays a role in the pathway by the hydrogenation of the oxide layer. Tafel slopes were used to ascertain the CO₂ reduction mechanism at various oxide compositions of the first reaction transfer is the rate-determining step. In addition, the dependence of the FE on the voltage was studied in 0.2 M Na₂SO₄ (pH 4.0); the result revealed that the FE falls strongly with increasingly negative potentials.

In a subsequent study, Popic et al. [160] studied the reduction of CO_2 on RuO_2 and modified RuO_2 electrodes in 0.5 M NaHCO₃. Three electrodes, Ru, Cu–Cd-modified Ru, and Cu–Cd-modified $RuO_x + IrO_x$, were used in electrolysis for 8 h while the potential was held at - 0.8 V. The adsorbed Cu and Cd ad-atoms seemed to improve the rate of CO_2 reduction. The IR spectrum revealed the presence of acetone and CH₃OH in the system. Acetone was formed in an early stage of electrolysis and remained constant thereafter on RuO_x and RuO_x modified electrodes. On the other hand, the amount of CH₃OH increased with time. RuO_x/Cu and RuO_x/Cu and RuO_x/Cu and RuO_x/Cu and RuO_x/Cu after 480 min of electrolysis.

Recently, Spataru et al. [167] studied the ECRC at RuO₂-coated diamond electrodes. The authors selected the polycrystalline boron doped diamond (BDD) as a substrate due to its excellent chemical and electrochemical stability. In addition, the substrate exhibits a high overpotential for hydrogen evolution which is important in suppressing the competitive HER and minimizing any substrate effect. The polarization measurements provided evidence consistent with those in the literature [160, 165, 168], i.e. that saturating the solution with CO₂ increases the overall current

in the hydrogen adsorption reduction. However, contrary to the claim of Bandi [168], the authors indicated the absence of CO₂ reduction prior to onset of hydrogen evolution. In addition, they suggested that the reduction of CO_2 is inhibited by strong hydrogen discharge in the acidic media and enhanced near neutrality. These findings agree with those of Popic et al. [160] who reported a high FE of CH₃OH in neutral NaHCO₃ unlike Bandi [160] who suggested that high pH electrolyte would lower the FE of CO₂ reduction. Tafel plots for various pH values were similar and ranged between 113 and 119 mV/decade; this indicated the existence of a similar reaction mechanism for the ECRC at RuO₂-coated diamond electrodes within the investigated pH range. The authors attempted long-time electrolysis for a range of pH values to identify the products of ECRC. The results indicated that the main products were CH₃OH and HCOOH with trace amounts of CO and CH₄, at a FE of 8 and 40%, respectively. The FE was highest at a pH of 3.9. The authors noted that the use of BDD as a substrate for RuO₂ results in a lower FE for CO₂ reduction to CH₃OH compared to that reported by Popic et al. [160] who used a titanium substrate. The authors suggested that TiO_2 contributes to CH₃OH production. Another distinction between the study of Spartu et al. [167] and Popic et al. [160] is the formation of HCOO⁻ and CH₄ in the former and their absence in the latter- a clear indication that the substrate effect is substantial in ECRC.

Another recent work that illustrated the importance of the substrate is that of Zhang et al. [170] who studied ECRC on RuO₂/TiO₂ nanotubes (NT)/nanoparticles (NP) composite modified Pt electrode – a composite electrode that has not been studied previously (**Figure 16**). The rationale is that TiO₂ nanotubes can provide a good support due to their low binding energy that promotes the diffusion of the electroactive reactants. The use of RuO₂ on TiO₂ can increase the active surface areas and create more active sites that enhance ECRC. CVs at different holding potentials revealed that the current is amplified at RuO₂/TiO₂ nanotubes upon saturating the medium with CO₂ at a larger extent than that at RuO₂/TiO₂ nanoparticles- an indication that the nanotubes structures exhibit a better catalytic activity toward the ECRC. Similar to the findings of Popic et al. [160], the increase in the holding potential in the presence of CO₂ caused an increase in the oxidation current in the region thought to be related to the oxidation of ECRC CO₂ electroreduction products. Interestingly, the oxidation current recorded in the ECRC product oxidation region was higher using the nanotubes substrate toward CO₂ electroreduction. To further

asses the catalytic activities of the electrode, steady state polarization curves were performed. Those test revealed the positive shift of CO₂ reduction potential on RuO₂/TiO₂ NTs compared to RuO₂/TiO₂ NPs. This was attributed to the high dispersion of RuO₂ on TiO₂ nanotubes; a feature that ensures a higher surface area and larger number of active sites. The prolonged potentiostatic electrolysis at -0.8 V in 0.5 M NaHCO₃ revealed that the main product of electrolysis was CH₃OH at a FE of 60.5% on RuO₂/TiO₂ nanotubes composite and 40% on RuO₂/TiO₂ nanoparticles composite. The FE for CH₃OH achieved on RuO₂/TiO₂ nanotubes composite is the highest achieved in the CH₃OH producing group.



Figure 16: TEM images of (a) RuO₂/TiO₂ NPs composite, (b) RuO₂/TiO₂ NTs composite [170].

3.2.1.1.4.3 Osmium (Os)

Osmium cathodes were used to selectively electroreduce CO_2 to CH_3OH at a FE of 57%. Traces of CO (FE 0.11%) were also formed. Nevertheless, when carbon electrodes were used as a support for electrodeposited Os, the electrode lost its selectivity toward CH_3OH [175].

3.2.1.1.4.4 Molybdenum (Mo)

Summers and Frese [176] studied the catalytic performance of Mo toward ECRC at a pH 4.2 in $0.2 \text{ M Na}_2\text{SO}_4$. They reported the production of CH₃OH at potentials as little as 160 mV negative of the reversible potential. The reduction took place at room temperature and at potentials between -0.57 V and -0.80 V with FEs greater than 55% in some cases. Interestingly, upon cycling the Mo electrodes in $0.2 \text{ M Na}_2\text{SO}_4$ between -1.2 and +0.2 V before electrolysis, a FE greater than 100% was obtained. CV measurements revealed that the corrosion of molybdenum metal and its oxidation to molybdenum dioxide (MoO₂) might be the source of electrons for the

electroreduction of CO_2 . Later, the group patented producing CH_3OH on Mo foils mounted on Cu wires, with up to 84% FE and without detectable corrosion [30].

3.2.1.1.5 Group 4 - Hydrogen (H₂) producing metals

Since this thesis is intended to provide a comprehensive review on the research progress on CO_2 electroreduction, focusing on electrocatalysts for the HER is beyond the scope of this report. However, it suffices to say that the overwhelming majority of H₂ producing metal electrocatalysts are characterized by a low overpotential for H₂ in addition to an affinity to CO poisoning [18].

Metals like Pt, Ni, Fe, Al, Ga and Ti will reduce CO_2 to form CO; however, due to the low turnover of CO, the principle product for these electrodes is hydrogen under ambient conditions [18]. However, in non-aqueous supporting electrolytes, Ni, Pd, and Pt are selective for CO while Al, Ga and group VIII elements (except Ni, Pd, and Pt) form both CO and oxalic acid [177].

In contrast to the usual classification system based only on the products of electrolysis, recently, some workers [19] proposed a new classification system according to the electronic configuration of the electrode material (sp or d group) and the solvent used for the supporting electrolyte (aqueous or non-aqueous solutions). As known, a standard 18-column periodic table could be deconstructed into four blocks, that is, s, p, d, and f blocks [14]. The new classification system offers the advantage of taking the effect of the electric configuration and the nature of the electrolyte into account for a better identification of the product distribution. The sp group includes principal group metals in the periodic table and transition metals whose d orbitals are fully filled (i.e. metals with a d^{10} electronic configuration) (e.g. Zn, Cd, Hg, Cu, Ag, Au). The d group refers to other transition metals in the d block of the periodic table. The d metals are described by the presence of vacancies in their d shells (e.g. Pt, Pd, Ru, Fe, Cr, Mo, Ni, Ti, Nb). The main product of CO₂ reduction on sp metals in aqueous electrolytes is HCOO⁻/HCOOH and to lower extent H₂ and CO. The catalytic activity of d group metals toward CO₂ electroreduction is lower than that of sp group. The main products for these metals is H₂ in aqueous media although the formation other products such as HCOOH, hydrocarbons and CH₃OH is possible. Operating in non-aqueous media has benefits of changing the product distributions of some metals in both metal groups by giving rise to new products such as oxalic acid [19, 49]. The main

electroreduction products obtained on sp and d group metals in aqueous and non-aqueous supporting electrolytes are systematized in **Table 2**.

Metals	Produ	cts
	Aqueous medium	Non-aqueous medium
	sp group metals	
Cu, Zn, Sn	HCOOH	-
In, C, Si, Sn, Pb, Bi, Cu, Zn, Cd, Hg	HCOOH, CO, hydrocarbon	-
In, Sn, Pb, Cu, Au, Zn, Cd	-	Hydrocarbon, CO, CO32-
In, Sn, Au, Hg	-	CO
In, Tl, Sn, Pd, Pd, Zn, Hg	-	Oxalic acid
	d group metals	
Ni, Pt	-	CO, CO ₃ ²⁻
Ni, Pd, Rh, Ir	НСООН, СО	-
Fe, Ru, Ni, Pd, Pt	Hydrocarbon	-
Ti, Nb, Cr, Mo, Fe, Pd	-	Oxalic acid
Mo, W, Ru, Os, Pd, Pt	MeOH	-
Zr, Cr, Mn, Fe, Co, Rh, Ir	СО	-

Table 2: Summary of the Metal Cathodes Employed for electroreduction of CO₂ [178].

3.2.1.2 Pressure

One of the major issues often encountered in the electrochemical reduction of CO_2 in an aqueous medium is the limited solubility of CO_2 in the liquid phase at ambient pressure and temperature [13, 16, 17]. The solubility of CO_2 in aqueous solutions under standards conditions is 0.034 M [18]. A simple solution to this limited solubility is elevating the pressure which would, in turn, increase the concentration of CO_2 in the solution as per Henry's law that directly relates the concentration of a given gas in a solvent to the partial pressure of that gas. Hence, if the partial pressure of CO_2 is to be increased then the concentration of CO_2 in the liquid phase will thereby go up. Many attempts were made in previous studies to investigate the effect of elevating the pressure on product distribution, selectivity and efficiency in the ECRC [41, 46, 49, 63, 71, 77, 144, 179-184]. It was reported that an elevated pressure does not only increase the CD of the process which is primarily due to the increase of CO_2 concentration but also leads to a different product distribution [49, 184-186]. **Table 3** illustrates the effect of pressure on different metals with regard to product distribution and FE.

Fe does not form any CO reduction products at ambient conditions (**Table 3**). However, increasing the pressure to 50 atm gives rise to some products (CO, $HCOO^{-}$ ion and hydrocarbons). Hence, in this case, raising the pressure alters the product distribution of the

process. Enhanced performance is observed with respect to Pd, and Pt. Elevating the pressure increases the FE of the primary products (CO and HCOO⁻).

	Processo of	Faradaic efficiency (%)							
Electrode	CO_2 (atm)	со	HCO0-	$\rm CH_4$	C_2H_4	$\rm C_2 H_6$	Other hydrocarbons		
Fe	1	0	0	0	0	0	0		
Fe	50	6.7	3.7	1.61	0.05	1.32	2.73		
Co	1	1.2	ť	0.31	t	0.2	0.28		
Co	60	14.4	4.1	0.93	0.13	0.45	0.81		
Ni	1	0	0.1	0.62	0.63	0	0.06		
Ni	60	10.4	23.2	1.78	0.44	0.88	0.77		
Pđ	1	5.3	4.4	0	0	0	0		
Pđ	50	57.9	4.4	0	0	0	0		
Pt	1	0	0	0.02	0	0	0		
Pt	60	9.3	24.1	0.31	t	0.08	0.08		
at = trace.									

Table 3: Effect of pressure on the electrochemical reduction of CO₂ on different metals [6].

The actual influence of increasing the pressure has been investigated and some theories were set to explain the behavior of the system under high pressure. The first possibility has to do with the relationship between pressure and heat of adsorption of the reaction intermediate on the surface of the electrode [20]. However, it was established that for metals that exhibit CO₂ reduction activity exclusively under high pressure (e.g. Ni, Pt), the increment of free energy due to the increase of CO₂ partial pressure is negligible compared to the heat of adsorption of CO thus the elevation of pressure will not energetically affect the adsorption on the electrode surface to a great extent [20]. Another possibility has to do with the conversion of CO₂ to carboxylic acid under high pressures [187]. If CO₂ is transformed into weak acid (bicarbonate (HCO₃⁻)) under high pressure, then the concentration of hydrogen ions near the electrode/electrolyte surface rises [187]. If this theory is true, then the formation of products in the ECRC depends on the presence of hydrogen ions. However, it was proven that the concentration of H⁺ is not the only factor responsible for the formation of products and hence the influence of increasing the buffer capacity under pressure was disregarded as the contributing factor for the improved process performance [20]. A third possibility relates to a higher CO₂ solubility that stems from a higher pressure; at high CO₂ pressure, the CO₂ molecule displaces some of the CO that are adsorbed on the electrode's surface thus making room for further reaction of products [187]. Sakata and coworkers [186] did bulk electrolysis experiments with Cu electrodes at a series of CO_2 pressures. They concluded that raising the pressure increases the yield of CO since CO_2 was actually displacing the absorbed CO molecules on the surface of the electrode.

Gatrell and coworkers [17] used an electropolished Cu to assess the effect of pressure on the performance of the ECRC. Upon increasing the pressure from 0 to 60 atm of CO_2 at a constant current of 163 mA cm⁻², the predominant reaction product shifted from hydrogen to hydrocarbons reaching a FE of 44% by 10 atm. At 20 atm, the FE of hydrocarbons decreased to 12% while those of HCOO⁻ and CO rose to 30%. At higher pressures, HCOO⁻ and CO were the primary products along with a FE of 54% for HCOO⁻ production at 30 atm. Hence, the authors concluded that with increasing the amount of CO₂ fed to the reactor, less reduction products were formed.

Ito and his coworkers [49] employed an elevated pressure, 20 atm, for the electrochemical reduction of CO_2 in aqueous and non-aqueous solutions. They reported that the CD of the products rises relative to ambient condition.

Hara et al. [49] reported that metals can be classified into four groups on the basis of their electrocatalytic activities at ambient high pressures. The first group includes Ti, Nb, Ta, Mo, Mn, and Al which do not show any change in product selectivity as a function of pressure since the only product they produce is hydrogen. This is attributed, to the poisoning of those electrodes following the formation of CO on their surfaces. The second group consists of Zr, Cr, W, Fe, Co, Rh, Ir, Ni, Pd, Pt, C and Si. The product selectivity of these metals changes from only hydrogen under atmospheric pressure to HCOOH and CO at high pressure. The third group includes Ag, Au, Zn, In, Sn, Pb, and Bi. These metals show higher a FE for their major products, CO and HCOOH, at elevated pressure. The last group contains only Cu which is characterized by a change in selectivity at higher pressure under which CO and HCOOH are the preferential products while CH_4 and C_2H_4 are the major products at 1 atm.

Indeed, pressure is a major determinant in the electrochemical reduction of CO_2 and hence any optimization attempts should take into consideration the influence of pressure on performance; especially if a new catalyst design is to be employed.

3.2.1.3 Temperature

Because the solubility of CO₂ in water is significantly higher at low temperatures, it is advantageous to carry out the ECRC under such conditions [2, 7, 14, 83, 187]. Similar to the effect of elevated pressure, conducting CO₂ electrolysis under low temperatures offsets the disadvantage that stems from the low solubility of CO₂ under atmospheric conditions. However, the effect of temperature is not as direct as it might seem. The influence of temperature is related to the nature of electrode material and other process conditions such as pH and pressure. To illustrate, Sakata et al [83] studied the effect of temperature on various metal electrodes. They noted that CH₄ and C₂H₄ are detected for all metal electrodes used in their study with varying efficiencies. They attributed this occurrence to the increased solubility of CO₂ and the increased stability of the reduction intermediates at low temperatures. Another interesting feature is that the ratio of products also changed at high temperatures, indicating that the adsorption states of CO₂ and therefore the reaction routes depend upon the temperature. Hori et al [17] investigated the influence of temperature on the product distribution by carrying out galvanostatic work over the temperature range from 0°C to 40°C. It was reported that lower temperatures resulted in a little change in the FE of HCOO⁻, a decrease in FEs of the HER and C₂H₄ and an increase in the FE of CH₄. An interesting insight on the effect of temperature was provided by Cabrera et al. [187] in their voltammetric study of CO₂ reduction on Cu through measuring of the peak current (the highest current in the cathodic region of a CV) with respect to temperature and solubility (Figure 17).

There are two distinct current-temperature dependence regions (**Figure 17**). Between 0°C and 20°C, the current is almost stable. However, beyond 20°C, the current increases at a high rate. That is despite the fact that the solubility of CO_2 drops down with increasing temperatures. This is counter-intuitive because one would think that an increase in the concentration of electroactive species (CO_2) gives rise to enhanced reduction and, subsequently, greater CDs. The authors explained this discrepancy by referring to the reaction pathway of CO_2 on Cu indicating that the rate determining step is not associated with the concentration of CO_2 , but rather the dissociation of CO_2 or its reduction to longer chain hydrocarbons.

Jitaru et al. [188] studied the influence of temperature and reported that an increase in temperature under ambient conditions leads to a decrease in the FE of HCOOH because of the decreasing CO_2 concentration in the electrolyte, which also promotes the HER.

It is apparent that the role of temperature in the ECRC is still not established among many workers. This is primarily due to the process conditions that differ from one experiment to another. Hence, it is important to carry out further in-depth experiments to elucidate the influence of temperature in CO_2 electroreduction.



Figure 17: Cathodic peak current as a function of temperature in the voltammetry of a 0.5 M KHCO₃ solution saturated with CO₂ on a Cu surface. The inset shows the solubility of CO₂ in pure water as a function of temperature [188].

3.2.1.4 Electrolyte

The electrolyte medium, which consists of a solvent, conducting salts and pH-balancing chemicals, exerts a major influence on the ECRC [12]. The nature of the electrolyte is of a particular interest since it is the medium where the CO_2 reduction process takes places [16, 18, 20]. In fact, even for the same metal electrode with the same purity, different supporting electrolytes can give different products at varying FEs [14]. Many different solutions were

investigated in previous studies and those fall into two broad groups (i) aqueous electrolytes, and (ii) non-aqueous electrolytes [10].

An aqueous electrolyte is usually a solution in which the ions are dissolved in a hydrosolvent mostly water [14]. The rational for using the former is the abundance of water and the simplicity of the process. In general, the stable electroconductivity and convenience of concentration adjustment of common aqueous electrolytes allows researchers to conduct control experiments on various electrode catalysts and structures [14]. The main drawback for using aqueous electrolytes is the occurrence of the HER, usually competing with CO_2 reduction, in addition to the low CO_2 solubility in aqueous electrolytes.

The non-aqueous electrolytes, on the other hand, are advantageous due to their ability to suppress the competing HER that takes place otherwise in aqueous medium [20]. Also, the concentration of water as a reagent can be controlled and hence the reaction mechanism can be more easily investigated. Another important point is the higher solubility that CO_2 exhibits in non-aqueous media relative to aqueous solutions (**Table 4**).

Solvent	Concentration (M)
Tetrahydrofuran (THF)	0.205 ± 0.008
Acetonitrile (AN)	0.279 ± 0.008
Dimethylformamide (DMF)	0.199 ± 0.006
Dimethylsulphoxide (DMSO)	0.138 ± 0.003

Table 4: Solubility of CO₂ in various solvents at 25°C [177].

It is notable that some solvents can have a much higher solubility toward CO_2 compared to water (0.033 M). Also, one of the advantages of using a non-aqueous electrolyte is to assess how different solvent properties such as dielectric constant, viscosity, and density contributes to the performance of the process compared to water [14]. Using non-aqueous electrolytes proved to be effective in some cases in increasing the CD and producing products using electrodes that were considered inert in aqueous solutions [14, 16, 18, 20]. However, the use of volatile and potentially toxic organic solvents such as acetonitrile and other non-aqueous electrolytes makes the isolation of the products and the recovery of the solvents costly [189].

The importance of the electrolyte does not only lie in the nature of the solvent used but it also extends to the type of the cationic and the anionic species. Various electrolytes such Na₂SO₄, K₂SO₄, KHCO₃, K₂CO₃, HClO₄, NaClO₄, NaCl, Na₂SO₄, H₃PO₄ have been used for the electrochemical reduction of CO₂ [7]. These inorganic salts are often employed due to their high electrical conductivities in water [7]. Few reports have investigated the role of the electrolyte composition in the electrochemical CO₂ reduction. However, it has been established that the electrolyte choice is a vital parameter that has an effect on the CD, product selectivity and distribution [7, 20]. Indeed, changing the cationic species of the electrolyte while holding all the experimental conditions constant can lead to a change in the product distribution and the FE [7].

Paik et al. [39] studied the electroreduction of CO₂ to HCOO⁻ on Hg in Li⁺, Na⁺, and (C₂H₅)N⁺ in hydrogen carbonate solutions. They reported that the reduction potential at a constant current increases in the order of Li⁺ < Na⁺ < (C₂H₅)N⁺. It was hypothesized that the size of the cationic components of salt plays an important in CO₂ reduction on several electrodes [7, 20, 190]. The authors indicated that larger cations favor CO production and suppress the HER [7, 20, 190].

Hori et al. [20] reviewed the effect of the cation size by carrying out electrolysis of CO_2 using various alkali hydrogen-carbonate solutions and a Cu working electrode at constant CD of 5.0 mA cm⁻² (**Table 5**).

V vs SHE CH. CO. FOULD ON HCOOT H. T (1)	2
$CH_4 C_2H_4 CO ETOH PFOH HCOO H_2 Total$	
LiHCO ₃ -1.45 32.2 5.2 tr 1.6 tr 4.7 60.5 104.2 6	5.19
NaHCO3 -1.45 55.1 12.9 1.0 4.2 0.6 7.0 25.1 105.9 4	1.27
KHCO3 -1.39 32.0 30.3 0.5 10.9 1.6 8.3 14.5 98.1 1	.06
CsHCO3 -1.38 16.3 30.5 2.4 7.2 4.4 15.8 24.4 101.0 0).53

Table 5: Effect of the cationic species in the electrolyte on the faradaic efficiencies of various products [20].

^aCurrent density: 5.0 mA cm⁻². Temperature: 18.5°C.

Table 5 indicates that the formation of CH_4 increases relatively in the order $Na^+>Li^+>K^+>Cs^+$. C_2H_5OH , on the other hand exhibits the highest concentration with K^+ followed by Cs^+ , Na^+ , and Li^+ . The undesirable hydrogen evolution reaction is favored when using Li^+ followed by Na^+ then Cs^+ and finally K^+ . Another apparent feature is the variation in the reduction potential with respect to each of the electrolyte. The reduction potential is the lowest with Cs^+ followed by K^+ , Li^+ and Na^+ ($Li^+=Na^+$). These features show that the nature of the cationic species in the electrolyte has an influence on the product distribution and the efficiency of the electrochemical reduction of CO_2 . The cationic effect can be derived from the extent of the specific adsorption of the cations [20, 190]. This is related to the reaction energetics and kinetics of the outer Helmholtz plane in the electrical double layer (EDL). The hydration number of Li^+ is the highest and that of Cs^+ is the lowest among the four alkali cations. Cs^+ is the largest and softest among the cations and hence it adsorbs to the electrode more readily than others [20]. Based on this, it is reasonable that Cs^+ exhibits the lowest reduction potential. On the other hand, Li^+ exhibits the highest potential due to its high hydration number that decreases the stability of this molecule on the surface of the electrode [20]. Since the highest hydrogen FE was recorded with Li^+ which is associated with the largest hydration number, it can be proposed that water molecules are involved in the HER.

Kenis et al. [190] also investigated the influence of electrolyte composition on the electrochemical reduction of CO_2 to CO in an electrochemical flow reactor. The authors specifically examined the effect of alkali cations on the partial current densities of the CO and H₂. It was reported that the presence of large cations such as Cs^+ enhances the performance of the process by improving the partial CD for CO production. In addition, the authors suggested that the presence of large cations suppresses the HER leading to an increase in the FE of CO_2 reduction. The rationale behind this was similar to that discussed by Hori and coworkers [20] as the authors related their results to the interplay between the level of cation hydration and the extent of their adsorption on the electrodes.

In addition to the effect of the cationic species in the electrolyte, the influence of the anionic species was also investigated. Hori et al. [28] reported that the anion choice (e.g. Cl^- , ClO_4^- , SO_4^- , HCO_3^- , $H_2PO_4^-$) is influential because each anionic component has a different buffer capacity which affects the acidity of the electrolyte and subsequently the nature and the amount of products formed [13]. This group also indicated that the choice of the anion influences the local pH at the electrode surface and thus governs the CO_2 electroreduction reaction pathway (**Table 6**). For the same concentration of 0.1 M, the FE of hydrocarbons exhibited the highest values using KHCO₃ followed closely by KCl, KClO₄ and K₂SO₄. Actually, KHCO₃ is one of the most representative aqueous electrolytes as many studies have been carried out with this solution to

assess and study many aspects of CO₂ electroreduction [14]. Using K₂HPO₄ (phosphate buffer) promoted HER while suppressing the reduction of CO₂ to desirable products. Also, it is interesting to note that the electrolytes that triggered the highest FE for production of hydrocarbons also required the highest cathodic potentials while the phosphate buffer that promoted HER showed the lowest potential. This occurrence is probably due to lower pKa of phosphate buffer (6.86) compared to that of KHCO₃ which entails a different pH at the electrode/electrolyte interface [17, 20]. A detailed explanation about the effect and the origin of the local electrode/electrolyte pH is presented in Section 3.2.1.5.

Table 6: Effect of the anionic species on the faradaic efficiency of CO₂ electroreduction products [20].

				~			v				
Solution	Conc.	ъЦa	Potential	Faradaic efficiency (%)							
	м р	рп	V vs.SHE	CH_4	C_2H_4	EtOH	PrOH	CO	HCOO	H ₂	Total
KHCO3	0.1	6.8	-1.41	29.4	30.1	6.9	3.0	2.0	9.7	10.9	92.0
KC1	0.1	5.9	-1.44	11.5	47.8	21.9	3.6	2.5	6.6	5.9	99.8
KC1	0.5		-1.39	14.5	38.2	Ь	Ь	3.0	17.9	12.5	
KClO ₄	0.1	5.9	-1.40	10.2	48.1	15.5	4.2	2.4	8.9	6.7	96.0
K_2SO_4	0.1	5.8	-1.40	12.3	46.0	18.2	4.0	2.1	8.1	8.7	99.4
K_2HPO_4	0.1	6.5	-1.23	17.0	1.8	0.7	tr	1.3	5.3	72.4	98.5
K_2HPO_4	0.5	7.0	-1.17	6.6	1.0	0.6	0.0	1.0	4.2	83.3	96.7

^apH values were measured for bulk solution after electrolysis.

^bNot analyzed

Another interesting feature is the enhancement of the HER upon increasing the concentration of the phosphate buffer from 0.1 M to 0.5 M. This is attributed to the lower pH value at the electrode/electrolyte interface as the concentration of the buffer increases [20, 28]. This feature is not associated with KCl, KClO₄, and K₂SO₄ that do not have buffer properties and thus for those solutions, the pH at the electrode/electrolyte interface rises and consequently the HER is enhanced to a greater extent. In addition, it is notable that FE is influenced by the nature of the anionic species. KCl, KClO₄, and K₂SO₄ provide higher FEs of C₂H₄ and alcohols than CH₄ in comparison with 0.1 M KHCO₃ and 0.1 M K₂HPO₄. This is related to the lower concentration of hydrogen ions present in non-buffer solutions such as KCl, KClO₄, and K₂SO₄ It is notable that the reaction pathway of C₂H₄ and CH₄ are different as CH₄ formation seems to be highly influenced by low pH,

Hence, the nature of the electrolyte and its composition play a significant role in the electrochemical reduction of CO_2 . Any future endeavours should focus on the influence of the

electrolyte composition on the performance of the reaction. A range of solution of different cationic and anionic species should be employed to determine the electrolyte that gives the best selectivity, the highest efficiency and the desirable product distribution.

3.2.1.5 pH

The pH of the solution in which CO_2 electroreduction occurs is a vital factor to consider when carrying out the process. Electrolysis has been performed in acidic, neutral, and basic conditions often depending on the desired electrolyte. In all aqueous media, the electrochemical reduction of CO_2 leads to the formation of hydroxide ions leading to a change in the electrolyte's pH particularly on the electrode/electrolyte interface as discussed in Section 3.2.1.4. It is important to recall that the nature of the supporting electrolyte (buffer or non-buffer) significantly impacts that pH at the electrode/electrolyte interface and consequently affects the product distribution, selectivity and FE in the process.

Figure 18 illustrates the significance of pH by showing an exemplary CO_2 to HCOO^{-/} HCOOH conversion. Thermodynamically stable regions of CO_2 and HCOOH related species are demonstrated as a function of potential and pH. It is notable that CO_2 cannot be present in basic aqueous solutions and that is due to the reaction of CO_2 with OH⁻ to produce HCO_3^- so the electrochemical reduction of CO_2 has to take place in neutral or acidic solutions. In addition, HCOOH takes places in strongly acidic media while $HCOO^-$ can be formed over a wider pH range (acidic, neutral, and alkaline).

The effect of pH on CO_2 electroreduction is not direct. In fact, the importance of pH in CO_2 electrolysis is related to the influence of pH on the competing HER that needs to be suppressed for a more efficient CO_2 reduction [17]. The HER is a strong function of pH and with increasing pH, the HER equilibrium potential becomes more negative (**Figure 19**). The equilibrium potential denoted by E_{rev} reflects the potential of the HER derived from thermodynamic principles. As the applied current density increase (galvanostatic electrolysis in this case), the equilibrium potential becomes more negative at any given pH value. On the other hand, although CO_2 reduction produces hydroxide anion, its equilibrium potential is not much influenced by the pH in comparison to the HER. Hence, slightly acidic media are more favorable for the HER since the latter is thermodynamically preferred in comparison to the reduction of CO_2 .



Figure 18: Potential versus pH value of CO₂ and related substances [14].



Figure 19: Hydrogen evolution polarization data at copper with varying solution pHs [17].

In addition, the bicarbonate buffering system that takes place when CO_2 is dissolved in the electrolyte is an important aspect to consider. Indeed, one of the many challenges in electrochemical CO_2 reduction chemistry is related to the interaction between CO_2 and water

[14]. The introduction of CO_2 into an aqueous solvent entails a complex series of reversible reactions (**Figure 20**).

$$CO_{2(g)} \xrightarrow{H_2O} CO_{2(aq)} \xrightarrow{H_2O} H_2CO_{3(aq)} \xrightarrow{H_2O} HCO_3^-(aq) + H_3O^+$$
$$HCO_3^-(aq) \xrightarrow{H_2O} CO_3^{2-}(aq) + H_3O^+$$

Figure 20: Equilibrium reactions of CO₂ with water from [18].

It is established that there is a correlation between pH and the concentration of CO_2 in the medium. Upon introducing CO_2 into the aqueous medium, the first equilibrium between CO_2 and water is shown below:

$$CO_2 + H_2O \leftrightarrow HCO_3 + H^+ pKa = 6.4$$
 (15)

The bicarbonate HCO₃⁻ can further dissociate through the following reaction:

$$HCO_3 \leftrightarrow CO_3^{2^-} + H^+ \qquad pKa = 10.3 \tag{16}$$

Reaction 15 results in the CO₂-saturated bulk solutions having pH values from around pH 6-8 (for bicarbonate concentrations of 0.04-2 M respectively). However, most of the buffer capacity near the electrode surface comes from reaction 16 (with a much higher pKa) due to instability of bicarbonate. This fact has a lot of implications in terms of the pH at the electrode/electrolyte interface and the bulk solution. That is because a significantly higher local pH can be created compared to the bulk solution. That is due to the slow rate of neutralization between CO₂ and the hydroxide ion as mentioned previously.

3.2.2 Reaction mechanism

Understanding the reaction pathway is an important step toward optimizing the process of the ECRC. By studying the reaction mechanism that yields a specific product distribution at a given metal electrode, predictions can be made about the metal groups that are likely to produce the best yield of a particular end product under a given set of conditions [19]. It is to be recalled that the reduction of CO_2 to different products is governed by several factors such as the surface of the electrode, electrolyte, reduction potential, temperature, pressure and pH. This adds a higher

level of complexity to the process. Hence, elucidating the reaction pathways and their dependency on the various experimental conditions can enhance the attractiveness of the ECRC as potential CO_2 mitigation method.

Many authors previously proposed reactions mechanisms for a variety of products. However, those attempts lacked, in many cases, sound and concentrate evidence. Recently, Chaplin et al. [178] constructed a diagram (**Figure 21**) that shows some of the common reduction products derived by a variety of workers in the field of CO_2 electroreduction. The reaction scheme depicting four principle pathways: (1) reaction between $\bullet CO_2^-$ (ads) and $CO_2(g)$ giving CO(g) through disproportionation; (2) formation of a $\bullet CO_2^-$ end product dependent upon the nature of the electrolyte; (3) formation of a $\bullet COOH_{(ad)}$ species leading to the production of HCOO⁻; and (4) formation of a range of adsorbed reduced CO_2 generating CO, hydrocarbons and alcohols.

To facilitate the understanding of the scheme, each competing reaction is given a reference letter.



Figure 21: Various reaction pathways of CO₂ electro-reduction from [178].

3.2.2.1 Reaction path A: the adsorption of CO₂ onto the electrode surface.

It is apparent that path A is a common intermediate for all the other pathways/products. Hence the first step is the adsorption of CO_2 on the metal surface. This step is reported to be the contributing factor to higher than calculated potential for CO_2 reduction predicted by thermodynamics. The reason for that is that CO_2^- is an unstable molecule on many metals and thus requires high energy to get stabilized. Also, in this first step, distinctive variations in electrocatalytic activity among electrodes take place. Some electrodes will stabilize M-CO₂ (M refers to the catalyst on which the reaction is taking place_ converting it to useful product. Other metals bond with hydrogen ions to form M-H, thus only yielding hydrogen.

3.2.2.2 Reaction path B: protonation of CO₂ to from MCOOH

In case $M-CO_2$ takes place, the protonation reaction occurs through reactions (17) and (18) to produce MCOOH which can lead eventually to the formation of HCOOH.

$$M-CO_2 + e^- + H^+ \rightarrow MCOOH$$
(17)

Another possibility includes a substitution reaction where the CO_2 molecule is interposed between an existing M-H bond as such:

$$M-H+CO_2 \rightarrow MCOOH$$

In this case, it is interesting to note that the occurrence of reaction (18) is dependent on the magnitude of the M-H bond. Catalyst metals with a strong M-H bond usually do not favor reaction (18) and therefore the formation of MCOOH has tp go through reaction (17). In such case, the acidity of the system is a controlling factor in the formation of MCOOH since reaction (18) occurs in low pH environment.

3.2.2.3 Reaction path C: CO₂⁻ radical released into the electrolyte

In this reaction pathway, CO_2^- that initially adsorbs on the electrode surface quickly desorbs into the aqueous solution. This path, however, is not favored at low pH due to the abundance of H⁺ ions that may promote other paths like path B. Upon the release of CO_2^- into the solution, $CO_2^$ reacts with either water or H⁺ to produce a 'COOH radical. This can either readsorb onto the surface (path C₂) or react further with water to give HCOOH_(aq) and a hydroxyl radical.

(18)

3.2.2.4 Reaction path D: removal of 'O' form the M- CO₂' species

The removal of one oxygen atom from CO_2^- takes places through an electrophilic attack represented by

$$M-CO_2^- + H_2O \rightarrow MCO^+ + 2OH^-$$
(19)

or:

 $M-CO_2^- + 2H^+ \rightarrow MCO^+ + H_2O$ ⁽²⁰⁾

In this case, a proton knocks out an oxygen atom instead of reacting with it. This path along with path G takes place on Cu electrodes under neutral or acidic environments.

3.2.2.5 Reaction paths E, F, G: reaction of species COOH (ad)

The M-OCOH species that is formed through pathway B will undergo a nucleophilic attack losing an OH⁻ according to the following reaction:

$$M-COOH + H^+ \rightarrow M-CO^+ + H_2O$$
(21)

The production of M-CO intermediates *via* paths D and G is considered common on Cu and Ru and some other *d*-group metal electrodes. Actually, these routes are believed to be present in systems which produce highly reduced products such as CH_4 , C_2H_4 , and CH_3OH . Some researchers proposed that such pathways are blocked by either high pH or elevated operating pressures [178]. Increasing the pH and pressure actually promotes route B giving HCOO⁻ rather than yielding CO.

3.2.2.6 Reactions H, I, J: further reduction reactions

When M-C=O⁺ forms following paths G or D, the production of CO through path H becomes mainly dependent on the transfer of one electron. Since CO requires an electron while the formation of $HCOO^-$ is largely dependent on adsorption and protonation, the peak production of CO occurs at a greater applied potential in comparison to that of $HCOO^-$.

Reaction I is of a particular importance due to the formation of the hydroxyl functional group which is a characteristic of alcohols. This is done by addition of a proton and an electron to $M-C=O^+$. Following this step, products like CH₃OH, C₂H₅OH, propanol, CH₄, C₂H₆ etc... can be formed.

In reaction path J, the addition of three electrons and two protons to $M-C=O^+$ results in the formation of a free carbon radical which further reacts with hydrogen and electrons to give C_2H_2 and CH_4 . Path J is promoted at low temperatures and is competitive with route I and this is the reason the yield of CH_4 goes up while that of C_2H_4 drops upon lowering the temperature.

3.2.2.7 Reaction path K: disproportionation

This reaction path gives rise to CO_3^{2-} and CO and it is a common occurrence in non-aqueous systems. This route involves the reaction of CO_2 with the adsorbed CO_2^{-} . This path is promoted by metals such Au and Ag while pathway H takes place on *d*-group metals. It is noteworthy that disproportionation is independent of both pressure and pH. Path H on the other hand is suppressed by raising pressure and promoted by low pH.
3.2.3 Conclusion

In conclusion, the product distribution in the electrochemical reduction of CO₂ is a function of electrode metals, electrolyte solution and process parameters such as pH, temperature, pressure and the mass transfer inside the cell. The selection of an appropriate electrocatalyst and operating conditions plays a significant role in determining the desired CO₂ reduction process pathway and its selectivity with respect to the desired product. Low temperature and pressure have been proved to enhance the performance of the process by improving the solubility of CO₂ in the electrolyte. The choice of the electrolyte influence the outcome of the process and it has been established that buffer electrolytes particularly KHCO₃ is favorable for high-achieving systems. In addition, the use of non-aqueous solutions can yield different product distribution relative to aqueous solutions. It is noteworthy that the proper selection of experimental conditions to achieve a certain performance is dependent on the nature of the electrode as some experimental conditions can produce good results with a given catalyst but prove unsuccessful in others. Any CO₂ system (catalyst, set of experimental conditions) is associated with a shortcoming (e.g. deactivation, low efficiency or high costs) and hence the performance of the process must be assessed by weight the benefits and the limitations. If a variety of value-added products is sought with high yields then Cu is the choice to make which would come with a high cost due to the high overpotential associated with this catalyst. In case a less costly system is required then Ru/RuO₂ is the material to choose but unfortunately this system will result in low yields. High efficiency systems can be achieved by formic acid- producing metals but those come at the expense of a low reaction rates

Chapter 4

4. Current Status

4.1 Recent progress

Many of the previously discussed studies offer a promising route for the conversion of CO_2 to value-added products in simple electrochemical setups. Despite the extensive development in this field, the process remains challenging due to:

- (i) A high CO₂ electroreduction overpotential required to produce value-added products.
- (ii) The low solubility of CO_2 in water at ambient temperature and pressure.
- (iii) The formation of a mixture of products implying a costly separation step.
- (iv) The deactivation of the electrodes by impurities and reaction intermediates.

The focus of most of the previous research has been on the use of bare metallic electrode as electrocatalysts; however, the interest has been gradually shifting toward employing non-conventional, non-metallic electrodes, new cell configurations and novel supporting media. What follows is a concise overview of the novel system configurations that have been integrated in the ECRC to address the above-mentioned drawbacks and improve the performance.

4.1.1 Ionic Liquids (ILs)

One of the new routes developed recently in the ECRC involves the use of ionic liquids. Ionic liquids (ILs) are organic molten salts composed merely of ions, and are a kind of novel medium for many chemical processes. Similar to strong acids, ILs completely dissociate into ions and are not diluted by any bulk solvent [19]. Besides, ILs are characterized by negligible vapour pressure at room temperature and are thermally and electrically stable [30]. Their non-volatility, non-flammability, exceptional solubility, high conductivity, and wide electrochemical windows has caught the attention in the CO₂ electroreduction field [191].

The use of ILs bring offers many advantages over the commonly used aqueous electrolytes including

- (i) The suppression of the HER which competes with the reduction of CO_2 .
- (ii) An increase in the conductivity of the electrolyte due to the presence of charged ions.

- (iii) A better solubility of CO_2 to that in aqueous systems in a large range of temperatures and subsequently better mass transfer.
- (iv) A lower environmental impact in comparison to conventional organic solvents.
- (v) A higher stability for the CO₂ pathway intermediates and therefore a better control.

A number of reports have discussed the use of ILs and the results have shown that this can be a promising route toward enhancing the performance of the process [189, 191-197].

One of the early studies involved the use of ionic liquid, 1-n-butyl-3-methylimidazolium hexafluorophosphat (BMIM-PF₆), and supercritical CO₂ in the ECRC [191]. It was shown that CO₂ and water can be converted into easily recoverable CO and H₂ using (BMIM-PF₆) as an electrolyte which can then be recycled for further use without any treatment.

In 2011, due to its high surface area, Liu et al. [196] prepared a novel silver-coated nanoporous copper composite electrocatalysts and employed it in the electrosynthesis of DMC (dimethyl carbonate) from CO₂. The ionic liquid (BMIM-BF4) was used as an electrolyte at a range of temperatures. The highest FE (80%) was achieved at 50°C. According to the authors, the temperature influenced the viscosity of the ionic liquid and the solubility of CO₂ in the ionic liquid.

Rosen et al. [195] investigated a mediated selective conversion of CO_2 to CO at Ag in 1-ethyl-3methylimidazolium tetrafluoroborate (EMIM-BF4). They reported the production of CO at low overpotentials, below 0.17 V. Also, the authors noted a decrease in the onset potential at Ag from -2.1 V in the absence of ILs (in an aqueous solution) to -1.5 V in its presence. The FE toward CO formation was always greater than 96% in addition to EE of 87% at -1.5 V. They suggested that EMIM-BF4 can lower the overpotential of CO₂ reduction by forming low energy reduction intermediates, thus shifting the CO₂ conversion to less negative potentials. Despite the clear improvement, the authors indicated a lower reaction rate than what is typically needed in a commercial process.

Although the approaches of using ILs have achieved significant reductions in the CO_2 electroreduction overpotential, they have been so far limited to low CDs. Moreover, the use of ionic liquids in the electrolyte may prove problematic for long-term operation of an electrolyser [87].

4.1.2 Metal Complexes

In the early 1980s, the use of metal complexes in CO_2 electrocatalytic reduction attracted interest stimulated by the good performance of some transition bare metals and the possibility of achieving very high selectivities and activities [198]. Metal complexes are usually thought of as operating in a homogeneous phase, dissolved in the reaction medium, in which they act as redox mediators in the CO_2 reduction process [91].

A metal complex consists of a central atom or ion which is usually metallic (coordination centre) and a surrounding array of bound molecules or ions that are in turn known as ligands or complexing agents. These are usually thought of as operating in a homogeneous phase, dissolved in the reaction medium, in which they act as redox mediators in the CO_2 reduction process [198]. However, such complexes can also operate in a heterogeneous mode, in which the complex is deposited on a solid electrode surface or on a gas diffusion electrode. There are two types of metal complexes, the planar and the octahedral coordination, and those can be coupled with any metal or ligands [198]. In general, the square planar complexes tend to catalyze CO_2 reduction in aqueous media, whereas octahedral complexes are more active in non-aqueous media [198].

Metal complexes require relatively mild conditions compared to the direct reduction of CO_2 at bulk metal electrodes. The main products in the ECRC catalysed by metal complexes include CO and HCOO⁻ although other products can be also obtained to a lower extent. The role of the transition-metal complexes is to direct the reactivity of the CO_2 radical anion toward a specific product and to achieve high selectivity and low potential relative to the reduction on a metal surface [18,199]. The role of metal complexes in the ECRC is illustrated by an example in **Figure 22**.

In step 1, the carrier molecule (quione in this illustration) is reduced to its anionic form. The anionic form binds selectively with CO_2 in step 2 to form a carbonate like "adduct". In step 3, the complex is oxidized and releases CO_2 at high pressure.

Various metal complexes such as copper [201, 202], palladium [201, 203-205], nickel [206-210], cobalt [203, 211], and iron [211, 212] have been reported to catalyse the electrochemical reduction of CO₂.



Figure 22: Reaction Scheme for Electrochemical CO₂ Pumping [200].

Copper complexes have been studied stimulated by the strong catalytic activity of Cu bare metal toward hydrocarbon and alcohol formation. Cu complexes have been shown to be able to fixate CO_2 directly from air when the pH is above 7 [199]. Angamuthu et al. [199] devised an electrocatalytic system based on a Cu complex to activate and convert CO_2 selectively into oxalate at readily accessible potentials, in a simple but very effective catalytic cycle. The authors reported rapid formation of oxalate at high selectivity.

Verdejo [202] used Cu^{II} Complexes of 5,5"-Terpyridinophane and reported that the reduction of CO₂ at this complex occurred between -1.4 V and -1.65 V.

Using palladium complexes at -1.10 V, Ogura et al. [213] obtained HCOOH at relatively low FEs, as small as 10%, while H_2 was the major product. Nickel cyclams have been shown to be highly selective in the reduction of CO₂ to CO under electrochemical conditions in water [208, 209]. In another study [91], a FE as large as 99% was obtained at -1.4 V using Nickel complexes of carbine-pyridine. Although these complexes had a high selectivity toward the formation of CO, the production rate of CO was relatively moderate and underwent rapid deactivation when used continuously at high applied potentials.

Despite the good selectivity and high catalytic activity of many of the metal complexes toward the formation of value-added products in the ECRC, they lack stability, and, therefore, present a challenge that must be resolved before any eventual application is set forward [198]. Furthermore, systems involving homogeneous molecular catalysts struggle to achieve high current densities, where they cannot compete with metallic catalysts for the most part. If those complexes are to be combined with a solid metallic catalyst, major problems currently facing electrochemical CO_2 reduction could be solved; however, many of these catalyst systems are still not economically efficient [18].

4.1.3 Gas Diffusion Electrodes (GDE)

Besides employing elevated CO_2 pressures, another possible means to reduce mass transfer limitations during electrolysis is the use of gas-diffusion cathodes loaded with electrocatalytically active metals. The success of gas diffusion electrodes (GDEs) in gas-fed fuel cells such as hydrogen-oxygen fuel cells and some electrosynthesis has led to consider GDEs for CO_2 reduction [31]. GDE usually consists of a Teflon-bonded carbon black matrix on which metal catalyst particles are dispersed. These electrodes are both porous and hydrophobic and have a structure that not only allows extensive utilization of the electrocatalyst but also increases the area of the three-phase interface (gas/electrode/electrolyte) which would enhance the diffusion of CO_2 to the catalyst (**Figure 23**) [18, 23, 198].

The key behind the efficient operation of this surface is the very short distances that dissolved CO_2 must travel through the liquid phase in order to react at the electrocatalyst [198]. The active layer provides a conjunction of solid, liquid and gaseous interface and minimizes the limitation encountered on bare metal catalysts which, otherwise, entail a low contact between CO_2 and the catalyst surface (**Figure 23**).

The ECRC on various metals and metals compounds loaded on GDE under 1 atm was conducted in several studies [46, 56, 64, 182, 183, 214-223]. Mahmoud et al. [64] used a metal-impregnated polytetrafluoroethylene-bonded (PTFE) carbon gas-diffusion electrode for the ECRC over a wide range of pH (1 to 5) with lead, indium and tin as catalysts. Electrolysis at lead-impregnated electrodes at -1.8 V and pH of 2 yielded a FE of nearly 100% for HCOOH product at a remarkable CD of 115 mA cm⁻² which is significantly higher than that obtained on bare metallic In. Impregnated Pb demonstrated the highest activity compared to indium and tin-impregnated electrodes. One of the drawbacks reported by the authors pertained to the presence of large cathodic overpotential for HCOOH (> 1.3 V) in addition to the high Tafel slopes. They attributed this formation of non-conducting barriers on the electrode surface.



Figure 23 : Schematic diagram of a gas diffusion electrode active layer [198].

In the following year, Sammells et al. [221] attempted for the first time to incorporate the most active ECRC metal, Cu, in a gas diffusion assembly. A FE of 71% was found for the formation of C_2H_4 at very high applied current densities (300-500 mA cm⁻²) and a large resulting negative potential of -2.5 to -3.6 V, in alkaline aqueous KOH. This result contradicts the majority of the studies on metallic Cu which asserted that CH_4 is dominant product of over C_2H_4 . The authors attributed this discrepancy to the alkalinity of the electrolyte and not the nature of the working electrode.

This is consistent with the results of Hara et al. [46] who reported C_2H_4 as the main product at a FE of 69% while that for CH₄ formation was 9% in galvanostatic electrolysis of 400 mA cm⁻² in alkaline aqueous KOH at 20 atm of CO₂ pressure. However, at near neutral medium of 0.5 M KHCO₃, the main products were CO and HCOOH at FE of 31% and 28% respectively, at an applied CD of 900 mA cm⁻² and a resulting voltage of -1.65 V; The FEs of CH₄ and C₂H₄ were only 0.5% and 0.2% respectively.

Cobalt phthalocyanine supported on a carbon gas-diffusion electrode is an active and stable electrocatalyst for the reduction of CO_2 to CO under mild conditions. The FE for the main product, CO, was 100% at current densities up to 80 mA cm⁻² [222]. An interesting feature of

this work was the increase in FE brought by the incorporation of GDE; an increase from 4% under CO_2 atmospheric conditions to 97% using GDE. The authors also pointed to the stability of their electrode which did not show any loss of catalyst activity during its 10 h operation. It was also found that the shift of potential toward negative values, the other conditions being equal, raises the CO yield. In addition, with an increasing pH from 2 to 10, the partial CD of CO formation increases substantially if low CDs are applied (galvanostatic electrolysis).

The good properties of GDE were also demonstrated in the work of Furuya et al. [217] who examined the reactivity and selectivity of CO₂ reduction at GDE made of Ru, Pd and their alloy (Ru:Pd 1:1). Furuya and coworkers established that Ru and its oxide form have good catalytic properties toward CH₄ and CH₃OH formation while Pd has moderate catalytic activity toward CO formation. At a constant potential of -1.3 V, the research group achieved a FE of 90% and a remarkable CD of 80 mA cm⁻² at the Ru-Rd GDE in aqueous 0.5 M KHCO₃. The formation of HCOOH was characterized by a parabolic trend in which a maximum was reached at -1.3 V. Another interesting feature relates to the change of product distribution of Pd upon loading it on a GDE. A FE% up to 70% was achieved on a Pd-GDE at -0.9 V while CO was formed at a FE of 4% at larger potentials (-1.7 V) on bare Pd. The authors concluded that the reduction of CO₂ to CO at Pd catalysts in a gas-diffusion electrode setup is accelerated more than at a plate electrode.

The effect of pressure on Pt-GDE was investigated, galvanostatically, by Watanabe et al. [182] in 0.5 M KHCO₃ between atmospheric and 50 CO₂ atm. Pt exhibits a low overpotential for the HER and hence its use as bare plate in the ECRC yields mainly H₂ under either ambient, or CO at elevated pressures. Watanabe and coworkers presented, yet, another evidence about the change of product distribution by using GDE since the main product they reported was CH₄ at a maximum FE of 44% and a partial CD of 315 mA cm⁻². Interestingly, in addition to CH₄, the authors reported the production of C₂H₃OH, CO, and HCOO⁻. The effect of the CD was studied at a constant pressure and the results showed the FE for CH₄ formation increases with rising CD whereas that for CO goes down. The FEs for HCOOH and H₂ were hardly changed by increasing the CD. The study of the pressure dependence of the reduction products indicated that the FE for CH₄ increased with increasing CO₂ pressure with no apparent signs of potential change. This suggests that the change of product selectivity is due to the change of CO₂ pressure not electrode potential. Despite the attractive features of using GDE, a common drawback is their rapid

deactivation and decay of catalytic activity. Watanabe et al. indicated that the activity of the electrocatalyst deteriorated after passing a charge of 250 C. This shortcoming was also observed recently in the work of Lee and coworkers [56] who attempted CO_2 electroreduction at a Sn-GDE in a zero gap cell at -1.6 V. This group reported a reduction in the production rate and FE toward HCOO⁻ after the first 500 s. They achieved a maximum FE of 18%.

In a novel approach, Liu and coworkers [218] assessed the catalytic activity of Pd-MWNTs (multiwall carbon nanotubes) gas-diffusion electrode in aqueous 0.5 M KHCO₃ toward the conversion of CO₂ to organic acids. The use of carbon nanotubes as a support was ascribed to their excellent properties such as low resistance, high surface area, chemical stability, and exceptional mechanical, and electronic properties. For the first time, workers in the field of CO₂ electroreduction at metal GDE reported the formation of acetic acid. The other main product was HCOO⁻. The authors also studied the effect of electrolyte concentration, voltage and reaction time on the performance of their system. They suggested that a high voltage and a high concentration electrolyte advance the formation of acetic acid and asserted in this respect that the process is controlled by electron transfer. The best reaction conditions for the electrochemical reduction of CO₂ to acetic acid were -4 V, 5 min and 0.8 M KHCO₃ while those for HCOO⁻ were 34.5% and 52.3% respectively at a maximum CD of 9 mA cm⁻².

Due to the high reaction rate (i.e. current density, CD) and selectivity toward the formation of valuable products in ECRC, gas diffusion electrodes have been considered as a potential solution for the problem of mass transport limitation often encountered in CO_2 electroreduction on planar electrodes. However, the short lifetime and the rapid catalytic degradation of GDEs vitiate their potential integration into any future large scale commercial process.

4.1.4 Poisoning/catalytic deactivation and mitigation

One of the major challenges that hinders a long-term efficiency of CO_2 electroreduction and limits its applicability is the degradation of the catalytic activity (electrode poisoning) [23]. Poisoning is characterized by the gradual degradation of the catalytic affinity of a given CO_2 catalyst toward the production of value-added products. Although the loss in catalytic activity has been an established phenomenon in the field of electrochemistry, the reasons behind this aspect is still subject to controversy. While some authors has proposed that deactivation, in part, takes place due to the conversion of some CO_2 to graphitic carbon which deposits on the active sites of the catalyst, others point to the trace amount of impurities/organic components present either in the electrolyte solution or water that might interfere with the process. The proponents of the first theory refer to the appearance of black deposits on the deactivated electrode after electrolysis attributed to graphite as evidenced by XPS analysis [224-232]. The supporters of the other theory have suggested that heavy ion impurities present in electrolyte may adhere to the catalyst surface and limit its catalytic activity [233].

Hori et al. [45] were one of the early workers who reported a degradation in the catalytic activity of Cu during CO_2 electroreduction as manifested by the drop in FE of CH_4 formation during the first 60 minutes of electrolysis. This effect was minimized by etching the electrode in an acid solution or by pre-electrolysis. Pre-electrolysis is a purification procedure in which a sacrificial large-area cathode is used prior to the experiment to clean the electrolyte solutions from impurities or organic material. Platinum black is usually used as the cathode [233].

DeWulf et al. [93] conducted CO_2 electroreduction using Cu under potentiostatic conditions at -2.0 V. They detected hydrocarbon molecules mostly CH_4 and to lesser extent C_2H_4 . This research group reported the appearance of a thin black coating along the edges of the working electrode by the end of their experiments (120 mins). In addition, they noted that the rate of hydrocarbon products showed a time dependence characterized by an induction period, a growth to maximum and then a decay. They attributed this behavior to the poisoning of the electrode due to the formation of graphitic compounds according XPS analysis. DeWulf et al. [93] studied the possible pathways of catalytic poisoning and concluded that this phenomenon occurred via the formation of HCOO⁻/HCOOH that eventually led to the appearance of graphitic carbon.

One of the effective ways of addressing poisoning is by operating a pulsing technique in which the potential is alternated between a negative value/cathodic bias (to reduce CO_2 to value-added products) and a positive value/anodic bias to breakdown any molecule adhered to the active sites to the catalyst. Nogami et al. did a series of experiments on the pulsed electroreduction of CO_2 [225, 229, 231, 234, 235]. This group initially worked on identifying the optimal cathodic and anodic bias voltages (V_c and V_a) and their corresponding durations t_c and t_a [235]. Subsequently, they were able to achieve a consistent long term FE of CH₄ and C₂H₄ unlike under their galvanostatic, constant-current electrolysis in which FE reached a maximum and then decreased to almost a zero value. In attempt to study the theory brought forward by DeWulf et al. [93] about the poisoning effect of HCOO⁻/ HCOOH, they carried out CO₂ electroreduction with an added amount of HCOOH. Using X-ray photoelectron spectroscopy (XPS) to analyze the surface of the electrode at the end of electrolysis, they reported the presence of graphite carbon, alcohol and HCOO⁻ which led to the conclusion that the reduction of HCOOH triggers the formation of adsorbed graphite carbon and alcohol on the Cu electrode. The group implemented a pulsing method to restore the catalytic activity of the electrode. Pulsed electrolysis suppressed the poisoning process by keeping CO₂ electroreduction intermediates from being transformed to the final product such as graphitic carbon. The XPS spectra also confirmed the formation of Cu₂O which is, according to the group, formed by the oxidation of the Cu surface during the anodic bias in the pulsing operation.

In a following study, Nogami et al. [225] studied the optimal conditions for generating hydrocarbons by varying t_a , t_c , V_a , V_c , electrolysis time and temperature. By varying one parameter while keeping the others constant, the researchers were able to identify, in their pulsed method, the required setting for generating hydrocarbons over a long-term period (**Figure 24**) highlighting the fact that the optimal anodic potential for the formation of C₂H₄ is more anodic than that of CH₄. The authors explained this by presenting a reaction mechanism in which the first step is the formation of CuO₂.

Augustynski et al. [226-228] studied the poisoning of Au, Ag and Cu during electroreduction of CO_2 . They reported that the heaviest deactivation occurred at Cu and the process was characterized by a drop in the FE for hydrocarbon formation, an increase in the HER and a constant CD regardless of the purity of Cu electrode or the purity of the electrolyte (preelectrolyzed vs regent-grade solutions) (**Figure 25**). An activation method employed by this research group consisted of a periodic anodic stripping using a series of 2-3 rapid voltammetric sweep repeated every 5-10 min over the entire electrolysis run (24 h). By applying this technique, the group observed that high FEs of CH_4 , C_2H_4 and C_2H_5OH can be maintained over long electrolysis runs (**Figure 26**).



Figure 24: Pulsed electroreduction techniques used by Nogami et al. [225, 229, 231, 234] where T_c and T_a represent the time cathodic and anodic biases (*Vc*, *Va*) are applied respectively.



Figure 25: Decrease of faradaic efficiencies of CH₄ and C₂H₄ observed during first 60 min of the electrolytic reduction of CO₂, at a 99.999% Cu cathode (0.28 cm²) in a 0.5 M KHCO₃, solution [226].



Figure 26: Results of CO₂ electrolysis in 0.5 M KHCO₃, involving a reactivation of the poisoned Cu electrode from [226].

In addition, they indicated that total rate of hydrocarbon formation remained constant using this activation technique but they also noted an increase in the amount of C_2H_4 and a drop in that of CH₄. They attributed this feature to the structural change occurring at the electrode namely the increasing presence of Cu⁺(s) species. The research group also explored the influence of pressure on the deactivation process of Cu, and they concluded that the deactivation occurs at a much slower rate under atmospheric pressure in spite of the higher CD recorded at elevated pressure.

In another attempt to address the issue of Cu poisoning, Friebe et al. [232] investigated the deactivation of Cu through differential electrochemical mass spectroscopy (DEMS) that monitors the formation of products in *in situ* electrochemical processes such as electrocatalysis. Similar to the other studies on catalytic deactivation, Friebe et al. indicated that at constant–potential electrolysis, the production rate of the CO_2 passes through a maximum a short time after the beginning (~ 20 min) and then drop back to a value close to zero. To sustain a long term activity of Cu, this group used anodic pulses of 50 mV every 50 s for 10 s. The study revealed that the features of the long term deactivation (decline in the FE and CD) may well be manifested in between the andic pulses – a clear indication that pulsing plays a role in altering the structure of the electrode through the removal/oxidation of poisoning material that adsorb irreversibly on the catalyst either originating from an intermediate in the CO_2 reduction pathway or a soluble reduction product. The group explored the possibility of a poisoning soluble reduction product and concluded that some poisoning intermediates are not necessarily adsorbed on the electrode

but present as soluble material in the electrolyte. To further establish the presence of solublepoisoning material, the researchers added Cu ions to the electrolyte to ensure a continuous renewal of the cathode surface in case of an irreversible deactivation. Initially, this procedure led to a higher production rate of CH_4 compared to control conditions despite showing features of catalytic deactivation. This implied that a poisoning adsorbate cannot be only contributing factor to the decay in the catalytic activity. The group varied the bubbling rate of CO_2 to verify the possibility of a volatile poisoning component but the deactivation pattern did not change. They concluded that the adsorbed soluble poisoning species is, just as the insoluble adsorbate, oxidized to a non-poisoning compound. This suggested that the formation rate of soluble poisoning components is the same as the rate of their oxidation in pulsed electrolysis.

In a study to reveal the nature of these poisoning components, Lee et al. [236] investigated the adsorption/desorption patterns in the ECRC using an electrochemical quartz crystal microbalance (EQCM). The group reported that the loss of electrolytic activity was manifested by a drop in the FE for CH_4 formation to 5% in the first hour of the experiment (**Figure 27**). This aspect was attributed to adsorption of graphitic carbon on the surface of the electrode as illustrated by AES (Auger Electron Spectroscopy) and SEM (Scanning Electron Microscopy) analysis of the surface of the cathode before and at the end of electrolysis.



Figure 27: Faradaic efficiency (%) of CH₄ by applying cathodic potential of -2.1 V at solution temperature of 5°C in 0.1 M KHCO₃[236].

To retain the activity of the catalyst, the group used pulse modulation (**Figure 28**) in which they alternated the cathodic potential between -2.1 V (10 s) and 0 V (5 sec) over the length of the experiment. The group explained this behavior by the electro-dissolution of Cu and the formation of copper oxide during the anodic bias; this was confirmed by XRD, SEM and mass change techniques.

In accordance with the findings of Lee et al. [236], Yano et al. [237, 238] discussed the poisoning of Cu and the catalytic activity of CuO₂. Unlike the previously mentioned workers, this group focused just on the influence of the anodic bias potential (E_a) and the anodic bias time (t_a) on the formation of CH₄ and C₂H₄. They revealed that the higher the E_a employed, the greater the FE obtained for C₂H₄. Using XRD patterns of Cu after electrolysis; they noticed that pulse modulation gave rise to Cu₂O and CuO supporting the claims of Lee et al [236].





The group proved the catalytic activity of Cu_2O and CuO toward C_2H_4 by using a copper oxide electrode and obtaining the same behavior as with pure Cu with pulsing. The authors explained the prevalence of the FE of C_2H_4 over that of CH_4 by presenting a reaction mechanism in which copper oxide prevented the adsorbed CO (the first intermediate in CO_2 electroreduction) from being protonated.

Wasmus et al. [224] reported on the poisoning of bulk Cu and Cu deposited on glassy carbon in an on-line mass spectroscopy study with rotating electrodes. As seen in several other studies, the formation of CH₄ dropped after 5 minutes while that of C_2H_4 dropped after 17 minutes at -2.4 V. In accordance with other workers, the group indicated that the color of working electrode turned into black after 10 minutes. The authors attributed that loss of catalytic activity and the color change to the formation of graphitic carbon on the electrode surface; the activity of the electrode was reinstated by etching the electrodes in diluted nitric acid or stepped anodic pulsing at -150 mV for no longer than one minute. In agreement with DeWulf et al. [93] and Wasmus et al. [224], the authors proposed a pathway in which HCOO⁻ is an intermediate in the formation of the poisonous graphitic carbon.

Anagnostopoulos et al. [239] conducted CO_2 electroreduction using differently prepared Cu electrodes and observed a drastic drop of FE (CH₄) from an initial value of 30% to 2% after 10 minutes, with a similar trend for the other gaseous products (CO, CH₄, C₂H₄). However, the authors noted that the surface of the electrode retained its shiny appearance in contrast to other studies that reported a blackened Cu surface after a short time of electrolysis.

In accordance with Anagnostopoulos et al. [239], Sammells and coworkers [150] conducted CO_2 electrolysis using *in situ* deposited copper on glassy carbon Cu cathodes. The electrodes became darker in appearance and sometimes black, as electrolysis proceeded; the authors attributed this phenomenon to the presence of elemental carbon as suggested by evidence from Auger spectroscopy.

Augustynski et al. [227] addressed the poisoning of Au in ECRC experiments. The poisoning of Au assessed at constant-potential electrolysis was characterized by a continuous decrease in the CD and the rate of CO formation. Nevertheless, unlike the deactivation features of Cu, the FE of CO remained unchanged under similar experimental conditions. Augustynski et al. used an activation treatment that aimed to strip the poisoning products anodically from the electrode by means of periodic potential excursions. Following the activation procedure, the group reported an increase in the mean CD and a constant FE for CO formation over a long-term period.

Augustynski et al. [228] also studied the deactivation of Ag and reported on its time dependence in the ECRC. According to the authors, the deactivation of Ag is primarily reflected through the drop in the FE of CO formation and an increase in the overall current; the features which are attributed to the progressive build-up of adsorbed species that impede CO_2 reduction and enhance the HER. In order to reactivate the poisoned electrode, the researchers employed sweeping scans from the cathodic to the anodic region. The method comprised a sequence of three anodic/cathodic scans performed at 0.2 V s^{-1} repeated at intervals of 5 mins with a cathodic bias of -1.4 V and an anodic bias of 0.6 V (selected to avoid the dissolution of the metal). The use of such a method suppressed the decay of the FE for CO formation and allowed a higher FE over prolonged electrolysis. To identify the origin of the poisoning process, the researchers carried out experiments in the presence small amounts of HCOOH, CH₃OH, CO and CH₂O. Augustynski et al. determined that the presence of CH₂O, albeit at low concentrations, could lead to the decay in the catalytic activity. This is similar to what they observed in their experiments of CO₂ electroreduction using Cu.

Shiratsuchi et al. [225] applied pulsing to Ag at which the main product is usually CO under galvano-/potentio-static electroreduction. In accordance with Augustynski et al. [228], the features of catalytic degradation associated Ag were the decrease in the FE of the main product, CO, over time and the increase of that of H₂. Also, the group reported a poisoning effect marked by the degradation of the FE with time in the potential range where CH₄ could be detected. Using pulsed electrolysis, the authors reached the optimum bias conditions for the formation of CH₄ at which the products were steadily produced. Surprisingly, the authors noted the formation of CH₃OH, CH₄ (products formed with Cu) and HCOOH under a cathodic bias more negative than -2.0 V. The results showed that when FE (CO) and FE (HCOOH) increased, the FE of the other products was suppressed, implying two different pathways from CO₂ to CO and to hydrocarbons. Unlike Cu where graphite is considered as a poisoning intermediate, the authors indicated that graphite is an intermediate in the reaction pathway for the formation hydrocarbons and is not part of the deactivation process. In addition, they suggested that the value of the anodic bias governs the product distribution in the process. At more negative anodic bias, there is a high chance that H_{ad} reacts with CO₂ (free radical intermediate) producing C₂ products while at less negative voltage where oxidation of H_{ads} is more likely, the production of CO and HCOO⁻ is preferential.

Given the established performance of both Cu and Ag in pulsed electrolysis, Ishimaru et al. [234] conducted pulsed electrolysis using Cu-Ag alloy of different atomic ratios. The authors reported the formation of C_2 compounds such as C_2H_4 , C_2H_5OH and CH_3CHO at varying FEs dependent upon the atomic ratio of Cu to Ag. The group indicated that the pulsed electroreduction of CO_2 on the Cu-Ag alloy electrode showed a higher FE for the production of C_2 compounds compared to that of bare Cu and Ag. On the other hand, the use of the alloy did not offer any improvements

in the FE of CH₄ since Cu showed a higher FE than any of the Cu-Ag alloy atomic ratio combinations. Further, the authors suggested that the production pathway of C₂ compounds on Ag might be different than that on Cu since the latter involves the formation of an oxide layer on the electrode surface upon an anodic bias while the former's standard reduction potential for Ag₂O cannot occur within the applied bias used in the pulse electrolysis. The group proposed that the formation of C₂ compounds on the alloy might be related to the desorption reactions of CO and the adsorption of H⁺ cathodic period; on the other hand, the desorption of CO does not occur on Cu over the applied anodic bias. Based on the similarity of the FE (C₂H₄), FE (C₂H₅OH) and FE (CH₃CHO), the authors suggested that the formation of C₂ compounds may proceed in the scheme proposed by Sammells and Cook [136, 150, 151] in which a series of reactions between surface CO species, surface carbene species and adsorbed hydrogen atoms produce CH₃CHO in the first step and C₂H₅OH in the second step while C₂H₄ forms in a later stage. The authors attributed the difference in the optimum anodic bias for CH₄ and C₂ compounds to the different degree of CO desorption at the optimal anodic bias

Another metal catalyst associated with catalytic degradation was Sn. Hui and Oloman [58, 59] observed a decrease from 70 to 39% in the FE of HCOOH during the first 100 min of CO_2 electrolysis. The authors attributed these observation to washing away of Sn electrodeposits on the Cu mesh, competitive HER and the deactivation of the catalyst due its exposure to concentrated CO_2 gas and prolonged electroreduction [65]. Similarly, Lee et al. [56] reported a drop in the FE for HCOOH on an Sn gas diffusion electrode a short time after the start of electrolysis (**Figure 29**). The FE of HCOOH rises in the first stage of the electrolysis then decays precipitously after 500 seconds. This is a main feature of catalytic deactivation.

Shironita et al. [166] investigated the ECRC using a Membrane electrode assembly and reported a drop in the current with time. The authors attributed that to catalyst poisoning as a result of the CH_3OH accumulation on the surface of electrocatalyst.

Frese et al. [165] used Auger spectroscopy to confirm the presence of a carbon build up on the Ru surface at high temperatures leading to the partial deactivation of the surface. The deactivation was attributed to the build-up of carbon atoms or the combination of surface C atoms. The authors proposed that the graphitic carbon is the most likely component to be formed following the dissociation of CO_2 to surface carbon and oxygen on the electrode surface. Popic et

al. [160] discussed briefly the poisoning of RuO₂ electrode and attributed that to the formation of strongly bound intermediates.



Figure 29: HCOOH production rate on Sn based gas diffusion electrode at -1.6 V for 1 h [56].

In an early study, Hori et al. [76] discussed catalytic degradation using HCOOH producing catalysts such as In, Pb, Sn, Zn and Hg in galvanostatic electrolysis and presented a different explanation to poisoning than the previously mentioned reports. The degradation of those metals was reflected by a drop in the FE of the main products and a decrease in the electrode potential. The authors were able to restore the activity of the electrode by interrupting the process and washing the electrode with HNO₃ and distilled water- a proof that poisoning is not related to the dissolution of the electrode but to the formation of adsorbed components such as heavy metals. Indeed, those heavy metals are generally present at small levels in any chemical solution and can be deposited on the electrode surface at a small overpotential. Hori and coworkers supported their claim by adding ferrous ions to the solution- a step that led to the acceleration in the decay of the catalyst. Using pre-electrolysis, the researchers were able to maintain a nearly constant concentration of HCOOH over the electrolysis period. Also, the addition of TEA (tetra-ethyl ammonium perchlorate) delayed the decay of In since the HER does not take place on an electrode surface covered with TEA ions and the adsorption of heavy metals is hindered in the presence of this compound.

Despite the positive features of anodic pulsing, it is not evident how the electric charge consumed during the anodic polarization is evaluated in the estimation of energy efficiency [138]. Furthermore, All of the authors who reported on this subject used invariably small size electrodes (1 cm²), and it is not obvious whether their methods are applicable on a practical scale. Also, periodic anodic polarization may render the surface of Cu rather rough owing to resultant anodic dissolution [240], which would shorten the life of the electrode. Hence, more effort has to be made to study the underlying principles of catalytic activation to gain a better understanding about procedure.

4.2 Practical applicability

An important step toward the commercialization of CO_2 electroreduction is the assessment of its economic viability in order to determine at what stage the electrochemical reduction of CO_2 could become justified [241]. A crude process cost analysis model was developed taking into account assumptions about the capital cost (non-linear correlation of capital cost and production rate) and the cost of electrical power (linear correlation of energy cost and production rate) (**Figure 30**) [13]. The cost in this model is for the production of CO₂ electrolysis. It is apparent that the specific and the capital costs are dependent on the CD of the process and follow almost the same trend (**Figure 30**).



Figure 30: Cost model for the specific cost of electro-reducing CO₂ to CO [13].

The electricity cost, on the other hand, is fixed and independent of the CD. This shows that the cost to produce a given amount of CO is relatively high and related to the CD when operated under 250 mA cm⁻². Beyond this number, the cost levels off as the process is operated at higher CDs. Today, the average CD recorded in CO₂ electrolysis is around 100 mA cm⁻² [13]. This implies that efforts should be made to optimize the reaction by undertaking developments on some major aspect of the process including the development of a more efficient and effective catalytic material.

Despite this, some industrial efforts have been made to convert CO_2 into useful products. For instance, DNV GL, a company with expertise in the energy sector, constructed a small-scale reactor powered by solar panels (**Figure 31a**) in 2011 aiming to reduce 1 kg of CO_2 per day into HCOOH [14]. This pilot device showed that the process is not only feasible but also that a high overall system performance can be achieved demonstrating the commercial viability of the process [14].

Simons initiated a project called CO2RRECT (**Figure 31b**), aimed to convert atmospheric CO_2 into useful products including HCOOH using energy from a solar panel [14]. The research was carried out at a coal-fired power plant to investigate the prospects of industrial-scale development.



Figure 31: Industrial application of electrochemical reduction of CO₂ to HCOO-: a) pilot reactor built and assembled by DNV GL and (b) project CO2RRECT conducted by Siemens [14].

Chapter 5

5. Experimental section

The initial goal of this master's project was to develop a new RuO₂-based catalyst for the electrochemical reduction of CO₂ into small organic molecules dissolved in a liquid phase that could be useful for further use (value-added molecules). Unfortunately, despite extensive effort invested in the experimental work, the final results did not look promising, i.e. no significant reduction of CO₂ into organic molecules <u>*dissolved*</u> in the liquid phase was achieved. Nevertheless, some of selected experimental results obtained by the thesis author are presented further in the text.

5.1 Electrode Preparation

 $RuO_2 + IrO_2$ layers on Ti supports were prepared by thermal decomposition of aqueous solutions in the required mole ratio. First, a 0.30 M coating precursor solution was prepared by dissolving IrCl₃ x 3H₂O (Acros Organics 195500050) and RuCl₃ x xH₂O (Sigma Aldrich 206229) in 5 ml isopropanol (purity 99.9%, Fisher Scientific A416-1). A titanium plate (purity 99.2% metals basis, Alfa Aesar 10398) in dimensions of 2.54 cm x 2.54 cm with a thickness of 0.2 cm was used as a substrate for the Ir-Ru and Ru oxide coating. The titanium substrate plate was first wetpolished using 600-grit sandpaper. Then, the polished plate was rinsed thoroughly with triply distilled water and acetone and sonicated for 30 minutes in a water bath to remove polishing residue. Next, the polished plate was etched in a boiling solution of hydrochloric acid (33 wt. %, Fisher Scientific) and deionized water in a 2 (HCl):1(H₂O) volume ratio for 45 minutes. After etching, the plate was washed with deionized water and then dried in argon. The already prepared Ir-Ru and Ru precursor coating solutions was applied uniformly on the freshly prepared titanium substrate with a paint brush. After the first coating, the sample was placed in an oven at 373 K for 10 minutes in order to vaporize the solvent, followed by annealing of the sample at 737 K in a furnace (type 1300) for 10 minutes. The sample was then removed from the furnace, allowed to cool for 5 minute before the application of a new coating layer. The same procedure was repeated for six times in order to form six coatings on the titanium substrate. Finally, the sample was annealed in the furnace for a period of one hour to convert the metal salts into

oxides. The experimental conditions used in the coating procedure (i.e. number of coating, drying and firing temperature) were based on many studies in literature and screening experiments carried out in the "Electrochemistry and Corrosion" lab in the department of chemical engineering at McGill University. The amount of RuO₂ and IrO₂ deposited on the Ti plates was determined by subtracting the mass of the substrate after etching and its mass after the coating procedure.

5.2 Electrochemical Reduction of CO₂

The electrochemical reduction of CO₂ was performed in a three-electrode, two compartment batch electrochemical reactor (250 ml Pyrex glass beaker) (Figure 32). A platinum wire was used as a counter electrode (CE) and was placed on the opposite side of working electrode plate. The platinum wire was, prior to each use, sonicated for 30 minutes in triply distilled water followed by drying with Argon. Afterwards, the cell and its components were thoroughly rinsed and sonicated with ultra-pure water several times, and dried at T = 360 K in a drying cabinet. During measurements, the counter electrode was separated from the working and reference electrodes by a glass frit (12mm Porosity C Tube, ACE glass) in order to limit the contact between oxygen gas evolved at the counter electrode, and the working electrode. A saturated Calomel electrode (SCE) (+0.241 vs. SHE) was used as a reference electrode. 40% $IrO_2 + 60\%$ RuO₂-Ti, 20% IrO₂ + 80% RuO₂-Ti electrode, and a 100% RuO₂-Ti were used as catalyst material (note that both sides of the plate were coated with the metal-oxide coating). A total geometric area of the electrode was 12.5 cm^2 . CO₂ reduction experiments were performed in the following aqueous electrolytes: 0.4 M Briton Robinson buffer solution, 0.1 M KHCO₃, (99%, Sigma Aldrich), 0.5 M KHCO₃ (99%, Sigma Aldrich), 0.2 M Na₂SO₄ (97%, Fisher Scientific), 0.05 M H₂SO₄ (99%, Sigma Aldrich) and 0.1 M KCl (99%, Sigma Aldrich). The effect of the pH was examined using different electrolytes such as 0.1 M KCl (pH 3.5), 0.2 M Na₂SO₄ (pH 4), 0.05 M H₂SO₄ (pH 1.5), 0.5 M KHCO₃ (pH 6.7). The total electrolyte volume was 100 mL.

In order to maintain an oxygen-free electrolyte, argon (99.9999% pure, MEGS) was purged through the electrolyte prior to electrochemical measurements, for 45 min. Then, CO_2 (99.999%, MEGS) was bubbled through the electrolyte for 45 min prior to electrochemical measurements, and it was continued to be bubbled during the electrochemical measurements to maintain the

supporting electrolyte saturated with CO₂. The pH of the saturated solution was determined by an analytical pH-meter.

Electrochemical measurements were carried out using an Ecochemic Autolab PGSTAT30 Potentiostat/Galvanostat. The quantification and identification of electrolysis products was determined by gas chromatography and ion chromatography. For this purpose, liquid phase samples were taken from the electrochemical cell at a regular time interval via a syringe septum. C_2H_5OH , CH_3OH , acetone and acetaldehyde were analyzed by gas chromatography (Agilent 6890N with a 5973 MSD) with a flame ionization detector (FID). HCOOH / HCOO⁻ were analyzed using an ion chromotography (Metrohm 820 with 838 Advanced Sample Processor). The detection limit of C_2H_5OH , CH_3OH , CH_3OH , acetone and acetaldehyde were 5 ppm while that of HCOOH / HCOO⁻ was 1 ppm.



Figure 32: A schematic of the CO₂ reduction experimental setup.

Since the working electrode potential is an important part of the optimization process, several electrochemical techniques were used determine the potential or range of potentials that yield the best performance. For this purpose, linear voltammetry (LV) was performed in the absence and in the presence of CO_2 to ascertain the potential regions of CO_2 reduction on 40% $IrO_2 + 60\%$ RuO₂-Ti, 20% $IrO_2 + 80\%$ RuO₂-Ti electrode, and a 100% RuO₂. CV measurements were carried out to identify and distinct redox-transition peaks for the prepared metal oxides in different electrolytes. Eventually, a prolonged electrolysis experiment with a CO_2 saturated solution at the same electrodes was carried out at constant electrode potential.

Chapter 6

6. Results and Discussions

6.1 Surface Characterization

Before conducting trials for CO_2 electrolysis, it was essential to ensure the adherence and the stability of the RuO₂ coating on the titanium substrate. In theory, this is done using characterization techniques such as XPS, XRD or imaging techniques such as SEM, TEM. However, with regard to RuO₂, their metallic features are easily demonstrated by electrochemical measurement such as CV [172].

Cyclic voltammograms recorded during 20 consecutive runs (sweep rate 50 mV s⁻¹) in pH 6 0.4 M Britton–Robinson buffer solution, for 100% RuO₂-Ti electrodes exhibited two broad peaks that are characteristic features for RuO₂ voltammetric behavior, mainly in acidic media (**Figure 33**). The peaks are seen at about 0.2 and -0.4 V. Peaks 2 and 3 can be attributed to the Ru₂O₃/RuO₂ redox couple and peaks 1 and 4 to the Ru₂O₃/Ru couple. The increase in current marked by 5 refers to the HER from the reduction of water. Fujishima et al. [167] obtained a similar voltammogram in the same electrolyte using the same coating composition on a Si (111). Also, other studies in literature on the features of RuO₂- Ti bore a very close resemblance to **Figure 33** [172, 173].

6.2 CO₂-Saturation Validation

Prior to electrolysis, it was important to ensure the saturation of the electrolyte with CO_2 . This was achieved using two techniques. The first one consisted of measuring the pH of the electrolyte continuously until a stable pH value was attained. This is due to the following equilibrium:

$$HCO_3^{-} \rightleftharpoons CO_2 + OH^{-}$$
(22)

As more CO_2 is pumped into the electrolyte, the equilibrium shifts to the left as per the Le Chatelier's principle, resulting in the drop in OH⁻ concentration and thereafter a drop in pH.

Table 7 shows the change in pH with respect to time at a constant bubbling rate. The other technique involved the use of TOC (total organic carbon) in which the concentration of CO_2 was

determined and compared to literature values. After 30 minutes, both values were in close proximity.



Figure 33: Cyclic voltammetric response of the RuO₂-Ti electrode in 0.4 M Britton- Robinson buffer (pH = 5.8). Scan rate, 50 mV s⁻¹.

Table 7: The pH value of 0.1 M KHCO₃ solution along with the time of bubbling CO₂ at a constant flow rate.

Time / min	0	5	10	15	20	25	30	40
рН	8.54	7.15	7.14	7.09	7.05	6.97	6.96	6.96

6.3 Screening Experiments

The focus of the initial screening experiments was on 100% RuO₂-Ti since the latter has an established catalytic activity toward converting CO₂ as mentioned previously. The plan was to carry on experiments on IrO_2/RuO_2 -Ti in case satisfactory evidence for CO₂ electroreduction products is obtained. Toward the aim of rapidly verifying whether the newly produced 100% RuO₂-Ti has a catalytic affinity toward CO₂ electroreduction, a simple yet viable electrochemical method, linear voltammetry (LV), can be used. Using LV, it is possible to carry out a scan of voltages in the cathodic region where CO₂ reduction takes places and record the corresponding

CD that also reflects the reaction rate. So if LV is done under an inert Ar atmosphere where the HER is the only reaction and then in the presence of CO₂ where CO₂ electroreduction (if the catalyst is selective for CO₂ reduction) and the HER simultaneously take place then it can be reasonably assumed that the reduction of CO2 proceeds if the cathodic current under CO2 atmosphere is higher than that under inert atmosphere. The net CO₂ reduction can be determined as the difference between the two cathodic currents in the absence (Ar atmosphere) and the presence CO₂. The assumptions made in this procedure are based on the fact that the current in CO₂ saturated solution is a sum of the CO₂ reduction current and the HER current, and that the HER current in CO₂ saturated solution takes the same value as that in inert gas saturated solution (Ar atmosphere). These assumptions are valid only if the pH of the system stays constant. However, this presents an obstacle since the introduction of CO₂ to the electrolyte would bring about a change in pH due to the formation of carboxylic acid (Figure 22). Since the HER depends on pH of the electrolyte as mentioned previously, it would be expected to a see a higher CD after saturating the solution with CO_2 if a non-buffer electrolyte is used. Also, during the electrochemical CO₂ reduction, the pH near the electrode surface is expected to be higher than that in the bulk due to proton consumption. The local pH can be up to 6 units higher than in the bulk pH in a non-buffer solution [242]. To ascertain that the increase in current is due to CO₂ reduction rather than the increase in acidity, experiments were done in 0.05 M H₂SO₄ under ambient conditions. H₂SO₄ is a very strong acid (pKa 1.81), the saturation with CO₂ cannot produce a change in pH since carbonic acid (pKa 10.32), is a weak acid in comparison to H₂SO₄.

The current in the Ar environment is solely due to the production of hydrogen (**Figure 34**). This current increases with potential since the HER is not hindered by mass transfer limitation in aqueous solution. After saturating the electrolyte with CO_2 , there is no change in the CD at low potentials (-0.45 to -0.65 V), however this trend is reversed at higher potentials (starting from ca. -0.7 V) as the current density due to the CO_2 electroreduction sets in.

Once the onset CO_2 reduction potential was determined from polarization experiments in **Figure 34**, electrochemical reduction of CO_2 was investigated in 0.05 M H₂SO₄ (pH 1.5) aqueous solution at voltages exceeding the onset potential (i.e. -0.7 V to -1.25 in increments of 50 mV) in experiments lasting 10 minutes to obtain a steady state reading for the CD. A control experiment was also done in Ar atmosphere to obtain the CD of the HER. Afterwards, the current density of CO_2 electroreduction (i_{CO2}) was estimated as the difference between the CD in the presence of CO_2 and that in its absence (i.e. The CD of the HER obtained from the control experiment) (**Figure 35**). It is important to mention that LV readings could not have been used since the fast scan rate would not allow an accurate steady state CD reading.



Figure 34: Current vs Potential profile in 0.05 M H_2SO_4 at 100% RuO₂-Ti after Ar purging (solid line) and CO₂ saturation (dotted line) at a (scan rate 50 mV/s) and T = 295 K.

The FE of CO_2 reduction derived from the above-mentioned analytical measurements reached its maximum of 65% at -0.9 V.

Another method to validate the ECRC involves using cyclic voltammetry (CV) to monitor the variation of the anodic peaks as a function of holding potential (**Figure 36**). In CV measurements, the rise in anodic current is due to the oxidation of molecules produced by CO_2 reduction, either those dissolved in the electrolyte or those adsorbed on the surface. This method can be used as a first indication about the possibility of CO_2 reduction [160]. It is notable that upon applying a fixed potential of -0.8 V for 5 minutes, the CV anodic (oxidation) current in the region between -0.4 V and 0.6 V increases. This increase is more pronounced upon using a higher voltage of -1.2 V for 5 minutes. Popic et al. [160] indicated that an increase in the anodic current in the area of potential from -0.15 to - 0.3 V can be attributed to the oxidation of the products originating from CO_2 reduction. The increase in the oxidation current when more

negative potentials are used is an indication to the accumulation of CO_2 reduction products in the system [170].



Figure 35: The ratio of CO₂ reduction current to the total current as a function of potential in 0.05 M H₂SO₄ at 295 K. The values are obtained from potentiostatic (chronoamperometry) experiments.

The LV and CV measurements presented in this section indicated that the 100% RuO_2 -Ti electrode can be used in CO_2 electroreduction. However, the results do not give any evidence on the chemical composition of the formed products and their existence in the liquid or gas phase, or on the electrodes surface (adsorbed products). It is important to mention that control experiment under inert Ar atmosphere were conducted and the trends established in **Figure 36** were not observed.

6.4 The Effect of Electrolyte/pH

The effect of the electrolyte was studied in three different buffer solutions which cover a wide range of pH: 0.05 M H_2SO_4 (pH 1.5), 0.4 M Britton Robinson (pH 4), and 0.1 M KHCO₃ (pH 6.8) to ensure that any change in pH is kept within a narrow range. The same method mentioned in Section 6.3 was implemented to compare the performance of the electrolytes. It was concluded, from these preliminary studies, that a pH of 6.8 is the most promising for ECRC. This

conclusion agrees with the results of Popic et al. [160] who conducted experiments on conductive metal oxides including $RuO_2 + TiO_2$.



Figure 36: Voltammetric curves at the 100% RuO₂-Ti electrode in CO₂ saturated 0.05 M H₂SO₄ as a function of the holding potential. Scan rate, 50 mV s⁻¹.

6.5 Long term Potentiostatic electrolysis

In order to identify the products obtained by the reduction of CO_{2} , long-term potentiostatic polarization experiments were performed using the optimum experimental conditions deduced in the screening trials, i.e. (0.1 M KHCO₃ (pH 6.8), -0.9 V).

Long term electrolysis for CO_2 -saturated and Ar-saturated 0.1 M KHCO₃ is shown in **Figure 37**. It is clear that the CD is higher under CO_2 atmosphere in relation to that under Ar atmosphere. This aspect can be attributed to CO_2 electroreduction as was mentioned in Section 6.3.

Liquid phase samples from CO_2 -saturated 0.1 M KHCO₃ were taken at regular intervals during electrolysis and analyzed using ion chromatography (IC) and gas chromatography (GC). The gas phase products were not analyzed since the electrochemical cell used was not airtight. The

analysis indicated the absence of CO_2 reduction products dissolved in the liquid phase, during the time over which the experiment was conducted at a potential of -0.9 V. Samples were also taken from the other experiments in other electrolytes (0.05 M H₂SO₄ and 0.05 M Britton Robinson) and yet the same observation was recorded. These results suggest that although the electrode can reduce CO_2 (as evidenced by measurements in Figures (34-37), the produced molecules might not be dissolved in the liquid phase, indicating that the reaction products could be CO, CH₄ and/or C₂H₄. Also, due to the constant bubbling of the electrolyte with CO₂, if some of organic molecules initially formed were in the liquid phase, they might have quickly evaporated as a results of constant CO₂ bubbling (assuming they have large vapour pressure).



Figure 37: Chronoamperometry measurements in CO₂ saturated and Ar-saturated 0.1 M KHCO₃ at -0.9 V 100% RuO₂-Ti.

6.6 Troubleshooting

In the light of the lack of evidence for the formation of liquid products from CO_2 electroreduction, several theories were set forth toward the aim of understanding the shortcomings and troubleshooting the system. The main reasons to consider are the following

(i) Catalyst poisoning due to the presence of contaminants in the electrolyte or in water.

- (ii) The purity of CO_2 used in the system.
- (iii) The low solubility of CO_2 in the electrolyte.
- (iv) The inactivity of RuO₂-Ti toward CO₂ electrolysis.
- (v) The formation of gas only products.

The following section outlines the major steps carried out to address the potential causes for the observed lack of analytical evidence in CO_2 electroreduction.

As mentioned in Section 4.1, the poisoning/deactivation of the electrode is a common occurrence associated with many catalysts used for CO_2 reduction. This can be due either to impurities or CO_2 electroreduction intermediates as mentioned in Section 4.1.4. Heavy metal impurities contained in reagent chemicals at extremely low levels might be present in the electrolyte. Such heavy metal ions would be cathodically reduced and deposited at the electrode during CO_2 reduction. In addition, reaction intermediate might adsorb on the surface of the catalyst limiting the accessibility of CO_2 to the active sites. To address this drawback, pulsing was used to remove any potential contaminants from the surface of the electrode, similar to the approach used by Nogami et al. [225], Lee et al. [236], and Yano et al. [237, 238] – see **Figure 24 and Figure 28**. Based on the extensive literature review done on this subject, the anodic bias voltages were chosen as to fall in the range that corresponds to oxidation of the impurities (-0.5 V to 0 V). The whole range was tested while keeping the cathodic voltage constant at -0.9 V. However, the experiments did not yield any products except for one time when CH₃OH and C₂H₅OH were detected on the GC without satisfactory reproducibility.

To improve the purity of CO_2 , an extra pure CO_2 (99.99%) was purchased and used in electrolysis. Unfortunately, this did not yield any positive outcome, as no products were detected. Thus, it was concluded that the purity of CO_2 used in our experiments was not the origin for the lack of liquid phase products.

The low solubility for CO_2 was addressed by carrying out experiments in a low temperature water bath at a range of voltages (-0.6 V to -1 V). It was notable that the CD decreased at the employed low temperatures compared to ambient conditions- a clear indication for the suppression of the HER. However, those low temperature experiments did not result in any improvement, i.e. no detectable liquid-phase CO_2 reduction products were obtained.

Toward the aim of understanding the effect of the coating composition on the results, a different set of coating compositions (40% $IrO_2 + 60\% RuO_2$ -Ti, 20% $IrO_2 + 80\% RuO_2$ -Ti) were experimented using the same experimental conditions as those used for 100% RuO_2 -Ti. Nevertheless, all the tested compositions did not show any evidence for liquid phase products.

The only explanation yet to be pursued is the presence of products only in the gaseous phase. There is a reason to believe (screening experiments presented earlier in this chapter) that this possibility is quite plausible for interpreting the results of the electrochemical measurements and the ensuing lack of products in the liquid phase. Due to the time restrictions of this master's project, this possibility was not investigated and hence no certain conclusions can be drawn until a gas tight cell is designed, produced and then used and the effluent is analyzed by analytical instruments.

Chapter 7

7. Conclusion

CO₂ electroreduction to value-added molecules is an important research and development research area that has attracted considerable attention due to the advantages it can bring to counter environmental hazards linked to mounting CO₂ levels in the atmosphere. This climate change mitigation technology does not only aim to reduce atmospheric CO₂ but also presents a pathway for utilizing a once thought waste product as a feedstock for many industrial processes. However, CO₂ is a highly stable molecule on the thermodynamic level and converting it electrochemically to value-added product requires energy input in the form of voltage. Another obstacle that negates CO₂ electroreduction in aqueous electrolytes is the presence of competing reactions, such as the hydrogen evolution reaction (HER) that consumes some of the energy supplied, thereby reducing the efficiency of the electrochemical reduction of CO₂. Early studies on the process relied on the metallic electrodes as catalysts; however, due to slow reaction kinetics, surface deactivation and low product selectivity, the performance of metal catalyst has not shown success at a satisfactory level to justify their use in a large scale operation. Toward the aim of providing an in-depth understanding on the fundamental aspects of CO₂ electroreduction, this thesis presented, in part, a comprehensive review on the major electrochemical studies that addressed the conversion CO₂ to valuable products and the approaches employed to optimize the process.

An important step toward the optimization of the catalyst lies in gaining a better understanding on the interaction between the surface of the electrode and the reaction intermediates [10]. Developing novel catalysts is one of the most important steps toward the enhancement of the process. The bare metallic catalyst used extensively in literature studies proved to be futile with regard to practical application under standard conditions. New unconventional materials, like composite catalyst materials and nanostructure catalyst material are emerging as promising electrodes for future studies [10].

Many unanswered questions remain as to the specifics of the reaction pathway on the catalyst. Various research groups have proposed reaction mechanisms for different products and process conditions but sound and fundamental proof is still lacking to entirely elucidate the mechanism [6]. By understanding the reaction mechanism, the process can be tailored toward the production of a desired product with high faradaic and energy efficiency, thus, increasing the selectivity and the economic viability of the process [11]. Fundamental studies will shed light on the dependency of the product selectivity on the nature of the electrode's material and, thus, this would be an important step in optimizing the process. Also, further understanding about the process parameters (temperature, pH, pressure and cell configuration) and the interaction between those factors and the electrode surface is required toward upscaling the technology of CO_2 electroreduction [4].

This report also presented an attempt to reduce CO_2 electrochemically to value-added products using RuO₂-Ti and IrO₂/RuO₂-Ti mixed metal oxide. Electrochemical techniques such as linear and cyclic voltammetry (LV and CV) were used to validate the process and obtain useful information about the electrode's surface. Despite some promising results obtained by those techniques, the analysis of the aqueous solution for products that remained dissolved in it did not yield any concrete evidence to support the catalytic performance of RuO₂-Ti and IrO₂/RuO₂-Ti toward the electrochemical reduction of CO₂

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