



**Understanding the Electrochemical Reduction of
Carbon Dioxide into Formate using a Tin-plated
Cathode**

by

**Tan Tiek Aun
(1431211307)**

A thesis submitted in fulfilment of the requirements for the degree of
Master of Science (Environmental Engineering)

**School of Environmental Engineering
UNIVERSITI MALAYSIA PERLIS**

2016

ACKNOWLEDGEMENT

I would first like to thank the Dean of Environmental Engineering, Dr Nasrul bin Hamidin; my supervisor Dr Sara Yasina binti Yusuf, co-supervisor, Dr Umi Fazara Md Ali; and the teaching engineers, Mr Affendi Derman and Mr Nazerry Rosmady Rahmat. Their guidance and patience proved invaluable and vital to the completion of this work.

I would also like to thank Kementerian Pengajian Tinggi for the Research Acculturation Grant Scheme 9018-00033, and MyMaster under the Mybrain15 program.

Finally, I must express my very profound gratitude to my family, Tan Tiong Ming, Lee Yoke Kuan, Tan Tick Yi; friends, Ong Hui Yen, Lim Gim Pao, Chu Sue Yin, Chin Yuk Ming, Thenmolhi Ravinder; and pets, Ah Meow, Ah Meow 2a and Ah Meow 2b for providing me with support and continuous encouragement throughout the study. This accomplishment would not have been possible without them. Thank you.

TABLE OF CONTENTS

| | PAGE |
|---------------------------------|-------------|
| THESIS DECLARATION | i |
| ACKNOWLEDGMENT | ii |
| LIST OF FIGURES | iii |
| LIST OF TABLES | vi |
| LIST OF ABBREVIATIONS | vii |
| LIST OF SYMBOLS | viii |
| ABSTRAK | x |
| ABSTRACT | xi |
| CHAPTER 1 INTRODUCTION | |
| 1.1 CO ₂ Utilization | 1 |
| 1.2 Problem Statement | 5 |
| 1.3 Aims | 8 |
| 1.4 Objectives | 8 |
| 1.5 Scope | 8 |

| | | |
|-----|--------------|---|
| 1.6 | Significance | 9 |
|-----|--------------|---|

CHAPTER 2 LITERATURE REVIEW

| | | |
|-----|---|----|
| 2.1 | Electrochemical Reduction of CO ₂ | 10 |
| 2.2 | Formation of CO ₂ ^{•-} | 11 |
| 2.3 | Standard Potential for HCOO ⁻ Formation | 16 |
| 2.4 | Sn as a Catalyst for CO ₂ Reduction into HCOO ⁻ | 17 |
| 2.5 | CO ₂ Transport by Catholyte Flow | 25 |
| 2.6 | Non-aqueous and Aqueous Electrolytes | 26 |
| 2.7 | Proton Exchange Membrane | 33 |
| 2.8 | Deactivation of the Electrode | 34 |
| 2.9 | Overall View | 35 |

CHAPTER 3 METHODOLOGY

| | | |
|-----|--|----|
| 3.1 | Electrochemical Reactor Set-Up | 38 |
| 3.2 | Materials | 39 |
| | 3.2.1 Apparatus | 39 |
| | 3.2.2 Reagents | 40 |
| 3.3 | Electrodeposition of Sn | 41 |
| 3.4 | Producing the Sn Electrodes and Pre-electrolysis | 42 |
| 3.5 | Variables | 43 |
| | 3.5.1 Cathode Rotating Speed | 43 |
| | 3.5.2 Cathode Applied Potential | 44 |
| | 3.5.3 Electrolyte pH | 44 |
| 3.5 | High Performance Liquid Chromatography (HPLC) Analysis | 45 |

CHAPTER 4 RESULTS AND DISCUSSION

| | | |
|-----|---|----|
| 4.1 | Deposition of Sn onto Glassy Carbon Electrode | 46 |
| 4.2 | Pre-electrolysis | 51 |
| 4.3 | Cyclic Voltammogram of the Reduction Process of CO ₂ | 52 |
| 4.4 | High Performance Liquid Chromatography (HPLC) Analysis | 56 |
| 4.5 | Effect of Cathode Rotating Speed on the Reduction Process | 57 |
| 4.6 | Effect of pH on the Reduction Process | 69 |
| 4.7 | Effect of Cathode Potential on the Reduction Process | 78 |
| 4.8 | Production of dead zones across the Sn cathode surface | 84 |

CHAPTER 5 CONCLUSIONS AND FUTURE WORK

| | | |
|-----|-------------|----|
| 5.1 | Conclusions | 85 |
| 5.2 | Future Work | 87 |

| | |
|-------------------|----|
| REFERENCES | 88 |
|-------------------|----|

| | |
|-----------------------------|----|
| LIST OF PUBLICATIONS | 96 |
|-----------------------------|----|

©This item is protected by original copyright

LIST OF FIGURES

| NO. | | PAGE |
|------|---|------|
| 1.1 | Possible pathways for CO ₂ utilization | 2 |
| 1.2 | Specific energy consumption as a function of Faradaic efficiency for CO ₂ reduction products | 3 |
| 1.3 | HCOO ⁻ / HCOOH as an energy storage medium | 4 |
| 1.4 | CO ₂ emissions projection from four main sectors | 6 |
| 2.1 | Molecular Orbital for CO ₂ | 12 |
| 2.2 | Walsh diagram for CO ₂ | 14 |
| 2.3 | Schematic potential energy diagram of linear neutral CO ₂ and bent $\cdot\text{CO}_2^-$ | 15 |
| 2.4 | Carbon coordination, oxygen coordination and mixed coordination | 18 |
| 2.5 | Potential as a function of heat of fusion of several metals. HCOO ⁻ forming metals | 20 |
| 2.6 | Possible formation of HCOO ⁻ from $\cdot\text{CO}_2^-$ desorped into the electrolyte | 21 |
| 2.7 | Possible formation of HCOO ⁻ from $\cdot\text{CO}_2^-$ coordinated on cathode | 22 |
| 2.8 | Formation of (COO ⁻) ₂ | 27 |
| 2.9 | Formation of CO ₃ ²⁻ | 27 |
| 2.10 | Effect of water on HCOO ⁻ formation | 28 |
| 2.11 | Carbonate species at different pH | 29 |

| | | |
|------|---|----|
| 2.12 | Pourbaix diagram of CO ₂ | 30 |
| 3.1 | Flow chart of methodology | 37 |
| 3.2 | Experimental setup | 38 |
| 4.1 | Linear sweep voltammogram of Sn ²⁺ saturated in 11% H ₂ SO ₄ | 46 |
| 4.2 | Potential against time profile of the electro-deposition process | 49 |
| 4.3 | Surface morphology of Sn plated onto the glassy carbon electrode | 50 |
| 4.4 | Surface morphology of Sn plated onto the glassy carbon electrode after being rotated for 2 hours under water | 51 |
| 4.5 | Current against time profile for pre-electrolysis | 52 |
| 4.6 | Cyclic voltammogram of the reduction process of CO ₂ | 54 |
| 4.7 | a) High Performance Liquid Chromatography of a HCOO ⁻ standard. b) High Performance Liquid Chromatography of a sample produced by applying a negative potential onto a CO ₂ -saturated electrolyte | 56 |
| 4.8 | Calibration curve for HCOO ⁻ | 57 |
| 4.9 | a) Obtained current density against potential b) Theoretical current density for HCOO ⁻ against rotating speed | 60 |
| 4.10 | HCOO ⁻ yield at different rotating speeds | 62 |
| 4.11 | HCOO ⁻ Faradaic efficiencies at different rotating speeds | 63 |
| 4.12 | Linear Sweep Voltammogram for CO ₂ reduction carried out at differing cathode rotating speed | 65 |
| 4.13 | Degradation of Sn plated onto the glassy carbon electrode after 2 hours reduction | 66 |

| | | |
|------|--|----|
| 4.14 | Degradation of current density at different rotating speeds | 68 |
| 4.15 | a) Obtained current density against potential b) Theoretical current density for HCOO^- against pH | 71 |
| 4.16 | HCOO^- yield at different pH | 72 |
| 4.17 | HCOO^- Faradaic efficiencies at different pH | 72 |
| 4.18 | Surface morphology of Sn plated onto the glassy carbon electrode after 2 hour reduction in a basic environment | 74 |
| 4.19 | Linear sweep voltamgram for CO_2 reduction carried out at different pH | 76 |
| 4.20 | Degradation of current density at different pH | 78 |
| 4.21 | a) Obtained current density against potential b) Theoretical current density for HCOO^- against potential | 80 |
| 4.22 | HCOO^- yield at different applied potentials | 81 |
| 4.23 | HCOO^- Faradaic efficiencies at different applied potentials | 82 |
| 4.24 | Degradation of current density at different applied potentials | 83 |
| 4.25 | Formation of dead zones on Sn plated onto the glassy carbon electrode after 2 hour reduction | 84 |

LIST OF TABLES

| NO. | | PAGE |
|------|--|------|
| 2.1 | CO ₂ reduction products selectivity of several metals | 19 |
| 2.2 | Summary of CO ₂ reduction using Sn cathodes from other works | 22 |
| 3.1 | List of apparatus | 39 |
| 3.2 | List of reagents | 40 |
| 4.1 | Diffusion layer thickness at the electrode/ electrolyte interface at different cathode rotating speed | 58 |
| 4.2 | Theoretical and observed limiting current density at different cathode rotating speed | 59 |
| 4.3 | Maximum theoretical amount of HCOO ⁻ that can be produced at different cathode rotating speed | 61 |
| 4.4 | HCOO ⁻ yield and Faradaic efficiency at different cathode rotating speeds | 62 |
| 4.5 | Theoretical and observed amount of HCOO ⁻ produced at different cathode rotating speed | 69 |
| 4.6 | Theoretical and observed limiting current density at different pH | 70 |
| 4.7 | HCOO ⁻ yield and Faradaic efficiency at different pH | 73 |
| 4.8 | Theoretical and observed amount of HCOO ⁻ produced at different pH | 77 |
| 4.9 | Theoretical and observed limiting current density at different applied potentials | 79 |
| 4.10 | Theoretical and observed amount of HCOO ⁻ produced at different applied potentials | 82 |
| 4.11 | Charge degradation at different applied potentials | 84 |

LIST OF ABBREVIATIONS

| | |
|---------|--|
| ads | Adsorbed |
| Ag/AgCl | Silver/ silver chloride electrode |
| CA | Chronoamperometry |
| CV | Cyclic voltammetry |
| HPLC | High performance liquid chromatography |
| LSV | Linear sweep voltammetry |
| RDE | Rotating disc electrode |
| SCE | Standard calomel electrode |

©This item is protected by original copyright

LIST OF SYMBOLS

| | |
|------------|---|
| C | Charge of one coulomb |
| D | Diffusion coefficient |
| E | Nernst potential |
| E° | Standard Nernst potential |
| f | Cathode rotating speed |
| F | Faradaic constant |
| g_{Sn} | Weight of Sn required to be deposited |
| h | Henry constant |
| I_l | Limiting current |
| I_{Sn} | Current to be applied |
| j_L | Limiting current density |
| k_m | Constant equal to $\frac{D}{\delta_N}$ |
| K_{ox1} | Dissociation constant of CO_2 to HCO_3^- |
| K_{ox2} | Dissociation constant of HCO_3^- to CO_3^{2-} |
| K_{red1} | Dissociation constant of formic acid, $HCOOH$ to $HCOO^-$ |
| MW_{Sn} | Molecular weight of Sn |

| | |
|--------------------------|---|
| n | Number of electrons that is consumed to reduce one mole of reactant |
| n_{Sn} | Number of electrons used to reduce one mole of Sn |
| $P(\text{CO}_2)$ | CO_2 pressure just above the electrolyte |
| Q | Total charge passed |
| R | Universal gas constant |
| t | Time passed |
| t_{sec} | Time required for Sn deposition |
| T | Temperature |
| ν | Kinematic viscosity |
| δ_{Nernst} | Nernst diffusion layer |

©This item is protected by original copyright

Reduksi Elektrokimia Karbon Dioksida kepada Formate menggunakan Katod bersadur Timah

ABSTRAK

Timah (Sn) telah menjadi pilihan utama dalam penyelidikan elektrokimia disebabkan keupayaannya untuk menukarkan karbon dioksida (CO_2) ke dalam bentuk terturun dengan cekap dan pada kos tenaga yang rendah. Walau bagaimanapun, kajian yang lengkap dan menyeluruh yang mana mengaplikasikan Sn dalam penurunan CO_2 secara elektrokimia masih belum dapat dijelaskan secara menyeluruh. Oleh itu, kajian ini membincangkan penyelidikan asas mengenai penurunan karbon dioksida kepada ion formate (HCOO^-) secara elektrokimia, menggunakan elektrod bersadur timah. Sn telah berjaya diendapkan pada permukaan elektrod karbon berkaca secara sekata dan rata. Elektrod Sn tersebut juga adalah stabil secara mekanikal dan menunjukkan ciri-ciri elektrokimia boleh-ulang. Kajian terhadap kesan-kesan pengangkutan CO_2 secara katodik, pH elektrolit, dan potensi gunaan katod telah dikaji. Didapati bahawa halaju putaran katod yang lebih tinggi akan mengurangkan kecekapan Faradaic ion HCOO^- . Molekul-molekul CO_2 yang memasuki reaktor mempunyai masa mastautin yang lebih pendek pada kelajuan katod-berputar yang lebih tinggi dan sebahagiannya meninggalkan katod tanpa menjalani tindak balas elektrokimia. Didapati bahawa keadaan beralkali adalah menjadi pilihan bagi proses penurunan CO_2 kepada HCOO^- . Pelepasan H_2 dan H^+ adalah lazim pada pH yang rendah disebabkan jumlah $[\text{H}^+]$ sedia ada yang perlu diturunkan adalah tinggi. HCO_3^- mungkin menyumbang sebagai bahan kimia prapenanda bagi pembentukan HCOO^- . Potensi elektrolisis bersesuaian bagi penghasilan HCOO^- terbaik adalah sekitar $-1,75 \text{ V vs SCE}$ selari dengan kesusasteraan. Sekiranya upaya dibenarkan menjadi semakin negatif, kecekapan Faradaic akan berkurangan disebabkan pelepasan H_2 meningkat pada upaya-upaya yang lebih negatif. Elektrod bersaduran Sn didapati berkurangan dan terlucut semasa penurunan elektrokimia terutamanya pada upaya negatif yang tinggi atau keadaan-keadaan berasid disebabkan oleh tekanan mekanikal akibat kerapuhan hidrogen. Apabila elektrolit adalah beralkali, penjelasan yang mungkin adalah apabila Sn- CO_2 terbentuk, ikatan antara kedua-duanya tidak mudah terurai selepas itu dan gabungan molekul itu akan bebas di dalam larutan elektrolit pukal. Secara rumusnya, Sn adalah bahan katod terpilih yang berpotensi dalam menurunkan CO_2 kepada HCOO^- secara elektrokimia. Peranan beberapa parameter penting dan terpilih telah dijelaskan untuk manfaat kajian masa depan. Kajian masa depan juga diharap akan lebih peka tentang kemerosotan Sn melawan masa sewaktu proses penurunan elektrokimia berlangsung.

Electrochemical Reduction of Carbon Dioxide into Formate using a Tin-plated Cathode

ABSTRACT

Sn has been a research interest for its ability in converting CO_2 into its reduced form very efficiently and at a relatively low energy cost. However, a complete and exhaustive study for the usage of Sn in electrochemical reduction of CO_2 still does not exist. Researchers often provide conflicting reports on the role of variables such as cathodic CO_2 transport or electrolyte pH. Cathode degradation also has been reported by various researchers in literature but however, disagreement as to the cause of the degradation exists. This thesis presents a fundamental study on the electrochemical reduction of CO_2 into HCOO^- using a tin plated electrode. Sn was successfully deposited on glassy carbon electrode satisfactorily with a good even surface. The Sn plated electrodes are mechanically stable and give reproducible electrochemical characterizations. The produced Sn electrode is used to investigate the effects of cathode rotating speed, electrolyte pH, and applied cathode potential on the Faradaic efficiency for HCOO^- . A higher cathode rotating speed is detrimental to the HCOO^- Faradaic efficiency. CO_2 molecules entering the reactor have shorter residence time at higher cathode rotating speeds and some leave without undergoing electrochemical reaction. Basic conditions are preferable for CO_2 reduction to HCOO^- . H_2 evolution is prevalent at low pH due to the high amount of available $[\text{H}^+]$ to be reduced. HCO_3^- may have contributed as a precursor chemical for the formation of HCOO^- . The Faradaic efficiency for producing HCOO^- increases until it tapers off to a maximum at -1.75 V vs SCE. When the potential is made negative further, the Faradaic efficiency decreases due to the enhancement of H_2 evolution which is consistent with literature. The Sn plated electrode was found to degrade and strip off during electrochemical reduction likely due to mechanical stress caused by hydrogen embrittlement. When the electrolyte is basic, it is possible that when the Sn- CO_2 is formed, the bond between the two does not always break afterwards and the complex is brought into the bulk electrolyte. Sn is a potential selective cathode material in electrochemically reducing CO_2 into HCOO^- . The roles of several, select, important variables have been made clear for the benefit of future studies. Future studies will also be made aware of the Sn degradation with time during electrochemical reduction.

CHAPTER 1

INTRODUCTION

This chapter provides introduction to the electrochemical utilization of carbon dioxide (CO₂). The need for a study on electrochemical reduction of CO₂ into formate using tin-plated electrode is discussed in the problem statement. The project aims, objectives, research scope, and significance are also presented.

1.1 CO₂ Utilization

Carbon dioxide can be used as a base material to produce a wide range of small organic molecules (Jiang et al., 2010; Mikkelsen et al., 2010; Quadrelli et al., 2011; Yu et al., 2008). Fig. 1.1 illustrates the possible pathways for CO₂ conversions such as hydrocarbons (kerosene, diesel), methanol, carboxylic acids, urea and formic acid. However, the valorization of CO₂ is usually an endergonic process i.e. it requires an input of energy because it is an unfavorable and non-spontaneous process.

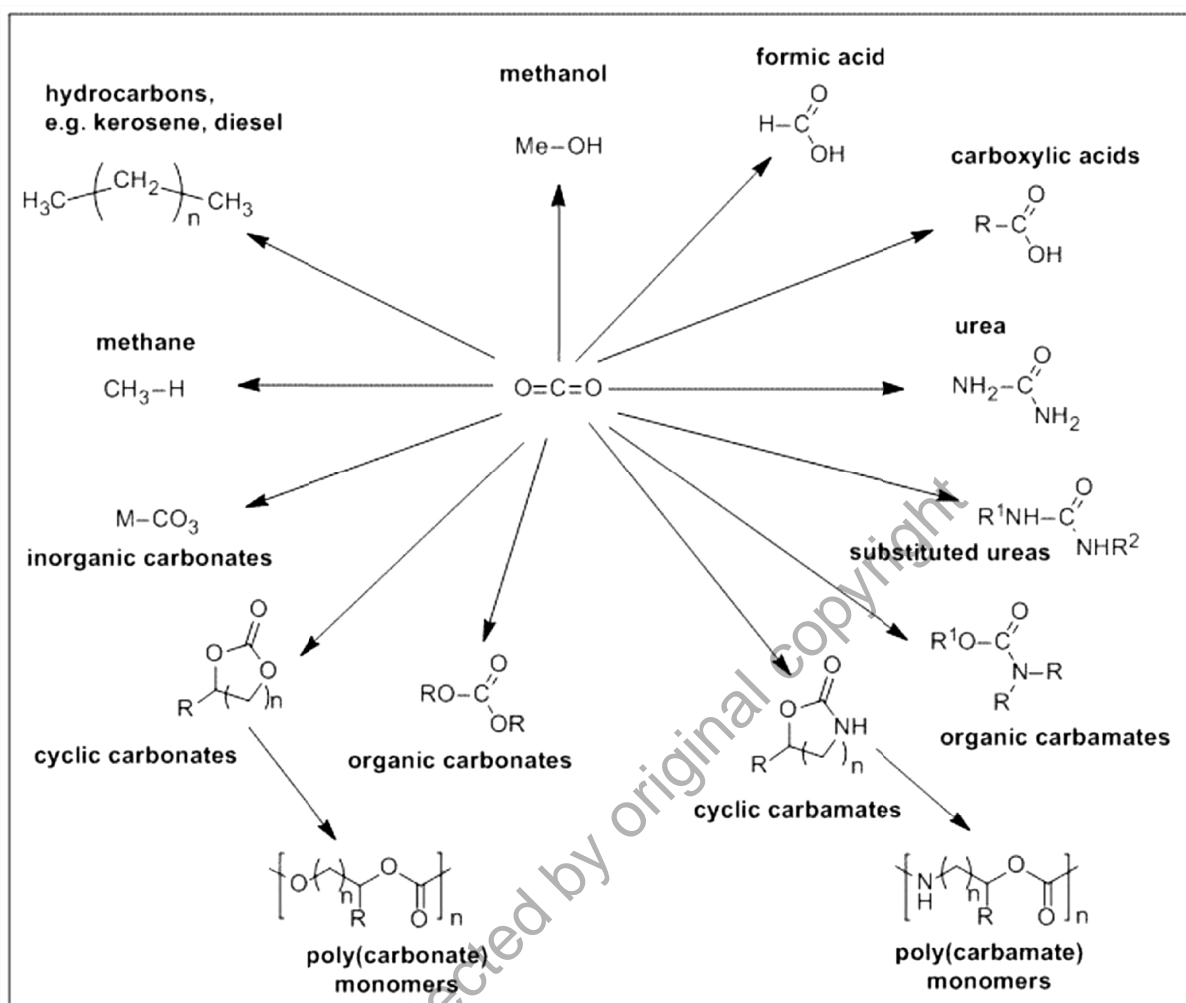


Figure 1.1: Possible pathways for CO_2 utilization (Energy Research Centre of the Netherlands, 2011).

Electrochemical valorization of CO_2 into formate (HCOO^-) can be carried out at ambient temperature and low pressure. The process does not require any consumable chemicals nor produce any harmful byproducts. However, the electrochemical process is energy intensive and for it to be carbon neutral, the energy must be derived from renewable sources. Also, for the process to be considered viable, the process must have high Faradaic efficiency and low overpotential requirements to be energetically efficient.

The specific energy consumption as a function of Faradaic efficiency for various CO₂ reduction products is shown in Fig. 1.2. Formate (HCOO⁻) and carbon monoxide (CO) require relatively little energy and can be converted with high Faradaic efficiencies. HCOO⁻ exist as a liquid in ambient conditions making it more practical to store and transport than CO which exist as a gas (Argarwal, Zhai, Hill, & Sridhar, 2011).

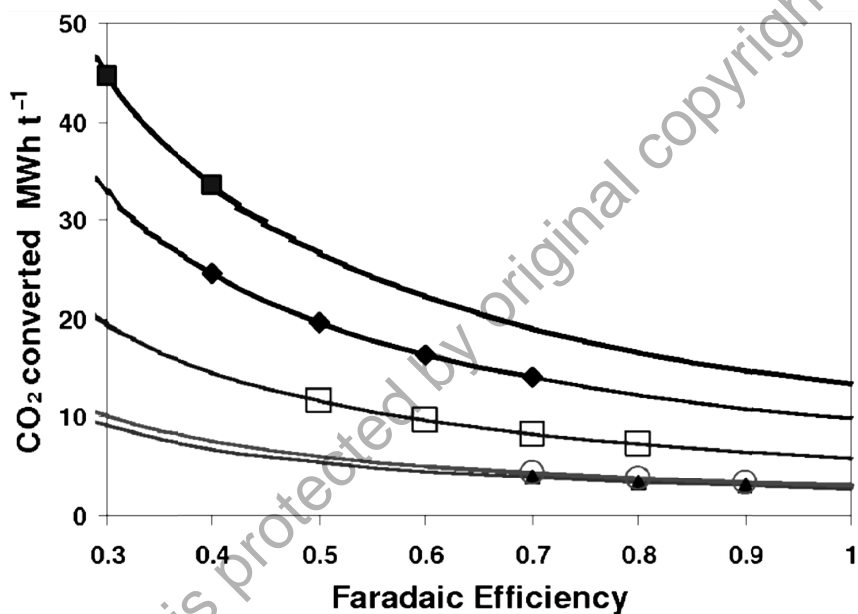


Figure 1.2: Specific energy consumption as a function of Faradaic efficiency for CO₂ reduction products. CH₄ (■), C₂H₄ (◆), CH₃OH (□), HCOO⁻ (○), CO₂ (▲) (Argawal et al., 2011)

Formate production from CO₂ has been widely targeted because it is an industrially valuable chemical. The expected average annual growth for the demand of HCOO⁻ is 3.7 %. HCOO⁻ is not yet replaceable for most applications. It is mainly used as an antibacterial agent in animal feed especially in Europe since the ban on antibiotic growth promoters in year 2006. Demands in silage preservation/ animal feed additives are also expected to grow significantly especially in China, Asia excluding Japan, Central and South America and Africa from year 2012 to year 2018. HCOO⁻ is also

used to create artificial flavoring, occasionally as food preservative and also to make perfume scents; in the leather tanning industry, especially in Central and South America, Africa, the Middle East, India, Italy, Spain and France; in textile and paper processing and as coagulant and anti-ozonant when processing raw latex into rubber. In India, Southeast Asia and Central and South America, HCOO^- serves as catalysts and plasticizers and pH regulator in chemical processes. HCOO^- preparations are also used to kill varroa and tracheal mites which invade honeybee hives and attack the bees (Crampton, 2016). HCOO^- is a potential sustainable liquid fuel due to its high energy density (Gattrell et al., 2006; Kuhlet et al., 2012; Narayanan et al., 2011; Olah et al., 2011; Prakash et al., 2013; Whipple et al., 2010). HCOO^- or formic acid (HCOOH) is also potentially useful as a storage medium for hydrogen (Grasemann & Laurency, 2012; Prakash et al., 2013) and the recoverable energy density of $\text{HCOO}^-/\text{HCOOH}$ is comparable with other storage methods as shown in Fig. 1.3 (Det Norske Veritas, 2011).

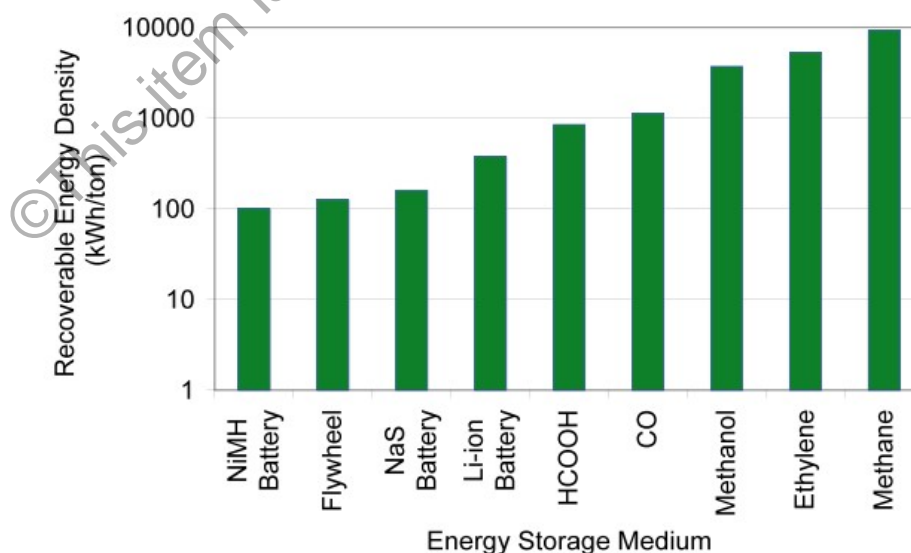


Figure 1.3: $\text{HCOO}^-/\text{HCOOH}$ as an energy storage medium (Det Norske Veritas, 2011)

1.2 Problem Statement

Carbon dioxide is non-polar and stable under standard conditions making it persistent in the atmosphere. This poses a threat to the environment because globally, CO₂ is a major cause of climate change (Figueroa, Fout, Plasynski, McIlvried, & Srivastava, 2008), contributing around 9 to 26 % to the greenhouse effect (Russel, 2007). The greenhouse effect is when gasses such as CO₂ trap infrared radiation from the sun in the lower atmosphere, warming up the earth's surface and atmosphere. The Intergovernmental Panel in Climate Change (2013) reported the globally averaged combined land and ocean temperature data show an average increase of 0.85 °C, from year 1880 to 2012, or about 0.89 °C from year 1901 to 2012, or about 0.72 °C from year 1951 to 2012.

Tropical countries (such as Malaysia) will be the first to experience unprecedented heat stress because of global climate change and this will damage the region's agriculture. Decreasing crop and livestock yield will lead to deficits or poorer food security (Battisti & Naylor, 2009). Global warming will also cause ocean thermal expansion and the melting of Greenland and Antarctica's glacier and ice sheets. This will cause a rise in sea level. The mean sea level rise along Malaysian coasts from year 1993 to 2010 is between 2.7 – 7.0 mm/yr. Sea level rise can cause destruction of assets or properties and disruption to economic sectors (Hydrolink, 2013). Fig. 1.4 shows the CO₂ emissions from year 2000, and projection to year 2020 from four main sectors.

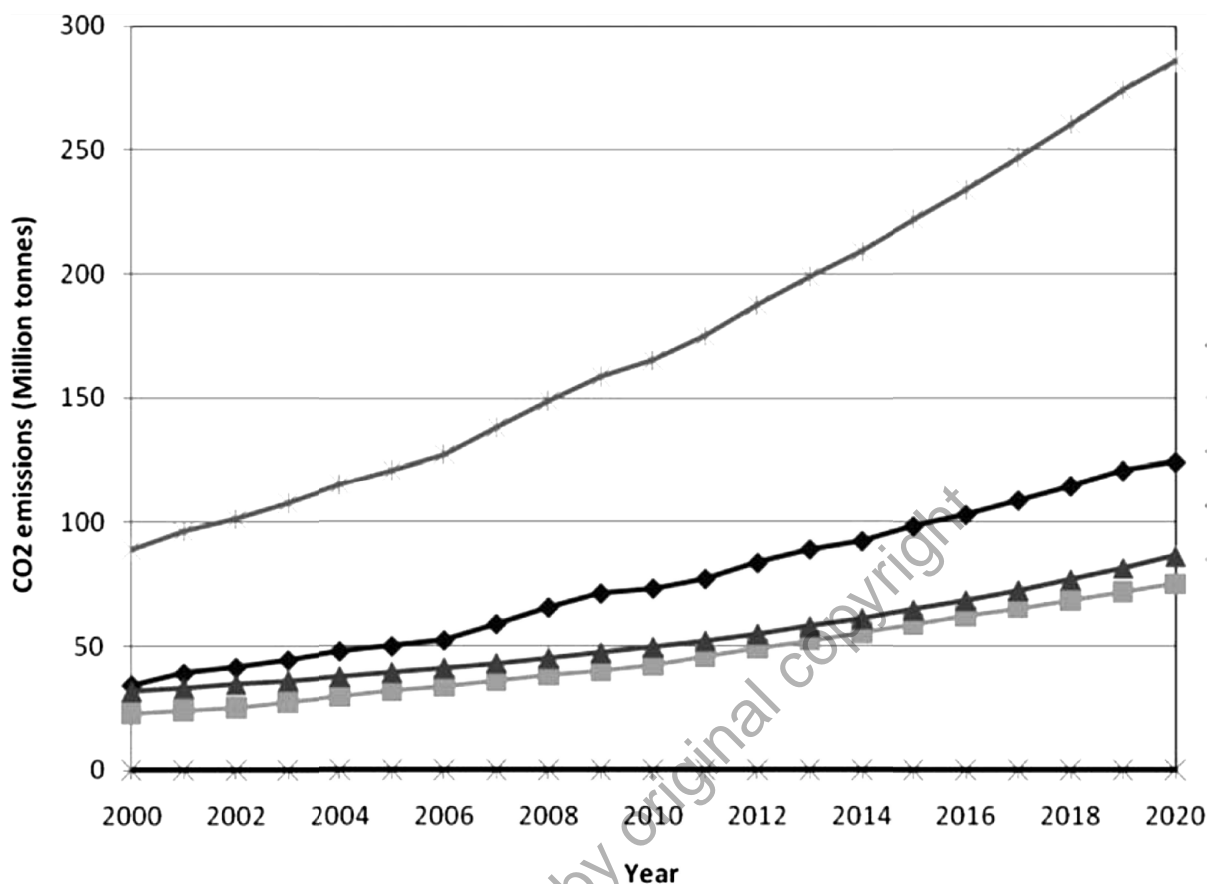


Figure 1.4: CO₂ emissions projection from four main sectors (electricity generation (◆), industrial (■), transportation (▲), and residential(×)) for the period 2000–2020 (Nor Sharliza Md. Safaai, Zainura Zainon Noor, Haslenda Hashim, Zaini Ujang, & Juhaizah Talib, 2010).

Malaysia is projected to contribute 285.73 million tonnes of CO₂ in 2020. Electricity generation will contribute 43.40 % of total CO₂ emission in 2020. More CO₂ will be produced due to the increase in the use of coals in combustion for electricity generation in line with the Five-fuel Diversification Strategy under the Malaysia’s Ninth Plan. The transportation sector will contribute 30.34 % of total emissions in 2020. The industrial sector is projected to contribute 26.26 %. Important industrial contributors include electronics, chemical, and rubber industries. The residential sector is expected to contribute 0.03 % (Nor Sharliza Md. Safaai et al., 2010).

The increase in atmospheric CO₂ must be slowed or reversed to avoid its contribution to the greenhouse effect. One of the ways to overcome this is via application of electrochemical technology. Electrochemical reduction of CO₂ into value-added chemicals utilizes CO₂ that would otherwise be released to the atmosphere. The process can also be used to store excess renewable energy in the reduced form of CO₂.

Electrochemical reduction of CO₂ can be defined as the conversion of CO₂ into its reduced form at the cathode using electrical energy. This work makes use of a 3 electrode system to investigate the reduction process, as well as several important factors that affects it. There are several types of potential cathode material; each will convert CO₂ into a different form or one form at differing efficiencies. Tin (Sn) has been a research interest for its ability to convert CO₂ into its reduced form very efficiently and at a relatively low energy cost (Det Norske Veritas, 2011; Jhong, 2013). However, a complete and exhaustive study for the usage of Sn in electrochemical reduction of CO₂ still does not exist. Researchers often provide conflicting reports on the role of hydrogen ion [H⁺]; some believe it to be detrimental to the CO₂ reduction process while others think it is beneficial. Cathode degradation also has been reported by various researchers in literature but however, disagreement as to the cause of the degradation also exists. This study addresses this information void by providing a clearer and correct picture of the electrochemical process.

1.3 Aims

This study aims to shed light on the potential of Sn as a selective cathode material in electrochemically reducing CO_2 into HCOO^- as well as the effects of selected important variables such as cathode rotating speed, applied cathode potential and electrolyte's pH that affects the process. It should form the basis for future, more detailed work that will fine tune operating conditions to optimally reduce CO_2 into HCOO^- .

1.4 Objectives

This study has 3 objectives:

1.4.1 To characterize the electrochemical behavior of Sn plated electrode via electrochemical deposition onto glassy carbon electrode.

1.4.2 To analyze effects of cathode rotating speed, applied cathode potential, and electrolyte's pH on the Faradaic efficiency for HCOO^- production from the reduction of CO_2 .

1.4.3 To study the current degradation of the developed Sn electrode during the electrochemical reduction of CO_2 as a function of time.

1.5 Scope

In this research, Sn is deposited onto a glassy carbon electrode by electrolysis in acidic plating solution. The plating solution is prepared in accordance to that described in the work of Lv, Zhang, Gao, & Lei (2014). The prepared electrode is then rotated

under water and subjected to a cyclic voltammetry (CV) test. Since Sn electrode degrades during CV and cannot be reused, the remaining Sn is stripped off and re-deposited using fresh acidic plating solution for each test. The electrodes are also inspected for visual defect or damage. Electrodes must provide stable, and predictable CVs, and are at least superficially even. When this is achieved, it is assumed that the Sn electrodes are produced in a reliable and reproducible manner. Electrodes used in electrolysis are prepared in the same manner, but not tested for stability to avoid deterioration. Cyclic voltammetry is carried out to ascertain the potential where CO_2 is reduced into HCOO^- . HCOO^- is then produced by applying a fixed potential SCE in a CO_2 saturated electrolyte using the Sn plated electrode. The HCOO^- yield is measured using high performance liquid chromatography. Other possible reduction products such as CO and H_2 are not measured explicitly. The amounts of HCOO^- produced under differing operating conditions are used as a measure to examine the effect of each variable on the reduction process. The current degradation of the developed Sn electrode is used as a measure of the Sn degradation with time during electrochemical reduction.

1.6 Significance

The results from this project will reinforce understanding on the potential of Sn as a selective cathode material in electrochemically reducing CO_2 into HCOO^- . The roles of several selected variables will also be made clearer for the benefit of future studies. Future studies will also be made aware of the Sn degradation with time during electrochemical reduction.

CHAPTER 2

LITERATURE REVIEW

This chapter discusses the previous studies on electrochemical reduction of CO₂, the mechanism of CO₂ adsorption onto the Sn surface to form CO₂, CO₂ transport to the Sn surface by catholyte flow, the importance of an aqueous component to HCOO⁻ formation, separation between the catholyte and anolyte, as well as deactivation of the working electrode.

2.1 Electrochemical Reduction of CO₂

The CO₂ molecule must first go through a difficult and energy consuming step, receiving an electron, e⁻ to form the CO₂^{·-} radical. This reaction is the rate limiting of the electrochemical reduction process. The CO₂^{·-} then receives a proton, H⁺ from water (H₂O) to form the radical HCOO[·]. The HCOO[·] may then receive another e⁻ to complete its electron pair and gain a negative charge to form HCOO⁻ (Hori, 2008). Equations 2.1, 2.2, and 2.3 explain the reduction process of CO₂ into HCOO⁻.

