ELECTROCHEMICALLY ASSISTED ORGANOSOL METHOD FOR NANO-PARTICLE DEPOSITION ON THREE-DIMENSIONAL ELECTRODES: APPLICATION FOR ETHANOL OXIDATION

by

DEREK ROGER LYCKE

B.A.Sc., University of Waterloo, 1999

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF APPLIED SCIENCE in

THE FACULTY OF GRADUATE STUDIES

Chemical and Biological Engineering

THE UNIVERSITY OF BRITISH COLUMBIA

December 2005

© Derek Roger Lycke, 2005
Abstract

The proton exchange membrane direct ethanol fuel cell (PEM DEFC) combines the beneficial properties of ethanol (i.e. low toxicity, high energy density and wide availability) with the theoretically high efficiency of electrochemical energy conversion but is challenged by poor anodic reaction kinetics, ethanol crossover, and CO₂ disengagement. A three-dimensional anode can mitigate these challenges by extending the reaction zone and more readily disengaging CO₂.

In the present work, the Bönnemann colloidal metal deposition method is extended to three-dimensional substrates (e.g. graphite felt) by conducting colloidal formation and deposition concurrently under the application of an electric field (e.g. 1.25 mA cm⁻² and 2 V) with the three-dimensional substrate serving as the cathode. The modified methods are primarily electrophoretic coupled with chemical reduction; however, faradaic effects (i.e. electrodeposition) are still apparent. Particle size, catalyst deposit composition, and loading are dependent on the reactant that is first allowed to electrophoretically adsorb to the substrate (i.e. reducing surfactant [N(C₇H₁₇)₄B(C₂H₅)₃H] or metal salt). Various Pt:Sn (an established ethanol electrocatalyst) ratios are studied. The 9:1 bulk atomic ratio produced the most active catalyst deposit measured by cyclic voltammetry, chronopotentiometry and chronoamperometry for both the surfactant and metal adsorption variants. Surfactant adsorption results in reduced particle size (3 - 10 versus 5 - 43 nm), loadings (0.44 versus 0.96 mg cm⁻²) and Pt:Sn catalyst ratios (3.1:1 versus 3.9:1). Active catalyst surface area, measured by copper underpotential deposition and stripping, is higher for the surfactant adsorption variant (98.0 versus 73.2 cm² catalyst cm⁻² substrate), whereas the surface Pt:Sn ratio is higher for the metal adsorption variant (7.7:1 versus 3.1:1). On an area basis, the metal adsorption variant outperforms the surfactant adsorption variant in half cell electrochemical testing.

Fuel cell tests of the 3-dimensional anodes show promising levels of activity when 0.5 M H₂SO₄ is added to the ethanol feed for protonic conductivity. The metal adsorption variant produces higher power densities on an area basis (e.g. 7.0 versus 2.0 mW cm⁻² at 30 mA cm⁻² ); however the surfactant adsorption variant performs better on a mass activity basis (e.g. 10.0 versus 8.7 mW mg⁻¹ at 30 mA mg⁻¹ ). This mass activity is comparable to literature data reported for the traditional, gas diffusion, Pt-Sn anode at substantially higher catalyst loads (i.e. 2.0 versus 0.44 mg cm⁻²).

In addition to fuel cell use, nano-catalyst deposited on three dimensional electrodes can be used for other applications, such as electrosynthesis.
# Table of Contents

ABSTRACT ........................................................................................................ ii
TABLE OF CONTENTS .................................................................................. iii
LIST OF TABLES .............................................................................................. vi
LIST OF FIGURES ............................................................................................ vii
NOMENCLATURE ............................................................................................. ix
ABBREVIATIONS .............................................................................................. xi
ACKNOWLEDGEMENT ..................................................................................... xi

1.0 INTRODUCTION ......................................................................................... 1

2.0 THEORETICAL BACKGROUND ......................................................................... 8
  2.1 ELECTROCHEMICAL THERMODYNAMICS .................................................... 8
  2.2 ELECTRODE KINETICS ............................................................................... 10
  2.3 FUEL CELL ELECTRODE DESIGN ................................................................ 13
  2.4 EXPERIMENTAL METHODS FOR ELECTRODE KINETIC STUDIES .............. 14
      2.4.1 Reference Electrodes ............................................................................ 15
      2.4.2 Cyclic voltammetry ............................................................................. 16
      2.4.3 Chronopotentiometry .......................................................................... 17
      2.4.4 Chronoamperometry .......................................................................... 18
      2.4.5 Surface Area Analysis ....................................................................... 20

3.0 OBJECTIVES ............................................................................................... 22

4.0 LITERATURE REVIEW ................................................................................ 24
  4.1 ETHANOL ELECTRO-OXIDATION ............................................................... 24
  4.2 PREPARATION OF NANO-PARTICULATE CATALYST .................................... 29
      4.2.1 Electrodeposition Techniques ............................................................... 30
      4.2.2 Sol-Gel Technique .............................................................................. 31
      4.2.3 Impregnation Methods ....................................................................... 33
      4.2.4 The Polyl Process ............................................................................... 33
      4.2.5 Protective Shell Colloids ................................................................... 34
      4.2.6 Summary ............................................................................................. 38

5.0 EXPERIMENTAL METHODS ......................................................................... 39
  5.1 ELECTRODE MATERIAL ............................................................................ 39
  5.2 SUBSTRATE PRETREATMENTS .................................................................... 39
      5.2.1 Pd nucleation ...................................................................................... 39
      5.2.2 Nitric acid oxidation ........................................................................... 40
  5.3 CATALYST DEPOSITIONS ........................................................................... 40
      5.3.1 Preparation of tetraoctylammonium triethylborohydride \( \text{N} \left( \text{C}_8 \text{H}_{17} \right)_4 \text{B} \left( \text{C}_2 \text{H}_5 \right)_3 \text{H} \) .................................................. 40
      5.3.2 The Binnemans colloid preparation method and deposition on 3-D substrates ............................................................... 42
      5.3.3 Electrochemically mediated colloidal metal deposition on 3-D substrates ............................................................... 45
  5.4 HEAT TREATMENT .................................................................................... 48
  5.5 CHARACTERIZATION OF NANO-PARTICULATE DEPOSITED CATALYST ........ 50
      5.5.1 Particle Size by Electron Microscopy ................................................... 50
      5.5.2 EDX ..................................................................................................... 51
      5.5.3 ICP-OES ............................................................................................. 52
Page intentionally left blank.
List of Tables

| Table 1-1: Fuel Cell Types | .......................................................................................................................... 2 |
| Table 5-1: Physical Characteristics of Graphite Felt | .......................................................................................................................... 39 |
| Table 6-1: Deposited Pt:Sn Ratios and Estimated Loadings on Catalysts - Electrochemically Mediated Colloidal Metal Deposition at Various Applied Current Densities | .......................................................................................................................... 69 |
| Table 6-2: Deposited Pt:Sn Ratios and Estimated Loadings on Catalysts - Electrochemically Mediated Colloidal Metal Deposition at Various Deposition Times | .......................................................................................................................... 71 |
| Table 6-3: Measured Reagent Quantities for Preparation of Pt-Sn Catalyst | .......................................................................................................................... 76 |
| Table 6-4: Quantitative Features of Cyclic Voltammetry Forward Scans Featured in Figure 6-9 | .......................................................................................................................... 78 |
| Table 6-5: Estimated Loadings on Catalysts Prepared - Electrochemically Mediated Colloidal Metal Deposition (Surfactant Adsorption) with Various Bulk Pt:Sn Ratios | .......................................................................................................................... 82 |
| Table 6-6: Deposited Ternary Catalyst Ratios Determined by EDX | .......................................................................................................................... 87 |
| Table 6-7: Deposited Pt:Sn Ratios Determined by EDX on Catalysts Deposited on Pd Nucleated Felt | .......................................................................................................................... 91 |
| Table 6-8: Deposited Pt:Sn Ratios Determined by EDX on Catalysts - Electrochemically Mediated Colloidal Metal Deposition (Surfactant and Metal Adsorption Variants) | .......................................................................................................................... 98 |
| Table 6-9: Tafel Slope and Exchange Current Densities - Surfactant Adsorption Variant | .......................................................................................................................... 116 |
| Table 6-10: Tafel Slope and Exchange Current Densities - Metal Adsorption Variant | .......................................................................................................................... 118 |
| Table 6-11: Maximum Power Density from Power Curves Featured in Figures 6-44 and 6-45 | .......................................................................................................................... 126 |
| Table 6-12: Comparison of 3-Dimensional Anode Fuel Cell to Conventional MEA Study | .......................................................................................................................... 126 |
# List of Figures

**Figure 1-1:** Schematic of a direct ethanol fuel cell .................................................. 6
**Figure 2-1:** Conventional membrane electrode assembly (MEA) design .......................... 13
**Figure 2-2:** Three electrode setup for electrochemical testing ...................................... 15
**Figure 2-3:** Cyclic voltammetry response signals ......................................................... 16
**Figure 2-4:** Chronopotentiometry response signals ........................................................ 18
**Figure 2-5:** Chronoamperometry response signals ............................................................ 19

**Figure 3-1:** Proposed MEA design utilizing a three dimensional electrode .......................... 22
**Figure 3-2:** Three dimensional electrode materials and their approximate thicknesses ............. 23

**Figure 4-1:** Effects of the addition of Ru to Pt based catalysts on methanol and ethanol electro-oxidation .................................................. 26
**Figure 4-2:** Effects of the addition of Sn and Ru to Pt based catalysts for ethanol electro-oxidiation .................................................. 28
**Figure 4-3:** Preparation of sol-gel particles and coatings ................................................. 32
**Figure 4-4:** Bönnemann adsorbed colloid with protective shell ....................................... 36
**Figure 4-5:** Electrochemical formation of N(C$_8$H$_7$)$_4$Cl stabilized nanometals ............ 37

**Figure 5-1:** Tetracylamonium triethylhydroborate production ........................................ 41
**Figure 5-2:** Bönnemann metal colloid formation ............................................................... 43
**Figure 5-3:** Bönnemann colloid deposition on the 3-D carbon substrate ............................. 44
**Figure 5-4:** Preparation of metal salt suspension for electrochemical mediated colloidal metal depositions .................................................. 46

**Figure 5-5:** Schematic of electrochemically mediated colloidal metal deposition on 3-dimensional substrates .................................................. 47
**Figure 5-6:** Stainless steel tubular reactor ................................................................. 49
**Figure 5-7:** Carbon substrate prepared for EDX measurements ..................................... 52
**Figure 5-8:** Electrochemical cell .................................................................................. 54
**Figure 5-9:** Mounted working electrode ................................................................. 55
**Figure 5-10:** Reference voltammogram used to verify catalyst cleanness .......................... 56
**Figure 5-11:** Direct methanol fuel cell test station ......................................................... 60
**Figure 5-12:** Fuel cell components .............................................................................. 61
**Figure 5-13:** Fuel cell reagent delivery ................................................................. 62

**Figure 6-1:** Electro-oxidation of ethanol on Pt$_2$Sn catalyst - Bönnemann method ............ 66
**Figure 6-2:** Electro-oxidation of ethanol at various scan rates on Pt$_2$Sn catalyst - Bönnemann method .................................................. 66
**Figure 6-3:** Diffusion control in ethanol electro-oxidation on Pt$_2$Sn catalyst - Bönnemann method .................................................. 67
**Figure 6-4:** Electro-oxidation of ethanol on Pt$_2$Sn catalyst - electrochemically mediated colloidal metal deposition at various applied current densities .................................................. 69
**Figure 6-5:** Electro-oxidation of ethanol on Pt-Sn catalyst - electrochemically mediated colloidal metal deposition with various deposition times .................................................. 71
**Figure 6-6:** Particle size - electrochemically mediated colloidal metal deposition (surfactant adsorption) .................................................. 73

**Figure 6-7:** Effect of time delay between the application of deposition current and the addition of metal salt .................................................. 74
**Figure 6-8:** Schematic of electrochemically mediated colloidal metal formation and deposition .................................................. 75
**Figure 6-9:** Electro-oxidation of ethanol on Pt-Sn catalyst - electrochemically mediated colloidal metal deposition (surfactant adsorption) at various bulk Pt:Sn metal salt ratios .................................................. 77
**Figure 6-10:** Electro-oxidation of ethanol (first scan) on Pt-Sn catalyst - electrochemically mediated colloidal metal deposition (surfactant adsorption) .................................................. 79
FIGURE 6-11: RELATIONSHIP BETWEEN Pt:Sn RATIOS IN THE CATALYST DEPOSIT VERSUS BULK CONDITIONS ........................................... 80
FIGURE 6-12: ELECTRO-OXIDATION OF ETHANOL ON Pt-Sn CATALYST - ELECTROCHEMICALLY MEDIATED COLLOIDAL METAL FORMATION (SURFACTANT ADSORPTION) AT VARIOUS EXPERIMENTAL SCALES .............. 83
FIGURE 6-13: ELECTRO-OXIDATION OF ETHANOL ON Pt-Sn CATALYST - ELECTROCHEMICALLY MEDIATED COLLOIDAL METAL DEPOSITION (SURFACTANT ADSORPTION) AT VARIOUS DEPOSITION CURRENT DENSITIES ........................................ 84
FIGURE 6-14: ELECTRO-OXIDATION OF ETHANOL ON TERNARY CATALYSTS - ELECTROCHEMICALLY MEDIATED COLLOIDAL METAL DEPOSITION (SURFACTANT ADSORPTION) ........................................ 86
FIGURE 6-15: ELECTRO-OXIDATION OF ETHANOL ON Pt-Sn CATALYST - ELECTRODEPOSITION IN ORGANIC MEDIA ........................................ 89
FIGURE 6-16: ELECTRO-OXIDATION OF ETHANOL ON Pt-Sn CATALYST - ELECTROCHEMICALLY MEDIATED COLLOIDAL METAL DEPOSITION (SURFACTANT ADSORPTION) ON Pd NUCLEATED FELT ......................... 90
FIGURE 6-17: ELECTRO-OXIDATION OF ETHANOL ON Pt-Sn CATALYST - ELECTROCHEMICALLY MEDIATED COLLOIDAL METAL DEPOSITION (SURFACTANT ADSORPTION) ON Sn SENSITIZED FELT ........................................ 92
FIGURE 6-18: ELECTRO-OXIDATION OF ETHANOL ON Pt-Sn CATALYST - ELECTROCHEMICALLY MEDIATED COLLOIDAL METAL DEPOSITION (SURFACTANT ADSORPTION) ON NITRIC ACID TREATED FELT .... 93
FIGURE 6-19: ELECTRO-OXIDATION OF ETHANOL ON Pt-Sn CATALYST - ELECTROCHEMICALLY MEDIATED COLLOIDAL METAL DEPOSITION (SURFACTANT AND METAL ADSORPTION) ........................................ 96
FIGURE 6-20: ELECTRO-OXIDATION OF ETHANOL ON Pt-Sn CATALYST - ELECTROCHEMICALLY MEDIATED COLLOIDAL METAL DEPOSITION (SURFACTANT AND METAL ADSORPTION) AT VARIOUS TEMPERATURES ......................... 100
FIGURE 6-21: CHRONOPOTENTIOMETRY ON Pt-Sn CATALYST - ELECTROCHEMICALLY MEDIATED COLLOIDAL METAL DEPOSITION (SURFACTANT AND METAL ADSORPTION) ........................................ 103
FIGURE 6-22: PARTICLE SIZE - ELECTROCHEMICALLY MEDIATED COLLOIDAL METAL DEPOSITION (METAL ADSORPTION) ........................................ 104
FIGURE 6-23: ELECTRO-OXIDATION OF ETHANOL ON Pt-Sn CATALYST - ELECTROCHEMICALLY MEDIATED COLLOIDAL METAL DEPOSITION (METAL ADSORPTION) AT VARYING CONDITIONS ........................................ 107
FIGURE 6-24: CHRONOPOTENTIOMETRY ON Pt-Sn CATALYST - THE ELECTROCHEMICALLY MEDIATED COLLOIDAL METAL DEPOSITION (METAL ADSORPTION) WITH VARYING DEPOSITION CURRENT DENSITIES ........................................ 108
FIGURE 6-25: REPRODUCIBILITY IN ELECTRO-OXIDATION OF ETHANOL ON Pt-Sn CATALYST - ELECTROCHEMICALLY MEDIATED COLLOIDAL METAL DEPOSITION (SURFACTANT ADSORPTION) ........................................ 109
FIGURE 6-26: REPRODUCIBILITY IN ELECTRO-OXIDATION OF ETHANOL ON Pt-Sn CATALYST - ELECTROCHEMICALLY MEDIATED COLLOIDAL METAL DEPOSITION (METAL ADSORPTION) ........................................ 112
FIGURE 6-27: EFFECT OF HEAT TREATMENT ON THE ELECTRO-OXIDATION OF ETHANOL ON Pt-Sn CATALYST ........................................ 113
FIGURE 6-28: Cu UPD AND BULK DEPOSITION ON Sn CATALYST ........................................ 114
FIGURE 6-29: Cu UPD STRIPPING FROM Sn CATALYST ........................................ 115
FIGURE 6-30: Cu UPD AND Cu BULK DEPOSITION ON Pt-Sn CATALYST (SURFACTANT ADSORPTION VARIANT) ........................................ 116
FIGURE 6-31: Cu UPD STRIPPING FROM Pt-Sn CATALYST (SURFACTANT ADSORPTION VARIANT) ........................................ 117
FIGURE 6-32: Cu UPD STRIPPING FROM Pt-Sn CATALYST (METAL ADSORPTION VARIANT) ........................................ 118
FIGURE 6-33: ELECTRO-OXIDATION OF ETHANOL ON Pt-Sn CATALYST - ELECTROCHEMICALLY MEDIATED COLLOIDAL METAL DEPOSITION (SURFACTANT ADSORPTION) AT VARIOUS TEMPERATURES ........................................ 119
FIGURE 6-34: CHRONOPOTENTIOMETRY ON Pt-Sn CATALYST - ELECTROCHEMICALLY MEDIATED COLLOIDAL METAL DEPOSITION (SURFACTANT ADSORPTION) AT VARIOUS TEMPERATURES ........................................ 120
FIGURE 6-35: CHRONOPOTENTIOMETRY ON Pt-Sn CATALYST - ELECTROCHEMICALLY MEDIATED COLLOIDAL METAL DEPOSITION (METAL ADSORPTION VARIANT) AT VARIOUS TEMPERATURES ........................................ 121
FIGURE 6-36: CHRONOAMPEROMETRY ON Pt-Sn CATALYST - SURFACTANT ADSORPTION ........................................ 122
FIGURE 6-37: TAFL PLOTS FOR Pt-Sn CATALYST - SURFACTANT ADSORPTION ........................................ 123
FIGURE 6-38: TAFL PLOTS FOR Pt-Sn CATALYST - METAL ADSORPTION ........................................ 124
FIGURE 6-39: TAFL PLOT FOR Pt-Sn CATALYST - METAL ADSORPTION ........................................ 125
FIGURE 6-40: ELECTRO-OXIDATION OF ETHANOL - METAL ADSORPTION ON VARIOUS SUBSTRATES ........................................ 126
FIGURE 6-41: CHRONOPOTENTIOMETRY - METAL ADSORPTION ON VARIOUS SUBSTRATES ........................................ 127
FIGURE 6-42: DEFC PERFORMANCE - SURFACTANT ADSORPTION VARIANT ........................................ 128
FIGURE 6-43: DEFC PERFORMANCE - METAL ADSORPTION VARIANT ........................................ 129
FIGURE 6-44: DEFC PERFORMANCE WITH 0.5 M H2SO4 - SURFACTANT ADSORPTION VARIANT ........................................ 130
FIGURE 6-45: DEFC PERFORMANCE WITH 0.5 M H2SO4 - METAL ADSORPTION VARIANT ........................................ 131
FIGURE 6-46: DEFC PERFORMANCE - COMPARISON TO TRADITIONAL GDL ANODE ........................................ 132

FIGURE 8-1: PROPOSED FUEL CELL ANODE FLOW FIELD DESIGN ........................................ 133
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>ai</td>
<td>chemical activity</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>Tafel slope</td>
<td>mV dec⁻¹</td>
</tr>
<tr>
<td>C_b</td>
<td>fuel concentration in bulk feed</td>
<td>M</td>
</tr>
<tr>
<td>C_s</td>
<td>fuel concentration at electrode surface</td>
<td>M</td>
</tr>
<tr>
<td>d</td>
<td>interelectrode gap</td>
<td>cm</td>
</tr>
<tr>
<td>D_l</td>
<td>diffusion coefficient</td>
<td>cm² s⁻¹</td>
</tr>
<tr>
<td>E_e</td>
<td>equilibrium cell potential</td>
<td>V</td>
</tr>
<tr>
<td>E⁰</td>
<td>standard cell potential (T = 298 K, a = 1)</td>
<td>V</td>
</tr>
<tr>
<td>F</td>
<td>Faraday’s constant (96485)</td>
<td>C mol⁻¹</td>
</tr>
<tr>
<td>i</td>
<td>current density</td>
<td>mA cm⁻²</td>
</tr>
<tr>
<td>I</td>
<td>cell current</td>
<td>mA</td>
</tr>
<tr>
<td>i_L</td>
<td>limiting current density</td>
<td>mA cm⁻²</td>
</tr>
<tr>
<td>i_o</td>
<td>exchange current density</td>
<td>mA cm⁻²</td>
</tr>
<tr>
<td>M</td>
<td>electrochemical species</td>
<td>-</td>
</tr>
<tr>
<td>n</td>
<td>number of electrons exchanged per mol of fuel</td>
<td>-</td>
</tr>
<tr>
<td>n*</td>
<td>number of electrons exchanged in a single charge transfer step</td>
<td>-</td>
</tr>
<tr>
<td>P</td>
<td>power density</td>
<td>mW cm⁻²</td>
</tr>
<tr>
<td>R</td>
<td>ideal gas constant (8.314)</td>
<td>J mol⁻¹ K⁻¹</td>
</tr>
<tr>
<td>s_i</td>
<td>stoichiometric coefficient</td>
<td>K</td>
</tr>
<tr>
<td>T</td>
<td>temperature</td>
<td>s</td>
</tr>
<tr>
<td>t</td>
<td>time</td>
<td>cm</td>
</tr>
<tr>
<td>α_a</td>
<td>anodic charge transfer coefficient</td>
<td></td>
</tr>
<tr>
<td>α_c</td>
<td>cathodic charge transfer coefficient</td>
<td></td>
</tr>
<tr>
<td>δ</td>
<td>diffusion layer thickness</td>
<td></td>
</tr>
<tr>
<td>ΔG⁰</td>
<td>standard system Gibbs free energy change (T = 273 K, a = 1 atm)</td>
<td>J mol⁻¹</td>
</tr>
<tr>
<td>ΔS⁰</td>
<td>standard system entropy change (T = 273 K, P = 1 atm)</td>
<td>J mol⁻¹ K⁻¹</td>
</tr>
<tr>
<td>Δφ_{ohm}</td>
<td>ohmic drop</td>
<td>V</td>
</tr>
<tr>
<td>η</td>
<td>overpotential</td>
<td>V</td>
</tr>
<tr>
<td>η_{c}</td>
<td>concentration overpotential</td>
<td>V</td>
</tr>
<tr>
<td>η_{s}</td>
<td>surface (kinetic) overpotential</td>
<td>V</td>
</tr>
</tbody>
</table>
## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAL</td>
<td>acetaldehyde</td>
</tr>
<tr>
<td>AFC</td>
<td>alkaline fuel cell</td>
</tr>
<tr>
<td>CA</td>
<td>chronoamperometry</td>
</tr>
<tr>
<td>CP</td>
<td>chronopotentiometry</td>
</tr>
<tr>
<td>CV</td>
<td>cyclic voltammetry</td>
</tr>
<tr>
<td>DAFC</td>
<td>direct alcohol fuel cell</td>
</tr>
<tr>
<td>DEFC</td>
<td>direct ethanol fuel cell</td>
</tr>
<tr>
<td>DMFC</td>
<td>direct methanol fuel cell</td>
</tr>
<tr>
<td>EDX</td>
<td>energy dispersive x-ray</td>
</tr>
<tr>
<td>GDE</td>
<td>gas diffusion electrode</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>inductively coupled plasma optical emission spectroscopy</td>
</tr>
<tr>
<td>MCFC</td>
<td>molten carbonate fuel cell</td>
</tr>
<tr>
<td>MEA</td>
<td>membrane electrode assembly</td>
</tr>
<tr>
<td>MSE</td>
<td>mercury – mercurous sulphate reference electrode</td>
</tr>
<tr>
<td>PAFC</td>
<td>phosphoric acid fuel cell</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>SHE</td>
<td>standard hydrogen electrode</td>
</tr>
<tr>
<td>SOFC</td>
<td>solid oxide fuel cell</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>UPD</td>
<td>underpotential deposition</td>
</tr>
</tbody>
</table>
Acknowledgement

This thesis would not have been possible without the support of many people. I am highly indebted to my supervisor, Dr. Előd Gyenge, for his continued assistance in working me through the many revisions of this written work, and continually encouraging me to challenge myself throughout the duration of my studies. He has taught me skills that will last a lifetime. I offer my gratitude to my friends and group members Alex Bauer, Tommy Cheng, Jonghyun Choi and Mohammed Atwan for their contributions to the laboratory and the many experiments that define this work. Many thanks to Horace Lam and the staff of the Chemical & Biological Engineering Stores and Workshop for all their assistance in delivering supplies and equipment often on short notice. I also give special thanks to the Natural Sciences and Engineering Research Council of Canada for financially supporting me over these two years. Finally I would like to express my deepest gratitude to my parents Roger and Maria Lycke, as well as my sisters Andrea, Brenda and Jenny, and many friends for supporting and encouraging me with my decision to return to school. I couldn’t have completed this without you.
1.0 Introduction

Human survival and technological advancement depends on the need for a continuing energy supply; however, increasing global demand for energy presents a problem. In the age of rising oil costs, much attention is focused on when global fossil fuel production will begin to peak and eventually diminish. Although there is no clear consensus on when this may occur, it is generally acknowledged that fossil fuels are in finite supply and eventually the global economy will need to shift emphasis from the use of traditional fossil fuels towards a mix of sustainable energy sources (Dell and Rand, 2004). A sustainable energy source, by definition, meets needs of the present without compromising the ability of future generations (Brundtland, 1987). It is believed that no one source of sustainable energy will dominate the energy market, as fossil fuels do today. Therefore research is progressing in a variety of areas including hydroelectric, solar, wind, and geothermal based renewables as well as bio-fuels, such as ethanol (Gosselink, 2002). Establishing sustainable energy sources; however, is only one piece of the solution. In parallel to this research, a need exists to find energy carriers, capable of storing and transporting the energy, and efficient means by which to convert this energy to a usable form, such as electricity. For these reasons, a large commitment has been made to fuel cell technology and advancement in recent years.

A fuel cell is an electrochemical system that continuously converts the chemical energy of a fuel and an oxidant directly into electrical energy and heat with high theoretical thermodynamic efficiency (e.g. 99%+ for \( \text{H}_2/\text{O}_2 \) systems, 97% for ethanol/\( \text{O}_2 \) systems at 298 K). The fuel cell is essentially comprised of two electrodes separated by an electrolyte, which serves to conduct ions, and generates electricity by means of electrochemical reactions. Unlike a battery, however, a fuel cell is an energy conversion system and does not store energy. A fuel cell requires a constant supply of fuel to the anode, and oxidant to the cathode, in order to produce electricity.

A variety of fuel cell types exist and are primarily classified by the type of electrolyte they employ. The nature of the electrolyte determines what kind of reactions take place in the fuel cell, which types of catalysts and fuels can be used, and what conditions (e.g. temperature and pressure) the fuel cell will normally operate at. All these factors combined determine which applications are appropriate for the fuel cell type. A summary of major fuel cell types and characteristics is included in Table 1-1.
Table 1-1: Fuel cell types (Source: US Department of Energy- Hydrogen, Fuel Cells & Infrastructure Technologies Program)

<table>
<thead>
<tr>
<th>Fuel Cell Type</th>
<th>Electrolyte</th>
<th>Temperature (°C)</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaline Fuel Cell (AFC)</td>
<td>Aqueous potassium hydroxide soaked in a matrix</td>
<td>90 – 100</td>
<td>Military, space</td>
</tr>
<tr>
<td>Phosphoric Acid Fuel Cell (PAFC)</td>
<td>Liquid phosphoric acid soaked in a matrix</td>
<td>175 - 200</td>
<td>Electric utility, transportation</td>
</tr>
<tr>
<td>Molten Carbonate Fuel Cell (MCFC)</td>
<td>Liquid lithium/sodium/potassium carbonates soaked in a matrix</td>
<td>600 – 1000</td>
<td>Electric utility</td>
</tr>
<tr>
<td>Solid Oxide Fuel Cell (SOFC)</td>
<td>Solid zirconium oxide matrix laced with yttria</td>
<td>600 – 1000</td>
<td>Electric utility</td>
</tr>
<tr>
<td>Polymer Electrolyte Membrane Fuel Cell (PEMFC)</td>
<td>Solid polymer perfluorosulphonic acid</td>
<td>60 – 100</td>
<td>Transportation, portable power, electric utility</td>
</tr>
</tbody>
</table>

It is noted in Table 1-1 that the fuel cell types listed can be classified as either low temperature (i.e. AFC, PAFC, PEMFC) or high temperature (i.e. MCFC, SOFC) systems. Low temperature systems hold the advantage of having a faster start up time, and may prove to be more convenient for applications such as portable power or transportation. The primary advantage to operating at higher temperatures is that heat is able to assist the kinetics of the sluggish electrode reactions. Therefore a variety of fuels can be used and potentially less expensive and lower activity catalysts could be employed.

Despite the recent surge in fuel cell technology development, the fuel cell concept has been around for a considerable amount of time. In 1839 Sir William Robert Grove, Welsh inventor and physicist, theorized that if water could be split into hydrogen gas and oxygen by applying electricity in the presence of an electrolyte, the reverse procedure could likely be accomplished. Grove combined hydrogen and oxygen gases in the presence of an electrolyte to produce water and electricity. Unfortunately not enough was known about electricity at the time, and the invention, later known as the “fuel cell”, wasn’t deemed to be useful.

In 1932, Francis T. Bacon, resurrected Grove’s research in fuel cell systems. It took several years for him to perfect his design, but the alkaline electrolyte product eventually proved to be successful. By the early 1960s the US National Aeronautics and Space Administration (NASA) adopted the principles of Bacon’s fuel cell, for use in the manned Apollo space missions program.
Fuel cell technology filled an important niche, and NASA funded numerous contracts exploring fuel cell research (Hoogers, 2003).

The first studies of low temperature PEM fuel cells, the focus of this work, did not occur until several decades after it was demonstrated by Grubb that solid polymer electrolytes held several advantages for use in battery technology (Grubb, 1959). The traditional fuel cell polymer electrolyte membrane (PEM) is a polymer membrane containing sulphonate (-SO\(_3\)H) groups which facilitate H\(^+\) transport through it by ion exchange. The primary advantage of the thin (~50 - 150 \(\mu\)m) electrolyte membrane is that it reduces the ohmic resistance present between the two fuel cell electrodes while affording a compact design. The most commonly used PEM electrolyte is DuPont Corporation’s Nafion®, a copolymer of tetra-fluoroethylene and sulphonyl fluoride vinyl ether. It has been demonstrated that Nafion® provides good protonic conductivity, selective permeability, and good chemical, thermal and mechanical stability (EG & G Services et al., 2000).

PEM fuel cells are being studied to generate electricity for a variety of purposes, where compact systems are favoured, including electric vehicles. Recently, however, the increasing power demand of portable electronics (e.g. laptop computers, cellular phones, digital cameras), has lead researchers to consider the use of fuel cell technology as a battery replacement. Fuel cells hold an advantage here, in that fuel can be continuously supplied to the system and no down time is required to recharge the power source by connecting the system to an electrical grid.

In a traditional PEM fuel cell, the fuel supplied is a hydrogen containing compound (e.g. hydrogen gas, methanol) and the oxidant is an oxygen containing compound or mixture (e.g. oxygen gas, air). Assisted by a catalyst, the fuel generates protons and electrons (among other products) at the anode electrode. Protons travel through the PEM electrolyte, and electrons travel by an external circuit, both to the cathode electrode. Protons, electrons and the oxidant combine, over a catalyst, at the cathode electrode to produce water. The electron current that travels from the anode electrode can be utilized for energy before reaching the cathode and completing the reaction.

By far the most studied fuel for the PEM Fuel Cell has been pure hydrogen gas. Rapid kinetics at the hydrogen fuel cell anode allows higher electrical efficiency to be obtained, relative to other fuel sources. In addition, hydrogen holds the promise of a zero emission fuel, producing only water when oxidized. Hydrogen as a fuel source; however, still has challenges to overcome. Issues exist with production, storage, and handling of the gas (Gosslink, 2002; Takeichi et al., 2003).
Low molecular weight alcohols, such as methanol or ethanol, are a promising alternative as a fuel cell feed source for the PEM fuel cell. The theoretical specific energies of methanol (6.1 kWh L\(^{-1}\)) and ethanol (8.1 kWh L\(^{-1}\)) are comparable to gasoline (10-11 kWh L\(^{-1}\)) and significantly higher than that of compressed hydrogen gas (0.4 kWh L\(^{-1}\) at 150 bar). Additionally their liquid state would make transportation and handling relatively easy. The use of alcohols is, of course, most advantageous in a direct alcohol fuel cell (DAFC), where low molecular weight alcohols are electro-oxidized directly without first reforming to produce hydrogen gas (e.g. steam reforming).

Methanol has been widely studied as a fuel source as it is the simplest primary alcohol. The reactions, and theoretical potentials, that occur in the liquid fed direct methanol fuel cell (DMFC) are shown in equations 1-1 through 1-3.

Anode Reaction:

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \quad E_{298K}^o = -0.02 \text{V SHE} \tag{Eq. 1-1}
\]

Cathode Reaction:

\[
\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O} \quad E_{298K}^o = 1.23 \text{V SHE} \tag{Eq. 1-2}
\]

Net Reaction:

\[
\text{CH}_3\text{OH} + \frac{3}{2}\text{O}_2 \rightleftharpoons \text{CO}_2 + 2\text{H}_2\text{O} \quad E_{298K}^o = 1.21 \text{V SHE} \tag{Eq. 1-3}
\]

Large advancements in catalysis and the operation of the direct methanol fuel cell (DMFC) have been made in the last decade, and the system has a promising future (Zhou et al., 2004). Methanol; however, also has some disadvantages, namely that it is relatively toxic, has a low boiling point (337.9 K), and is not a primary fuel source (i.e. it is largely produced from natural gas).

In parallel with DMFCs, research is starting to progress on the direct ethanol fuel cell (DEFC). Ethanol is safer than methanol, has a higher energy density than methanol and can be readily produced from available biomass. "Bioethanol" is also not believed to disrupt the global carbon balance, as carbon dioxide emitted during ethanol oxidation is absorbed by the plant during growth (Vigier et al, 2004A). This is a definite advantage to its direct use over fossil fuels, or to the reforming of fossil fuels to produce hydrogen gas as a fuel source. The DEFC realizes two
converging paths of opportunity: the use of a renewable energy source, and potentially efficient electricity production.

Within Canada, ethanol is an especially attractive fuel. In 2003, Natural Resources Canada introduced the “Ethanol Expansion Program”. The Ethanol Expansion program is a $100 million funding initiative designed to increase Canada’s annual bio-ethanol production from 245 million litres to nearly 1 billion litres by 2010. This initiative will position Canada to be a global leader in renewable ethanol production.

The reactions, and theoretical potentials, that occur at the both the anode and cathode in the DEFC are given in equations 1-4 through 1-6.

Anode Reaction:

\[ \text{C}_2\text{H}_5\text{OH}_\text{(l)} + 3\text{H}_2\text{O}_\text{(l)} \leftrightarrow 2\text{CO}_2\text{(g)} + 12\text{H}^+\text{(aq)} + 12\text{e}^- \quad E_{298K}^\circ = -0.08\text{V SHE} \quad \text{(Eq. 1-4)} \]

Cathode Reaction:

\[ \text{O}_2\text{(g)} + 4\text{H}^+\text{(aq)} + 4\text{e}^- \leftrightarrow 2\text{H}_2\text{O}_\text{(l)} \quad E_{298K}^\circ = 1.23\text{V SHE} \quad \text{(Eq. 1-5)} \]

Net reaction:

\[ \text{C}_2\text{H}_5\text{OH}_\text{(l)} + 3\text{O}_2\text{(g)} \leftrightarrow 2\text{CO}_2\text{(g)} + 3\text{H}_2\text{O}_\text{(l)} \quad E_{298K}^\circ = 1.14\text{V SHE} \quad \text{(Eq. 1-6)} \]

The process by which ethanol is electro-oxidized directly in the fuel cell is shown schematically in Figure 1-2. In addition to the electrodes and catalyst layers, Figure 1-1 depicts gas diffusion layers on both the anode and cathode side of the cell. Gas diffusion layers aid in the delivery/disengagement of reactants/products from the catalyst layer.
As with the PEM DMFC, the PEM DEFC system faces several challenges not normally associated with the traditional PEM H₂/O₂ system. The most important of these challenges include poor anodic reaction kinetics, ethanol crossover, and CO₂ product disengagement.

Although other noble metals, such as Au (Tremiliosi-Filho et al., 1998), have been proposed as primary catalysts, activity remains low and Pt has been shown to be the only stable catalyst viable for the direct oxidation of ethanol (Zhou et al, 2004). It has been demonstrated that Pt is capable of breaking the C – H bonds as well as the C – C bond in ethanol (Vigier et al, 2004B). Platinum; however, is readily poisoned by CO and CO – like intermediates of ethanol oxidation, lowering the oxidation rate (Zhou et al, 2003; Lamy et al, 2003; Vigier et al, 2004A).

The phenomenon of fuel crossover has been documented to be problematic in both the DMFC and DEFC, although in the case of the latter it has not been widely studied (Song et al, 2005). Fuel crossover occurs because ethanol is soluble in the Nafion® electrolyte membrane, and is able to diffuse from the anode, where it is delivered, to the cathode. In fact, the diffusivity of ethanol in Nafion® is comparable with that of water (10⁻⁴ – 10⁻⁷ cm² s⁻¹), and the properties of Nafion® do little to stop ethanol diffusion (Gong et al., 2001). At the cathode, ethanol can react directly with
oxygen, without producing electricity, establishing a mixed potential between oxygen reduction and ethanol oxidation. For a Pt based cathode it is also likely that ethanol, and reaction by-products of ethanol, can poison the cathode catalyst.

The simplest way to reduce fuel crossover is to increase pressure on the cathode side of the cell, which in turn limits the diffusion of aqueous ethanol across the membrane. Recently, however, several innovative membrane designs have been proposed for the DMFC that could also help combat the problem for the DEFC. These designs largely focus on chemical modification of the membrane by polymer crosslinking to reduce alcohol permeability (Wycisk et al, 2005) or creation of multilayered membranes that contain methanol barriers, such as Nafion-poly(vinylidene) fluoride (Youngchao et al, 2004) or sulphonated poly(etheretherketone) (Yang and Manthiram, 2004), on the cathode side. It is likely; however, that both of these approaches come at the loss of some protonic conductivity. Another novel approach, involves providing void spaces in the membrane to collect diffused methanol. The collected methanol can be physically removed or removed electrochemically by inclusion of a catalyst layer in the void space (Salinas et al, 1999), the latter approach works to effectively provide an extended reaction zone for the slow reacting methanol.

Finally, as carbon dioxide is produced in the anode compartment of the DEFC, pressure will build up in the compartment and gas that adheres to the surface of the electrode will block active catalyst sites (Prentice, 1991), lowering oxidation rates in much the same way as catalyst poisoning. Due to these concerns, CO$_2$ will typically need to be removed from the re-circulating fuel stream using a separation system, such as membranes (Malhotra, 2005) or adsorbers (Okuyama and Normura, 2003), both of which have been proposed for the DMFC. Improved disengagement of CO$_2$ from the anode using effective gas diffusion layers (Argyropoulos et al, 1999), or porous anode electrodes (Allen et al, 2005) have also been discussed, both again for the DMFC.
2.0 Theoretical Background

2.1 Electrochemical thermodynamics

Every electrochemical system is comprised of two electrodes (anode and cathode), where reactions occur, an electrolyte for ionic conduction, and an external conductor to allow electron flow. As a result, any measurements conducted on a single electrode must also involve a second electrode to complete the circuit, and it follows that the potential of any electrode must be measured against a second electrode. The international standard to which all electrochemical half cell systems are measured against is the standard hydrogen electrode. The reaction which occurs in the standard hydrogen electrode (SHE) is shown in Equation 2-1. Under the system conditions of 298 K, and unit hydrogen activity, the potential of the SHE is defined as 0 Volts.

\[ 2H^+ + 2e^- \leftrightarrow H_2 \quad E_{298K}^0 = 0V; \ Pt/H^+ (a = 1), H_2 (P = 1\ atm) \]  \hspace{1cm} (Eq. 2-1)

The equilibrium potential of a system, under standard conditions (i.e. 298 K, a = 1) is related to the standard Gibbs free energy (\( \Delta G^0 \)) of the system by Faraday’s constant (F) and the number of electrons involved in the reaction per unit mole of reactant (n):

\[ \Delta G^0 = -nFE^0 \]  \hspace{1cm} (Eq. 2-2)

Thermodynamics dictates that the Gibbs free energy of a system is related to the standard Gibbs free energy of a system by the activities (\( a_i \)) of the system products and reactants, and temperature (T) as shown in Equation 2-3.

\[ \Delta G = \Delta G^0 + RT \ln \left( \frac{\prod a_i^{s_i}}{} \right) \]  \hspace{1cm} (Eq. 2-3)
Here, \( s_i \) is the stoichiometric coefficient of the reactants/products which is, by definition, positive for products and negative for reactants, in the reduction direction, as expressed in the general electrochemical equation given in Equation 2-4.

\[
\sum s_i M_i + n e^- = 0 \quad \text{(Eq. 2-4)}
\]

(e.g. \( 2CO_2 + 12H^+ - C_2H_5OH - 3H_2O + 12e^- = 0 \) for ethanol oxidation)

From the relation given in Equation 2-3, it follows that equilibrium cell potential is related to the standard equilibrium cell potential by Equation 2-5, referred to as the Nernst Equation.

\[
E_e = E^0 - \frac{RT}{nF} \ln(\Pi a_i^{s_i})
\quad \text{(Eq. 2-5)}
\]

At low pressures the chemical activity of a gaseous compound is approximately equal to the gas pressure expressed in atmospheres, and at low aqueous reactant concentrations, the activity of substances in solution can be approximated by their molar concentrations.

The cell potential is also a function of system temperature as indicated by the thermodynamic relation given in Equation 2-6.

\[
\left( \frac{\partial E^0}{\partial T} \right)_a = -\frac{\Delta S^0}{nF}
\quad \text{(Eq. 2-6)}
\]

\[= 1.2 \times 10^{-4} \text{ V K}^{-1} \text{ for ethanol} \]

Where \( \Delta S^0 \) is the standard change in entropy of the system, under constant pressure. Assuming \( \Delta S^0 \) is constant, integration of Equation 2-6 yields a simple linear relationship between the standard equilibrium potential and temperature:

\[
E^0_2 - E^0_1 = \frac{\Delta S^0}{nF}(T_2 - T_1)
\quad \text{(Eq. 2-7)}
\]
Consequently equations 2-5 and 2-7 can be used to calculate equilibrium cell potentials \((E_{\text{e, cell}})\) at actual conditions from the standard equilibrium cell potential. When these equations are employed on the half cell reactions separately, the overall equilibrium cell potential can be defined as the difference between the cathodic and anodic half cell potentials, as measured against the SHE.

\[
E_{\text{e,cell}} = E_{\text{e,cathode}} - E_{\text{e,anode}}
\]  
(Eq. 2-8)

### 2.2 Electrode Kinetics

In all electrochemical systems, oxidation reactions occur at the anode and reduction reactions occur at the cathode. By definition current leaving the electrode is positive (i.e. anodic current), and that coming into the electrode is negative (i.e. cathodic current).

A deviation of cell potential from the equilibrium conditions is referred to as overpotential \((\eta)\).

\[
\eta = E - E_0
\]  
(Eq. 2-9)

Overpotential is a result of resistances that occur at the electrode, primarily related to electrode kinetics and mass transfer limitations, and represent net losses in the electrochemical system. As with current, by definition cathodic overpotentials are negative and anodic overpotentials are positive.

Overpotential brought on by kinetic limitations is called activation or surface overpotential \((\eta_a)\). The Butler-Volmer-Erdelyi-Grüz Equation (Equation 2-10) implicitly relates surface overpotential to the cell current density \((i\), current produced per electrode geometric surface area\) by three parameters: the anodic transfer coefficient \((a_a\)), the cathodic transfer coefficient \((a_c\)), and the exchange current density \((i_0\)). These parameters are characteristic of the reaction and catalyst employed. Transfer coefficients are generally independent of species concentrations and cell temperature, where as the exchange current density is strongly dependent on both (Prentice, 1991).
The Butler-Volmer-Erdey_Grúz Equation is often simplified under conditions of very large and very small overpotentials. Where large overpotentials are concerned (~50 to 100 mV, either negative or positive), one term in the Butler-Volmer-Erdey_Grúz Equation will approach to zero and the other will dominate. As a result the Equation simplifies to that given in Equation 2-11.

\[ \eta_s = b \log \left( \frac{|i|}{i_o} \right); b = \frac{2.303RT}{|\alpha|F} \]  

(Eq. 2-11)

Where \(|\alpha| = \alpha_s\) for anodic reactions and \(|\alpha| = -\alpha_c\) for cathodic reactions.

Equation 2-11 is referred to as the Tafel Equation and parameter ‘b’ is referred to as the Tafel slope. Charge transfer coefficients are usually between 0.2 and 2 so the Tafel slope is generally 30-300 mV/decade. Under conditions in which the Tafel Equation applies (i.e. high current densities), the Tafel slope and exchange current density can be determined graphically by plotting the overpotential against the log of current density.

Where very small overpotentials (e.g. <10 mV) are concerned, the exponential terms in the Butler-Volmer-Erdey_Grúz Equation can be approximated with a two term Taylor series expansion. The resultant Equation is referred to as the linear approximation of the Butler-Volmer-Erdey_Grúz Equation and is valid at low current densities (Equation 2-12).

\[ i = i_o \left( \frac{\alpha_s + \alpha_c}{RT} \right) F \eta_s = i_o \frac{nF}{RT} \eta_s \]  

(Eq. 2-12)

Overpotentials that result from mass transfer limitations within the cell are referred to as concentration overpotentials (\(\eta_c\)); due to the concentration gradient between the electrode surface (\(C_s\)) and the bulk cell conditions (\(C_b\)). The simplest approach to understanding mass transfer limitations is to assume that concentration gradients within the cell exist only in a thin diffusion layer of thickness (\(\delta\)), adjacent to the electrode surface. Thus, the current density is related to the
surface concentration of reactants by the Nernst diffusion layer model. This relationship is given in Equation 2-13 (cathodic reaction).

\[ i = \frac{-nFD(C_b - C_s)}{\delta} \quad \text{(Eq. 2-13)} \]

Where D is the diffusivity of the reactant in the electrolyte corrected for porosity.

Mass transfer limiting current density \(i_L\) occurs when the concentration of reactants at the surface of the electrode approaches zero, that is they cannot diffuse to the surface of the electrode faster than they react. The expression for mass transfer limiting current density is given in Equation 2-14:

\[ i_L = \frac{-nFDC_b}{\delta} \quad \text{(Eq. 2-14)} \]

It can be shown that the concentration overpotential is related to limiting current density by Equation 2-15.

\[ \eta_c = \frac{RT}{nF} \ln \left( 1 - \frac{i}{i_L} \right) \quad \text{(Eq. 2-15)} \]

In addition to the surface and concentration overpotentials, the ohmic drop \(\Delta \phi_{\text{ohm}}\) between the electrodes must be taken into account in the overall cell potential. This resistance is a function of the electrolyte conductivity \(\kappa\) and electrode spacing \(d\). For two plane, parallel electrodes, the ohmic drop is given in Equation 2-16.

\[ \Delta \phi_{\text{ohm}} = \frac{id}{\kappa} \quad \text{(Eq. 2-16)} \]

Upon collecting all cell overpotentials and the ohmic drop, the actual cell potential can be calculated, as shown in Equation 2-17.
\[ E_{\text{cell}} = E_a + \eta_s,\text{cathode} - \eta_s,\text{anode} + \eta_c,\text{cathode} - \eta_c,\text{anode} - \Delta \phi_{\text{ohm}} \]  

(Eq. 2-17)

### 2.3 Fuel Cell Electrode Design

The gas diffusion electrode design (GDE) used in the \( \text{H}_2/\text{O}_2 \) fuel cell is also the common anode in liquid feed direct alcohol fuel cells. In the conventional GDE design, Pt based nanoparticles (2 – 20 nm in diameter) are deposited on high surface area supports, such as Vulcan XC-72 carbon (Cabot Corp.), and then painted, or otherwise adhered, to the membrane or diffusion layer substrate using a protonically conductive medium, such as Nafion® (Figure 2-1).

![Figure 2-1: Conventional membrane electrode assembly (MEA) design for the direct alcohol fuel cell](image)
Recently some attention has been given to alternates to GDEs in anode design for DMFCs, which may show parallel interest in the realm of DEFCs. These designs are largely focused on the use of alternate catalyst supports and substrates. The simplest of these variations is to deposit unsupported catalyst onto the membrane side of the gas diffusion layer (Mann et al, 2004), this however does not significantly change the overall anode structure and does not appear to significantly affect the overall cell performance. An attempt to improve the overall surface area of the catalyst support has also been made and has included in-house made ordered porous carbon structures (Chai et al, 2004) and the use of multi-walled carbon nanotubes (Zhao et al, 2004). Both of these methods show some improvement in available catalyst support area and subsequently in overall fuel cell performance.

It has also been noted that the structure of the traditional gas diffusion electrode, is far from suitable for use in a liquid fed anode, and in particular for the transport and release of carbon dioxide (Allen et al, 2005). Allen et al. propose the use of a titanium mesh catalyst substrate in order to assist in carbon dioxide disengagement. The results show some promise.

Although the thickness of the titanium mesh used in the study of Allen et al was not reported, it must have had a thickness of at least 300 μm, and therefore it could be considered a three-dimensional anode. Three-dimensional electrodes have shown little cross over to the fuel cell and energy conversion domain; however, their use is common in electrosynthesis (Pletcher, 1997; Gonzalez-Garcia et al, 1998). The interfacial properties of 3-dimensional electrodes are advantageous for use in slow reactions due to the high specific surface area and porosity enhancing the convective mass transfer rate though them (Gonzalez-Garcia et al, 1998).

2.4 Experimental methods for electrode kinetic studies

Electrode kinetic studies are often conducted in a tri-electrode system (Figure 2-2) consisting of a working electrode, a counter electrode, and a reference electrode. The potential of the working electrode is measured against the reference electrode, as a function of the flowing current in the working and counter electrode circuit. In addition to the presence of reactants in solution, a supporting electrolyte is often added to ensure conductivity.
2.4.1 Reference Electrodes

Although the standard hydrogen electrode serves as an IUPAC reference to half cell potentials, it is rarely used as a reference electrode in electrochemical testing. The hydrogen electrode requires a constant gas supply making it bulky and inconvenient. As a result there are several other reference electrodes commercially available. Chloride based reference electrodes (e.g. Hg/Hg₂Cl₂ and Ag/AgCl in saturated KCl electrolyte) can be problematic for Pt based working electrodes due to potential Cl⁻ poisoning of Pt. Thus, when chloride contamination is of a concern, and/or in strong acidic media, the mercury/mercurous sulphate electrode in an aqueous K₂SO₄ electrolyte can be used. The reaction in the mercury-mercurous sulphate electrode is given in Equation 2-18.
\[ \text{Hg}_2\text{SO}_4 + 2e^- \leftrightarrow 2\text{Hg} + \text{SO}_4^{2-} \]  

(Eq. 2-18)

When a saturated aqueous K\textsubscript{2}SO\textsubscript{4} solution serves as an electrolyte, the Hg/Hg\textsubscript{2}SO\textsubscript{4} electrode has a potential of 0.642 V versus the standard hydrogen electrode.

2.4.2 Cyclic voltammetry

Cyclic voltammetry (CV) is perhaps the most published electrochemical research method. In this technique, the potential of the working electrode (against the reference electrode) of the cell is adjusted linearly with time from an initial set value \((E_i)\) to an end value \((E_f)\) and then back again. The resultant current that is produced is measured and plotted against the changing potential, in a plot known as the polarization curve. A typical potential – time response and polarization curve for a reversible reaction are depicted in Figure 2-3.

![Cyclic voltammetry response signals](image)

Figure 2-3: Cyclic voltammetry response signals

The scan rate at which the potential is changed can be adjusted and valuable information can be obtained from the curves. Two pieces of information generally cited are the potential at
which the oxidation of the reactant begins to occur, as well as the magnitude and potentials of any peak current densities that exist. Measuring a change in peak current density, at various scan rates, can give an indication as to why the peak occurs (i.e. poisoning, diffusion limitation, kinetic control, or mixed diffusion and kinetic control).

When the peak is diffusion controlled, the current will increase as the potential reaches the reduction potential of the analyte, but then falls off as the concentration of the analyte is depleted close to the electrode surface. In this scenario for a reversible reaction, the peak current, \( i_p \), is described by the Randles-Sevcik Equation (Equation 2-19a).

\[
i_p = 0.4463nFAC \left( \frac{nFvD}{RT} \right)^{\frac{1}{2}}
\]

(Eq. 2-19a)

For an irreversible reaction the Randles-Sevcik Equation takes the form of Equation 2-19b.

\[
i_p = 0.4961nFAC \left( \frac{\alpha n^*FvD}{RT} \right)^{\frac{1}{2}}
\]

(Eq. 2-19b)

Where \( \alpha \) is the charge transfer coefficient, and \( n^* \) is the number of electrons exchanged in the charge transfer step (Wang, 2000). In either case, should the Randles-Sevcik Equation be observed (i.e. the peak is diffusion controlled), a linear relationship will exist between \( i_p \) and the square root of the scan rate, \( v \).

### 2.4.3 Chronopotentiometry

The experimental setup for chronopotentiometry is identical to that of cyclic voltammetry. Unlike cyclic voltammetry; however, chronopotentiometry is a time based technique, in which the current is fixed between the working electrode and counter electrode for a set period of time. The potential of the working electrode, versus the reference electrode, is then measured and plotted with
time. A typical current density – time response and potential – time response curve are depicted in Figure 2-4.

**Figure 2-4: Chronopotentiometry response signals**

Chronopotentiometry provides valuable information about how an electrode functions over time, and how it will ultimately perform in the fuel cell under a constant current load. A stable electrode system should remain at a relatively constant potential with time; however, drift is expected due to catalyst poisoning, changes in electrode microstructure, and changes in electrolyte concentration/contamination with time.

### 2.4.4 Chronoamperometry

The experimental setup for chronoamperometry again uses the tri-electrode setup. Like chronopotentiometry, chronoamperometry is a time based technique. In this case the potential is fixed between the working electrode and reference electrode for a set period of time, while the total cell current is measured between the working and counter electrodes and plotted with time. Typical chronoamperometry response signals are given in Figure 2-5.
Figure 2-5: Chronoamperometry response signals

Chronoamperometry is a convenient method to determine whether the electrochemical reaction is under diffusion control. For linear diffusion control, the Cottrel Equation (Equation 2-20) defines current-time dependence and when a plot of \( i \) versus \( t^{0.5} \) is a linear relationship, linear diffusion control is said to occur in the system.

\[
i = nFC\sqrt{\frac{D}{\pi t}}
\]  
(Eq. 2-20)

If pure diffusion control can be ruled out, chronoamperometry can be used to determine the Tafel slope for the kinetic regime. In using chronoamperometry to extract this data, the current density is taken after a predetermined amount of time where quasi-steady state has been achieved (as noted in Figure 2-5). The slope of the plot of \( E \) versus \( \log(i) \) yields the Tafel slope, or parameter ‘b’, in Equation 2-11. The exchange current density for the system, \( i_0 \), can subsequently be determined by calculating the system current density at the theoretical equilibrium cell potential, \( E_c \).
2.4.5 Surface Area Analysis

Measurements of true catalytic surface area are important in electrocatalysis in order to make effective comparisons in the inherent activities of different catalysts. In heterogeneous catalysis, a high mass specific surface area is desirable, that is a low catalyst loading and high active catalyst surface area. Where Pt based catalysts are concerned, electrochemically active surface area is traditionally determined by hydrogen (Essalik et al., 1995) or CO adsorption (Schmidt et al, 1997). Hydrogen adsorption is accomplished by cyclic voltammetry in an aqueous acid media. Each active Pt atom has the capacity to adsorb about one hydrogen atom, and the charge associated with adsorption/desorption is used to determined the active surface of Pt as shown in Equation 2-21.

\[
Pt + H^+ + e^- \leftrightarrow Pt - H \quad 210 \mu C cm^{-2} \quad (Eq. 2-21)
\]

CO stripping voltammetry is a similar method for measuring the electrochemically active surface area of Pt. In this instance, the charge associated with desorption of CO can be used to calculate the active surface area.

A third approach for determining electrochemically active surface area is by Cu underpotential deposition (Green and Kucernak, 2002). In this method, a Cu monolayer is deposited on the active surface of the catalyst, at a potential slightly more positive than the potential at which the bulk deposition of Cu occurs (e.g. 0.30 versus 0.18 V SHE on bulk planar Pt). This is referred to as underpotential deposition (UPD). The copper UPD layer is subsequently stripped from the surface of the catalyst using a linear potential scan. Analogous to H and CO stripping, the charge associated with stripping of the Cu UPD layer (Equation 2-22) can be used to determine the active surface area of the Pt catalyst. Charge can be determined by integration of the area under the stripping polarization curve and a background voltammogram recorded without Cu deposition.

\[
Cu_{UPD} \rightarrow Cu^{2+} + 2e^- \quad 420 \mu C cm^{-2} \quad (Eq. 2-22)
\]
The major assumption of the Cu UPD method is the monolayer saturation of the Pt sites and that no Cu deposition occurs on the carbon substrate/support.

For Pt alloy catalysts, such as Pt – Ru, both the hydrogen adsorption and CO stripping methods can be problematic. It has been reported that monoatomic adsorption of H atoms and CO on Ru may not necessarily occur and that multiple modes of adsorption and/or dissolution in oxide layers are possible. For these reasons, Cu underpotential deposition has become the preferred method for determining the surface area of Pt based alloys (Green and Kucernak, 2002), and it is used in this study. In the case of Pt – Sn alloys, some success with Cu UPD deposition has been reported (Boucher and Alonso-Vante, 2003), although it was not clear if mono-atomic adsorption of Cu on the Sn catalyst surface is occurring at all, as multiple stripping peaks were not observed (i.e. one each for Pt and Sn) as was in the case of Pt – Ru alloys for Green et al.
3.0 Objectives

This study considers a solution to the major challenges of the DEFC discussed in Section 1.0: notably improved anode kinetics; fuel crossover; and carbon dioxide disengagement, using a novel anode electrode design.

As noted in Section 2.3, porous so called three-dimensional electrodes may show some promise as the liquid feed direct ethanol fuel cell anode, where reaction kinetics are generally slow and CO₂ disengagement in conventional GDEs can be problematic. Additionally, it is believed that extending the reaction zone will allow ethanol to react more completely before it reaches the membrane interface, leaving less opportunity for fuel cross over.

It is proposed here that the three dimensional electrode could serve as both the catalyst layer and the diffusion layer in the fuel cell anode as depicted in Figure 3-1.

![Figure 3-1: Proposed MEA design utilizing a three dimensional electrode](image)

Substrates considered for three dimensional electrode materials are carbon based and include graphite felt (Type Grade GF, Carborundum Co.), compressed graphite felt (GF-S3, Electrolytica)
Inc.) and carbon cloth (GC-10, Electroytica Inc.). Images of these substrates, and their uncompressed thicknesses, are shown in Figure 3-2.

Central to the challenge of creating a three-dimensional anode for use in the direct ethanol fuel cell is both the uniform deposition of nanoparticulate catalyst throughout the three-dimensional substrate, and the impartment of protonic conductivity across the electrode reaction zone.

Although many methods have been developed for creating nanoparticulate catalyst, their applicability towards direct deposition on 3-dimensional substrates has not been evaluated. In consideration of protonic conductivity, the use of solid or immobilized electrolytes, within the three-dimensional substrate, maybe the preferred operating practice; however, challenges will exist with diffusional and ohmic resistance in the electrolyte, warranting a full study on its own. As a proof of concept, the focus of this work is on creating effective unsupported nanoparticulate catalyst on three-dimensional substrates for use as a DEFC anode, and finally evaluating their performance in a DEFC using a flowing acid electrolyte to establish protonic conductivity.

In addition to its use in a fuel cell, three-dimensional electrodes prepared by this method may prove to be useful in areas of electrosynthesis where the three-dimensional electrode concept is already commonly employed.
4.0 Literature Review

4.1 Ethanol electro-oxidation

Extensive research in ethanol electro-oxidation has, for the most part, coincided with an interest in the direct ethanol fuel cell, whereas the production of ethanol based derivatives, such as acetaldehyde or acetic acid, has been primarily the domain of direct oxidation and heterogeneous catalysis. Prior to the mid 1990s very little attention was given to the electro-oxidation of ethanol, with only a few papers published largely concerning electrolyte choice for Pt catalysed oxidation reactions (Snell and Keenan, 1982). Large improvements in PEM fuel cell design came about in the early 1990s, and with it was a renewed interest in the direct alcohol fuel cell (Hoogers, 2003). The challenge remains to find a catalyst that is capable of the deep oxidation of ethanol to carbon dioxide and that is not prone to poisoning by CO and CO like derivatives of ethanol oxidation as is Pt (Vigier et al, 2004A; Lamy et al, 2002).

By electrolysis experiments at various potentials, and monitoring of products and intermediates with infrared reflectance spectroscopy, a mechanism for the electro-oxidation of ethanol on Pt has been proposed (Vigier et al, 2004A; Lamy et al, 2002).

1. Ethanol can adsorb on Pt following two modes:

\[
\text{Pt} + \text{CH}_3 - \text{CH}_2\text{OH} \rightarrow \text{Pt} - \text{OCH}_2 - \text{CH}_3 + e^- + H^+ \quad \text{(Eq. 4-1)}
\]

\[
\text{Pt} + \text{CH}_3 - \text{CH}_2\text{OH} \rightarrow \text{Pt} - \text{CHOH} - \text{CH}_3 + e^- + H^+ \quad \text{(Eq. 4-2)}
\]

2. At potentials less than 0.6 V SHE acetaldehyde (AAL) is produced according to the following reactions:

\[
\text{Pt} - \text{OCH}_2 - \text{CH}_3 \rightarrow \text{Pt} + \text{CHO} - \text{CH}_3 + e^- + H^+ \quad \text{(Eq. 4-3)}
\]

\[
\text{Pt} - \text{CHOH} - \text{CH}_3 \rightarrow \text{Pt} + \text{CHO} - \text{CH}_3 + e^- + H^+ \quad \text{(Eq. 4-4)}
\]
3. At potentials less than 0.4 V SHE AAL can also adsorb onto Pt:

\[ \text{Pt} + \text{CHO} - \text{CH}_3 \rightarrow \text{Pt} - \text{CO} - \text{CH}_3 + e^- + H^+ \]  
(Eq. 4-5)

4. At potentials greater than 0.3 V SHE the adsorbed AAL species can react with a neighbouring Pt atoms to yield adsorbed CO and adsorbed \(-\text{CH}_3\):

\[ \text{Pt} - \text{CO} - \text{CH}_3 + \text{Pt} \rightarrow \text{Pt} - \text{CO} + \text{Pt} - \text{CH}_3 \]  
(Eq. 4-6)

5. Subsequently, at potentials less than 0.4 V SHE, methane gas can be produced:

\[ \text{Pt} + H^+ \rightarrow \text{Pt} - H_{\text{ads}} \]  
(Eq. 4-7)

\[ \text{Pt} - \text{CH}_3 + \text{Pt} - H_{\text{ads}} \rightarrow 2\text{Pt} + \text{CH}_4 \]  
(Eq. 4-4)

6. At potentials greater than 0.6 V SHE, dissociative adsorption of water occurs:

\[ \text{Pt} + \text{H}_2\text{O} \rightarrow \text{Pt} - \text{OH} + H^+ + e^- \]  
(Eq. 4-9)

allowing for the complete oxidation of adsorbed CO to CO\(_2\):

\[ \text{Pt} - \text{CO} + \text{Pt} - \text{OH} \rightarrow 2\text{Pt} + \text{CO}_2 + H^+ + e^- \]  
(Eq. 4-10)

and; additionally acetic acid can be produced from AAL:

\[ \text{CHO} - \text{CH}_3 + \text{Pt} - \text{OH} \rightarrow \text{Pt} + \text{CH}_3 - \text{COOH} + H^+ + e^- \]  
(Eq. 4-11)

It can be immediately seen from the above mechanism that the reaction of ethanol, on pure Pt at low potentials, is problematic and ends in the production of methane, AAL and poisoned catalyst (i.e. step 6 does not occur). This incomplete reaction produces only a fraction of the electrons
available from complete electro-oxidation of ethanol. The problem of CO poisoning can be overcome by increasing the anode half cell potential. At half cell potentials greater than 0.6V SHE, Pt is able to adsorb water providing –OH oxidation groups to further oxidize the CO intermediates (Vigier et al, 2004B). However, anode potentials above 0.6 V SHE provide fuel cell voltages that are unsatisfactorily low, giving rise to low power delivery from the cell. Alloying Pt with a second or third metal has become the main focus to overcoming this problem.

Since the Pt – Ru alloy has been demonstrated to dramatically improve the electro-oxidation of methanol (Petry et al, 1965; Fujiwara et al, 1999; Lamy et al, 2002), it has possibly been the earliest studied Pt alloy combination for the electro-oxidation of ethanol. As a result of its ability to activate water molecules at low potentials, Ru has shown effectiveness in the oxidation of ethanol (Fujiwara et al, 1999; Lamy et al, 2002; Oliveria et al, 2004; Zhou et al, 2004), as it has done with methanol, although in most cases the results have been less dramatic (Figure 4-1).

![Figure 4-1: Effects of the addition of Ru to Pt based catalysts for both methanol (left) and ethanol (right) electro-oxidation by cyclic voltammetry (Zhou et al, 2004).](image)

Reference Electrode: Standard Calomel Electrode (SCE); 0.242 V SHE. Operation Temperature: 298 K. Scan rate: 10 mV s⁻¹. Electrolyte: 0.5 M H₂SO₄ + 1 M EtOH/MeOH

In addition to activating water molecules (equations, 4-12 and 4-13), it is proposed that the presence of Ru also changes the crystalline structure of the Pt catalyst which enables CO and CO like products to disengage from the surface more easily.
\[ Ru + H_2O \rightarrow Ru-OH + H^+ + e^- \quad (at <0.6 \text{ V SHE}) \]  
\[ Pt-CO + Ru-OH \rightarrow Pt + Ru + CO_2 + H^+ + e^- \]  
(Eq. 4-12)  
(Eq. 4-13)

On the basis of ability to activate water molecules at low potentials, Sn and Mo have received a fair amount of attention (Lamy et al, 2001). The mechanism in either case is believed to be similar to that of Ru. In one recent study, quantum chemistry calculations were conducted to determine how CO and OH interact with Pt-Ru, Pt-Sn and Pt-Mo alloys (Shubina and Koper, 2001). The theoretical results drew many interesting conclusions with respect to the relative binding energies of CO and OH on the different alloy metals. The study indicates that as Ru content is increased in a Pt-Ru alloy catalyst, the Pt–CO bond will theoretically weaken. The study also confirms that OH radicals preferentially bond with Ru atoms. Additionally, the study provides information on the binding energy of the Ru–CO bond. Ru is shown to have a higher affinity for CO than Pt, such that CO would preferentially bond with Ru, although this affinity also decreases with increased Ru content. Due to this it could be concluded that a portion of the Ru atoms in the Pt–Ru alloy are poisoned by CO or CO like derivatives.

In contrast, the Pt–Mo alloy simulations found that in the presence of Mo, binding energies for CO on either metal were comparatively low, with a slight preference for Mo. In addition, a strong preference for OH binding on Mo was shown. Thus Mo should theoretically make a good alloying metal choice.

The simulations of Pt–Sn alloy indicate that this system could function as a truly bifunctional catalyst. In this alloy combination, CO is found to interact only with Pt, and OH is found to interact preferentially with Sn. The binding energies of CO atop Pt; however, indicate that the Pt–CO bond isn’t weakened as significantly by the addition of Sn as it is with Ru or Mo.

There are several shortcomings to this study, a few important ones being the limited species considered, no reference to temperature/potential, and the fact that calculations are equilibrium based. The model considers the oxidative species to be OH and all poisoning species to be CO. CO-like derivatives are not considered. Even with these shortcomings; however, the results probably have some value and have consistency with what has been determined experimentally.

In published studies where Pt–Ru and Pt–Sn alloys are both considered (Zhou et al, 2004; Lamy et al, 2002), Pt–Sn appears to be the better performer for ethanol electro oxidation.
(Figure 4-2). This coincides with its ability to function as a truly bifunctional catalyst, as indicated in the above study. Fuel cell tests comparing the relative activity of Pt, Pt – Ru and Pt – Sn catalysts confirm the same findings (Lamy et al., 2001).

![Figure 4-2: Effects of the addition of Sn and Ru to Pt based catalysts for ethanol electro-oxidation by cyclic voltammetry (Zhou et al., 2004). Reference Electrode: Standard Calomel Electrode (SCE); 0.242 V SHE. Operation Temperature: 298 K. Scan rate: 10 mV s\(^{-1}\). Electrolyte: 0.5 M H\(_2\)SO\(_4\) + 1 M EtOH](image)

Still unexplained, however, is that the alloying metal that is optimal for ethanol oxidation (Sn) is not the same as that optimal for methanol oxidation (Ru) (Fujiwara, 1999; Lamy 2002). Since ethanol is the more complex of the two alcohols, one explanation is that the alloying properties of Sn, have an additional role to supplying the oxidative species in ethanol electro-oxidation. It has been demonstrated that Sn is able to change the electronic structure of Pt, in a way not completed by Ru, which could assist in the breaking of the C – C bond. An observation was made that the addition of Sn to Pt increases the Pt crystal lattice parameter, whereas Ru decreases it, and it could be this increase that favours ethanol electrocatalysis (Zhou et al, 2003).

Although theoretically promising the Pt – Mo alloy is a poor performer for the electro-oxidation of ethanol (Oliveria et al, 2002). In cyclic voltammetry studies the onset of oxidation is not improved from pure Pt catalysts by the addition of Mo, and in fact appears to slightly delay it. Some improvement at higher potentials is evident, but these potentials (>0.75 SHE) are of little practical interest in the DEFC.
Other binary and ternary alloys such as Pt – W, Pt – Pd (Zhou et al, 2004) and Pt – Re (Vigier et al, 2004B) have been discussed in literature, although none have shown promise beyond the Pt – Sn alloy. The basis for exploring a Pt – Re alloy stems from the known heterogenous catalytic properties of Re that would make it a good catalyst for cracking the C – C bond. Ternary systems have been somewhat less investigated, with Pt – Ru – Mo, Pt – Ru – W and Pt – Ru – Pd systems all showing improved activity over Pt – Ru alloys, but not beyond that of the preferred Pt – Sn alloy (Zhou et al, 2004). Additionally the performance of Pt – Sn – Ru (Zhou et al, 2003) alloys appears to fall between that of Pt – Sn and Pt – Ru alone. In fact until very recently no catalyst combination studied showed improvement beyond that of Pt – Sn. Recently, it has been demonstrated that Pt – Sn – Ni alloys (50:40:10) show moderate improvement over Pt – Sn alone (Spinacé et al, 2005).

There is little consensus on the exact ratio in which Pt and Sn should be alloyed to form an effective catalyst for ethanol electro-oxidation, with optimal ratios from 1.5:1 (Zhou et al, 2005) to 9:1 (Lamy et al., 2004) being cited in literature. It appears that the exact ratio is dependent on the method of catalyst preparation, presumably due to associated changes in the catalyst surface properties. In support of this, members of the same research group have cited different optimal Pt:Sn catalyst ratios when using different catalyst preparation techniques (Lamy et al, 2004 and Lamy et al, 2003). For this reason, studies using new catalyst preparation techniques for Pt – Sn alloys should also include variation of the Pt – Sn ratio to find a preferred alloy combination. Various catalyst preparation techniques are discussed in the next section.

4.2 Preparation of nano-particulate catalyst

It is known that in the Pt cubo-octahedral crystal structure, corner and edge sites are not very active in comparison to the (111) and (100) crystal faces. A model considering the mass averaged distribution of (111) and (100) Pt crystal faces, as a function of particle size, was developed in 1990 by Kinoshita, and concluded that Pt catalysts in the 2-4 nm range were most active for oxygen reduction on a mass activity basis. In addition, studies have also confirmed that nano-sized particles in the 4-5 nm range are most active for methanol (Frelink et al, 1995). It is believed that this particle size effect in electrocatalysis is extended to that of ethanol electro-oxidation and the creation of Pt
based nanoparticles, with a narrow size distribution, has been a primary focus of DEFC anode catalyst research. Various methods of creating Pt nanoparticles are described herein.

4.2.1 Electrodeposition Techniques

Electrochemical deposition of catalyst directly on the chosen support is perhaps the easiest and most convenient method of creating a catalyst and it is mostly this technique that has been applied on three-dimensional supports. In this method, metal ions are simply reduced and deposited directly on a carbon support that serves as the cathode.

Direct current electrodeposition of metals; however, can lead to large particle formation, and/or an inevitable coating of metal on the cathode support, instead of well dispersed nanoparticles as would be desired for fuel cell catalysis. Additionally at higher current densities, hydrogen evolution can cause the loss of the deposition layer and lower the current efficiency. A variety of methods can be used to overcome these problems and guide the generation of nanoparticles during deposition. These methods can include pulse deposition and templating, or a combination of the two.

In pulse deposition, the current is applied and stopped at regular intervals as opposed to a continuous application of current as in direct current deposition. Choi et al. (1998) were successful in pulse depositing Pt on carbon black affixed to a carbon cloth electrode. The plating bath was an aqueous solution of $\text{H}_2\text{PtCl}_6\cdot6\text{H}_2\text{O}$ and applied current densities varied from 10 – 50 mA cm$^{-2}$. Choi et al. found that higher catalyst surface areas were achieved during pulse deposition at high current densities. Using a 50 mA cm$^{-2}$ current applied for 100 ms and then stopped for 300 ms, a specific surface area of 124 m$^2$ g$^{-1}$ Pt was achieved and particle sizes averaged 1.5 nm. By contrast the specific surface area of direct current deposition increased with applied current density up until 25 mA cm$^{-2}$ when the layer began to be peeled off due to hydrogen evolution. Even at 25 mA cm$^{-2}$ the specific surface area was lower than that achieved using the pulse deposition. The activity of these samples, and its correlation to catalyst specific surface area, was confirmed by $\text{H}_2/\text{O}_2$ fuel cell tests. Success in creating nanoparticles of Pt by pulse deposition, averaging 5 nm in size with good distribution, has also been reported on a graphite basal plane surface (Zoval et al, 1998). Zovla et al., made another prominent observation in their study that deposition is more likely to occur on the
step edges and irregularities of the surface. The deposition was also noted to be spontaneous (i.e. at open circuit). Zovla et al. attempted to retard this spontaneous deposition during the off pulse period, by maintaining the carbon surface at a potential at which the spontaneous deposition did not occur. Another study by Liu et al. (2000), pre-treats the surface of highly orientated pyrolytic graphite (HOPG) with a 4-aminophenyl monolayer, prior to the adsorption and pulse deposition of Pt. The aminophenyl monolayer serves to suppress spontaneous deposition of Pt at defects. Liu et al. were successful in producing deposited particles averaging 3 nm, with good dispersion, when combining the pre-treatment with pulse deposition.

As an alternative to, or in addition to, pulse deposition, templating has also been explored to produce nanoparticles of catalyst by electrodeposition. In templating, a nano-porous structure is placed over the surface of the catalyst support and electrodeposition is subsequently conducted. In theory, metal will only deposit through the pores of the structure and particle size and distribution can be controlled by the properties of the structure. Elliott et al (1999) have reported success in electrodepositing Pt on planar Au using liquid crystal templating. In this study non-ionic surfactants (specifically: octaethylene glycol monohexadecyl ether \([\text{CH}_3(\text{CH}_2)_{15}(\text{OCH}_2\text{CH}_2)_8\text{OH}]\)) which exhibit liquid crystalline structures at high concentrations were used in a plating bath with water and hexchloroplatinic acid. It was observed that the liquid crystalline structure is a function of surfactant concentration and temperature. Therefore, different templates could be created. Employing direct current electrodeposition, Elliott et al. were able to create a porous Pt film with wall thicknesses and pore sizes in the vicinity of 2.5 nm. This was achieved in both a cubic and hexagonal liquid crystalline structure. In cyclic voltammetry studies involving methanol oxidation, the catalyst was able to pass currents more than 100 times greater than a polished Pt electrode of the same geometric surface area.

4.2.2 Sol-Gel Technique

Catalyst preparation by the sol-gel method is only one application of this technique that is widely employed in the preparation of amorphous materials such as ceramic and glass. Since the end product is a porous amorphous metal material, the sol-gel process may have a wider application
in the production of solid-oxide fuel cell catalysts, as opposed to PEM fuel cell catalysts (Chiba et al, 2004).

The sol-gel process involves the transformation of a liquid colloidal system (sol) into a solid gel phase. A synopsis of two possible routes of the sol-gel process is shown in Figure 4-3.

![Diagram of sol-gel process](image)

**Figure 4-3: Preparation of sol-gel particles and coatings**

The precursors for the preparation of “sol” are typically metal salts or metal organics such as metal acetylacetonates. The precursor materials are dissolved in an organic solvent, and a hydrolyzing agent is added to initiate a series of hydrolysis and polymerization reactions. These reactions produce a colloidal or “sol” suspension, from which the solvent is evaporated to produce a more viscous gel phase. Further drying and heat treatment of the gel solution, to remove liquid and organic materials, produces a solid, porous agglomeration of metal particles. The agglomeration of particles can be crushed to a powder and applied directly to the gas diffusion layer, using a protonically conductive media, such as Nafion® and incorporating carbon black for electronic conductivity (Kim et al, 2003). Alternatively, the sol or gel phases can be used to coat support materials followed by evaporation and heating of the coated support material to form a hardened metal film directly on the material (Suffredini et al, 2004).

One of the primary advantages of the sol-gel process, is that organic metal precursors can be used as opposed to halide salts. The catalyst particles left by halide salt precursors require extensive
washing and thermal heat treatments, in order to remove the halide byproduct, during which, significant noble metal may be lost (Kim et al, 2003). Unlike many other catalyst preparation methods; however, the sol-gel process produces an agglomeration of metal particle nanoparticles, rather than discretely deposited particles on a support or substrate.

4.2.3 Impregnation Methods

Synthesis of metal nanoparticles by impregnation is almost always accompanied by calcination and/or reduction to reduce the metal particles from their ionic precursors. In the impregnation method, hydrochloric acid solutions of soluble metal salt precursors (such as H₂PtCl₆·6H₂O, RuCl₃ and SnCl₂) are prepared and slowly added to aqueous suspensions of carbon support, such as carbon black. Overtime (1 hour or more) the salt suspension becomes impregnated on the support (Arico et al, 1995). The impregnated metals are subsequently reduced, either chemically in the liquid phase, with reducing agents such as sodium borohydride (Arico et al, 1995) or hydrazine (Roth et al, 2004), or by calicination and drying at high temperatures in air, followed by reduction in pure hydrogen. Both calcinations/reduction processes are conducted at high temperatures (300-500 °C) (Vigier et al, 2004B; Pieck et al, 1996; Roman-Martinez et al, 2000).

Impregnation methods are typically accompanied by pre-treatments of the carbon support to modify the surface. The purpose of this surface modification is to provide more or better active sites for the metal to adhere to. Surface modification techniques include oxidation in aqua regia to generate functional groups (Vigier et al, 2004B) and oxidation in H₂O₂ (Roman-Martinez, 2000). In the case of the latter, samples prepared without the surface modification underperformed those in which the carbon was first oxidized.

4.2.4 The Polyol Process

The polyol process is commonly employed to produce “unprotected” metal colloidal particles, that is metal nanoparticles that are stabilized by the solvents in which they are formed, or by simple anions, or both (Wang et al, 2000). In the polyol process, a viscous polyhydroxylic
alcohol (polyol), such as ethylene glycol, is used as a work up solvent. The high viscosity of the solvent in this case serves to minimize particle diffusion and agglomeration.

Metal salt precursors, that are soluble in ethylene glycol (such as H$_2$PtCl$_6$•6H$_2$O and SnCl$_2$), are dissolved in the metal solution under an inert atmosphere. The solution is stirred and heated to a refluxing temperature between 120 – 200 C when chemical reduction of the metal ions by the polyol occurs over a period of 1 to 3 hours (Kurihara et al, 1995). The size of the colloidal particles can be somewhat controlled with variations of reaction time and temperature; however, they remain on the larger size for many metals including Ru (5 nm) and Sn (36 nm). The colloidal particles that result can precipitate from solution and remain relatively stable. Particles produced by the polyol method are adsorbed to high surface area supports, such as carbon black or Al$_2$O$_3$.

In order to produce nanoparticles of noble metals, the polyol process is often modified by adding sodium hydroxide (Zhou et al, 2004; Wang et al, 2000) or water (Zhou et al, 2003) to the polyol solution prior to heating. Sodium hydroxide reacts with the metal salt precursors to produce metal hydroxides, and these in turn will be reduced by the polyol on heating. Water lowers the solution temperature and reduces viscosity. Using the modified method which includes sodium hydroxide addition, the particle sizes are much smaller at ~ 1-3 nm for Pt, Ru, Sn and their alloys (Wang et al, 2000, Zhou et al, 2004; Zhou et al, 2003).

4.2.5 Protective Shell Colloids

Another approach to producing metal colloids is to encapsulate small metal particles in a protective shell to prevent them from agglomerating. This is in contrast to the polyol process, where agglomeration is prevented due to the high viscosity and limited diffusivity of the particles in the solvent. The protective shell is most often a sterically demanding organic molecule, which prevents agglomeration by physically coming between the metal centres. Prepared colloids are readily suspended in water and/or organic solvents, depending on the nature of the protective shell. For the most part the particles are neutral and the metal itself is fully reduced from the ionic precursors that are usually employed to create them. The affinity of the protective shell for the carbon support material is the primary method of depositing metal colloidal particles on carbon catalyst substrates.
Creating metal colloids of this nature from a metal salt precursor is by far the most published method as it generates reproducible and reliable results. In these methods two things need to be achieved. The metal ion needs to be reduced to a zero-valent state, and agglomerates of metal ions need to be stabilized with a protective agent to inhibit particle growth. The primary advantage of the salt reduction method is that nano-particles with a narrow size distribution are consistently prepared, even at the multigram level for a variety of metals and alloys (Bönneemann and Richards, 2001). Different stabilizers and reducing agents have been employed to create colloid particles surrounded by a protective shell. Hydrogen can be used as the reducing agent and has been demonstrated for metal salts stabilized by polymers and tetrabutylammonium (Bönneemann and Richards, 2001). Additionally chemical reductants such as hydrazine, and borohydride (BH$_4^-$), have been used with similar stabilizers. Borohydride is a widely used reduction agent; however, metal borates commonly form as a secondary reaction (Bönneemann and Richards, 2001).

The colloid method developed by Bönneemann et al (1991) has been widely referenced and used in creating fuel cell catalysts. Bönneemann’s method uses a unique class of molecules referred to as tetraalkylammonium hydroorganoborates, such as tetraoctylammonium triethylhydroborate [N(C$_8$H$_{17}$)$_4$B(C$_2$H$_5$)$_3$H]. This class of molecules has a dual role, with the hydroorganoborate [e.g. B(C$_2$H$_5$)$_3$H$^-$] portion of the molecule functioning as the reducing agent and the tetraalkylammonium [e.g. N(C$_8$H$_{17}$)$_4^+$] portion serving as the stabilizer. Hydroorganoborates hold an advantage over borohydride in that no metal borates form alongside the metal salt reduction (Bönneemann and Richards, 2001). The reaction that results in the case of PtCl$_2$ salt reduction in the presence of tetraoctylammonium triethylhydroborate is shown in Equation 4-14.

\[
\text{PtCl}_2 + 2N(C_8H_{17})_4B(C_2H_5)_3H \rightarrow \text{Pt}[N(C_8H_{17})_4\text{Cl}]_2 + 2B(C_2H_5)_3 + H_2 \uparrow \quad (\text{Eq. 4-14})
\]

Due to the sensitivity of hydroorganoborates to oxidizing substances, such as water and air, the reaction is conducted in dry tetrahydrofuran (THF) under an inert atmosphere. The metal salt is first dissolved or suspended in THF, followed by the dropwise addition of the tetraalkylammonium hydroorganoborate, which is also in a THF solution. Salt reduction is noted by the evolution of trialkylboron and hydrogen gases, as well as a characteristic change in colour. For Pt this colour change is from an opaque brown to a deep black. The reaction is allowed to proceed at a set temperature for several hours to allow the metal colloid particles to fully form. The resultant highly
stable colloid can be filtered from the solution using a glass frit and dried to a powder that is readily redistributed in THF for use at any time. Suspended in THF, the colloid is adsorbed on the catalyst support, typically carbon black, by mixing it with the support over time. A depiction of the protective shell colloid adsorbed to carbon black is given in Figure 4-4. Removal of the surfactant shell is accomplished by a combination of washing the absorbed catalysts in alcohol and by thermal heat treatment, at temperatures of 373 to 573 K, under an inert atmosphere.

![Figure 4-4: Bönnemann adsorbed colloid with protective shell](image)

The Bönnemann method has been successfully applied for a variety of metals and alloy metal combinations including Ru, Os, Ir, Ni, Pd, (Bönnemann et al, 1991), Pt-Ru, Pt-Ru-Mo, Pt-Ru-Sn (Götz and Wendt, 1998) and Pt-Sn (Bönnemann et al, 1998). The temperature and time required for the colloidal reaction vary (e.g. PtCl\(_2\): 2 h at 25 °C; RuCl\(_3\): 2 h at 53 °C; PtCl\(_2\)/SnCl\(_2\): 3 h at 30 °C).

A modification of Bönnemann’s method published by Götz and Wendt (1998), involves addition of the tetraalkylammonium salt to the metal salt suspension prior to treatment with the tetraalkylammonium hydroorganoborate. The additional tetraalkylammonium stabilizer helps keep undissolvable metal salts (e.g. PtCl\(_2\)) in suspension during the reaction and assists in keeping particle sizes small.

Preparing protective shell stabilized colloids by electrochemical synthesis is a novel method that has been explored by Reetz and Helbig (1994). The method consists of a two electrode setup suspended in an acetonitrile (CH\(_3\)CN)/THF (4:1) solvent with tetraoctylammonium chloride supporting electrolyte (Figure 4-5). Under applied current, several things occur. Firstly, metal from
the sacrificial anode is oxidized to produce cations, which migrate towards a Pt cathode where they are reduced to the zero-valent state. Tetraoctylammonium ions; however, also migrate towards the Pt cathode and they are able to surround and stabilize the newly formed metal particles to form a colloid. If the colloidal particles are insoluble in the chosen working solvent, the colloid precipitates from the solution and can easily be collected. The process is shown schematically in Figure 4-5.

![Figure 4-5: Electrochemical formation of N(C₈H₁₇)₄Cl stabilized nanometals according to Reetz and Helbig. Figure taken from Bönne mann and Richards (2001).](image)

The resultant colloid can be distributed in THF and adsorbed to carbon carriers in much the same way as Bönne mann’s method. A primary advantage of the method by Reetz and Helbig, is that the colloidal particle size can be easily controlled. By applying various current densities to a Pd system, it was shown that higher current densities (5mA cm⁻²) produce smaller colloidal particle sizes (1.4 nm) than lower current densities (0.1 mA cm⁻², 4.8 nm). An obvious limitation to the method of Reetz and Helbig; however, is that the method is restricted to producing colloids from a sacrificial metal that is anodically soluble. For metals that are less anodically soluble (e.g. Pt, Ru
and Mo), metal salt precursors have to be added to the reaction in order to provide the cations required (Bönnermann and Richards, 2001).

4.2.6 Summary

Of the deposition methods outlined in this section, the colloidal method established by Bönnermann and coworkers, reliably produces appropriately sized nanoparticles and was deemed to be a suitable starting point for attempted deposition of nanoparticles on three-dimensional substrates. It is also hypothesized that the robustness of the methods’ results will allow the process to be modified without significantly affecting the end result. Variants of this method, including current mediated depositions, will be applied to graphite felt.
5.0 Experimental methods

5.1 Electrode material

All experiments were initially conducted using graphite felt (Type Grade GF, Carborundum Co.) as a three-dimensional support (see also Figure 3-2). Physical characteristics of the felt are included in Table 5-1 (Oloman et al, 1991).

Table 5-1: Physical characteristics of graphite felt

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity, $\varepsilon$</td>
<td>0.95</td>
</tr>
<tr>
<td>Mean fibre diameter (µm)</td>
<td>20</td>
</tr>
<tr>
<td>Fibre density (kg m(^{-3}))</td>
<td>1500</td>
</tr>
<tr>
<td>Uncompressed thickness (mm)</td>
<td>2.0</td>
</tr>
</tbody>
</table>

5.2 Substrate Pretreatments

The need to improve deposition sites is important in any application. In effort to increase catalyst deposition sites on graphite felt, chemical pretreatments were trialed.

5.2.1 Pd nucleation

It has previously been demonstrated by others (Rye and Ricco, 1993) that Pd\(^0\) nucleation sites can be created on polytetrafluoroethylene (PTFE) surfaces using a two step process involving sensitization of the surface with Sn(II) ions and subsequent reduction of Pd(II) by adsorbed Sn(II). In the study by Rye and Ricco, the Pd\(^0\) deposits were successful in providing nucleation sites for the electroless deposition of Cu.

In an attempt to increase the number of nucleation sites on graphite felt, Pd nucleation was evaluated as a substrate pretreatment. In this process, a sensitization solution was created by combining 3.5 g of SnCl\(_2\) and 0.05 g of PdCl\(_2\) in 100 mL of 20 v\% of reagent grade HCl (Fisher Chemicals Inc.). The carbon felt was immersed in the solution for 5 minutes, and then washed with
3 L of distilled water by vacuum filtration. The sample was allowed to air dry overnight before deposition was conducted. The proposed reactions for this process are given in Equation 5-1.

\[
\begin{align*}
C + Sn^{2+\text{(aq)}} & \rightarrow C - Sn^{2+\text{(ads)}} \\
C - Sn^{2+\text{(ads)}} + Pd^{2+\text{(aq)}} & \rightarrow C - Pd^{2+\text{(ads)}} + Sn^{4+\text{(aq)}}
\end{align*}
\]  

(Eq. 5-1)

5.2.2 Nitric acid oxidation

By oxidizing the substrate in nitric acid, an attempt was made to increase surface roughness and deposition sites on the graphite felt. In this treatment a 60 v% solution of A.C.S. certified nitric acid (Fisher Scientific Inc.), was made with deionized water and the felt was immersed in the acid solution for 20 hours. Following acid treatment, the felt was washed with 3 L of deionized water.

5.3 Catalyst Depositions

5.3.1 Preparation of tetraoctylammonium triethylhydroborate

\((N(C_{8}H_{17})_{4}B(C_{2}H_{5})_{3}H)\)

Tetraoctylammonium triethylhydroborate solution in THF was prepared in house from tetraoctylammonium bromide and potassium triethylhydroborate precursors. A saturated solution of tetraoctylammonium bromide in THF was first prepared by combining 5.00 g (9.1 mM) of tetraoctylammonium bromide (Sigma-Aldrich, 98% purity) in 11.0 mL of dry (0.008% H\(_2\)O) certified reagent grade THF (Fisher Scientific Inc.) in a 50 mL Erlenmeyer flask. Nitrogen (Praxair, Industrial grade), passed first through a Driedent® drying column and subsequently saturated with THF, was bubbled through the mixture while stirring, with a magnetic stirrer, at room temperature until the tetraoctylammonium bromide was completely dissolved (approximately one hour). The experimental setup is shown by Figure 5-1.
Following preparation of the saturated tetraoctylammonium bromide solution, the nitrogen bubbling tube was lifted above the THF solution to provide a nitrogen blanket, under which the reaction was to occur. Using a glass syringe, 9.1 mL of 1 M potassium triethylhydroborate (Sigma-Aldrich) solution in THF, was added dropwise to the tetraoctylammonium bromide solution, via the nitrogen venting tube, over approximately 10 minutes and under continuous stirring. The quantity of potassium triethylhydroborate added was in the stoichiometric requirements of the reaction set out in Equation 5-2.

\[
\text{N}([C_8H_{17}]_4\text{Br} + \text{KB(C}_2\text{H}_5)_3\text{H} \rightarrow [C_8H_{17}]_4\text{B(C}_2\text{H}_5)_3\text{H} + \text{KBr}}
\]  

(Eq. 5-2)

As shown in Equation 5-2, the formation of tetraoctylammonium triethylhydroborate by this method is accompanied by the formation of KBr salt as a precipitate. Following addition of the potassium triethylhydroborate solution, the stirring of the solution under a nitrogen blanket was continued for one hour, at room temperature, to allow the reaction to proceed. The reacted mixture was then fully stoppered and stored at -18 °C for at least 16 hours to allow maximum precipitation of KBr from solution. Prior to initial use, KBr was vacuum filtered from the solution using a glass frit (porosity 4), and the KBr filter cake were washed with 5 mL of THF. The resultant tetraoctylammonium triethylhydroborate solution had a molarity of approximately 0.37 M in THF (assuming complete conversion) and was stored at -18 °C in a stoppered 50 mL Erlenmeyer flask.
when not in use. Solutions were kept for approximately two weeks after which any residuals were discarded.

5.3.2 The Bönnemann colloid preparation method and deposition on 3-D substrates

The Bönnemann method, in the variant developed by Görtz and Wendt, was used to prepare metal colloids in a 2:1 Pt:Sn ratio. 0.2086 g (0.78 mmol) of PtCl$_2$ (Sigma-Aldrich, 98% purity), 0.0743 g (0.39 mmol) of SnCl$_2$ (Sigma-Aldrich, 98% purity), and 1.9293 g (3.53 mmol) tetraoctylammonium bromide stabilizer where added to 105 mL of THF, in a jacketed vessel warmed to 30 °C with a circulating water bath. The quantity of tetraoctylammonium bromide added was in 50% excess of the molar equivalent required for each metal charge present (Equation 5-3). The composition of the solution and required temperature for Pt – Sn had been previously determined (Bönnemann et al, 1998). Dry, THF saturated, nitrogen was again purged into the system, while stirring with a magnetic stirrer for approximately 1 hour until the stabilizer and SnCl$_2$ salts were dissolved and the PtCl$_2$ salts were completely suspended in the solution. The experimental setup is shown schematically in Figure 5-2.

Following dissolution/suspension of the metal salts, the nitrogen purge was lifted from the solution to form a nitrogen blanket over the mixture. 9.1 mL of 0.37 M tetraoctylammonium triethylhydroborate in THF was subsequently added dropwise to the suspension using a glass syringe via a rubber septum. Addition was completed slowly over approximately 30 minutes to allow the reaction shown in Equation 5-3 to occur. The amount of tetraoctylammonium triethylhydroborate added was in 50% excess of the stoichiometric requirements shown in Equation 5-3.

\[
2\text{PtCl}_2 + \text{SnCl}_2 + 6\text{N(C}_8\text{H}_{17}\text{)}_4\text{B(C}_2\text{H}_5\text{)}_3\text{H} \rightarrow \\
\text{Pt}_2\text{Sn}[(\text{N(C}_8\text{H}_{17}\text{)}_4\text{Cl})_6 + 6\text{B(C}_2\text{H}_5\text{)}_3\text{H} \uparrow + 3\text{H}_2 \uparrow \\
\text{(Eq. 5-3)}
\]
Evidence and progress of the reaction was monitored by the visible formation of hydrogen and triethylborate gases, as well as the change in colour of the suspension from an opaque brown to deep black. Following addition of the reducing agent, the reaction was allowed to proceed under constant stirring for three hours, after which 2 mL of acetone was added to the solution, to destroy any remaining reducing agent, and the mixture was allowed to react for a further 30 minutes. The resulting colloidal solution was deep black in colour and stable in solution for at least twelve months.

A 40 x 40 x 2 mm piece of graphite felt, cut with a “tab” from which it could be suspended in solution, was used as the substrate for colloidal deposit. Prior to use the felt was clipped to a stainless steel alligator clip mounted on a steel rod and suspended in 125 mL of pure anhydrous ethanol (Commercial Alcohols Inc.) in a 125 mL Erlenmeyer flask using a neoprene stopper. The felt/ethanol suspension was placed in a sonic bath (Branson, model 5200) for 5 minutes to wash away adsorbed impurities and remove loose fibres generated during cutting. The felt was then removed from the ethanol bath, rinsed several times with distilled water and left to air dry overnight, after which the mass was recorded using an analytical balance (Mettler AE100).

In order to adsorb the encapsulated Pt₂Sn colloid onto the graphite felt, the dry graphite felt was remounted on the alligator clip and suspending in 300 mL of THF at room temperature.
exposed metal surfaces on the clip and rod were wrapped in Teflon tape. The felt/THF suspension was subsequently bubbled with dry, THF saturated, N₂ for one hour, after which the N₂ tube was raised above the solution to create a nitrogen blanket. The experimental set up for adsorption is depicted in Figure 5-3.

![Figure 5-3: Bönneemann colloid deposition on the 3-D carbon substrate](image)

The colloidal solution was removed from the nitrogen blanketed jacketed vessel (maintained at 30°C and under constant stirring), using a glass syringe via the rubber septum and subsequently added dropwise to the nitrogen blanketed THF/felt suspension over the course of 1 hour. Following addition of the colloidal solution, the mixture was stirred with a magnetic stirrer for 16 to 24 hours, under nitrogen blanket, to allow adsorption to occur. The colloidal suspension was then drained from the adsorption vessel, and filtered by vacuum filtration onto filter paper (Fisherbrand, grade P5, 4.25 cm) to collect loose carbon fibres. Following filtration, the paper was rinsed with approximately 5 mL each of ethanol and distilled water and left to air dry over night.

To wash off the encapsulating shell from the deposited colloid, the drained suspension vessel, containing the suspended felt sample, was then filled with 300 mL of dry anhydrous ethanol and stirred, under nitrogen blanket, for 10 minutes. The felt was then removed from the vessel and
sonicated in 125 mL of ethanol for 5 minutes in the same manner it was washed prior to deposition. The ethanol from both the initial washing and sonication was filtered in the same manner as the colloid to collect loose fibres. The filter paper was rinsed with approximately 5 mL of distilled water and left to dry over night. Finally the felt was washed in 125 mL of distilled water at room temperature, using the same setup as for ethanol sonication, but using a magnetic stirrer. The distilled water wash was conducted for 15 minutes, occasionally changing the water, until no ethanol odour was prevalent on the sample.

The deposited felt sample was left to air dry overnight and then weighed, together with the colloid and ethanol wash filter papers, to determine the overall mass difference from the original felt sample.

5.3.3 Electrochemically mediated colloidal metal deposition on 3-D substrates

In order to improve catalyst loadings from the original Bönnemann deposition method detailed in Sections 5.3.1 and 5.3.2, a variant of the Bönnemann colloidal method involved the preparation of metal colloids and the co-current deposition of the colloid on graphite felt under the action of an electric field.

a) Surfactant addition first: electrophoretic adsorption of surfactant on the felt

In this method, 0.2086 g PtCl$_2$ (0.8 mmol), 0.0743 g SnCl$_2$ (0.4 mmol) and 1.9293 g (3.5 mmol) of tetraoctylammonium bromide were measured on an analytical balance and added to 50 mL of THF in a 250 mL roundbottom flask with a septum covered sample port (Figure 5-4). This produces metal salt molarities in the reaction vessel at values similar to that previously reported for the Bönnemann method (Bönnemann and Britz, 1998). The reagent quantities were chosen with the goal of obtaining 5 mg cm$^{-2}$ of catalyst deposit, at an estimated deposition yield of 10%. Dry, THF saturated, nitrogen was bubbled through the metal salt/stabilizer solution, while stirring on a magnetic stirrer, for approximately 1 hour, until the salts became dissolved or suspended. Subsequently the nitrogen tube was lifted above the metal salt solution to form a nitrogen blanket over the suspension.
Graphite felt was washed and prepared as indicated in Section 5.3.2, and subsequently suspended in 50 mL of THF in a 100 mL jacketed vessel warmed to 30°C via a circulating water bath. The felt was positioned between two Pt/Ti counter anode electrodes, and the tri-electrode system was connected to multimeter and regulated power supply as shown in Figure 5-5. Dry, THF saturated, nitrogen was bubbled into the system for approximately 20 minutes before the tube was lifted above the solution to create a nitrogen blanket.
Following the nitrogen purge, 9.1 mL of 0.37 M tetraoctylammonium hydroborate was introduced dropwise, over approximately 10 minutes, to the felt/THF suspension via a septum covered sample port, using a glass syringe. Subsequent to the addition of tetraoctylammonium hydroborate, the felt sample was fully submerged. The solution was allowed to mix for approximately 1 minute, using a magnetic stirrer and then the power supply was turned on in galvanostatic mode, to a predetermined superficial current density (1.25 – 6.25 mA cm\(^2\), with corresponding voltages of 2 - 6 V).

The system was subsequently allowed to equilibrate for 0 to 60 minutes, adjusting the current supply as needed, and then the metal salt/stabilizer (i.e. tetraoctylammonium bromide) solution was added dropwise, over approximately 45 minutes, to the felt system by transferring the suspension from the roundbottom flask (Figure 5-4) to the jacketed vessel using septum covered sample ports and a glass syringe.

Figure 5-5: Schematic of electrochemically mediated colloidal metal deposition on 3-dimensional substrates
The reaction was allowed to proceed for 3 to 14 hours from the time the metal salt suspension was first introduced. Afterwards, the colloidal solution was drained from the vessel and filtered, as indicated in Section 5.3.2, and 100 mL of anhydrous ethanol was introduced to the vessel to wash the graphite felt sample under constant stirring for 10 minutes. Following the initial ethanol washing, the felt sample was sonicated in ethanol and washed in deionized water as detailed in 5.3.2. Additionally, loose fibres from both ethanol washes were again collected by vacuum filtration. The felt sample and filter papers were allowed to air dry overnight before determining the after deposit felt weight.

b) Metal addition first

In a variant of the electrochemically mediated colloidal metal deposition technique, the order in which the two key reaction components, namely the tetraoctylammonium triethylhydroborate reductant and the metal salt suspension, are introduced is reversed. In this method variant, 0.2086 g PtCl\textsubscript{2} (0.8 mmol), 0.0743 g SnCl\textsubscript{2} (0.4 mmol) and 1.9293 g (3.5 mmol) of tetraoctylammonium bromide were measured on a microbalance and added to 45 mL of THF in a 100 mL jacketed reaction vessel maintained at 30 °C. The mixture was bubbled with dry, THF saturated, nitrogen for approximately 1 hour until the components were dissolved or suspended. Subsequently, the nitrogen tube was raised to create a nitrogen blanket for the remainder of the experiment.

After nitrogen purging, the felt electrode assembly was placed in the reaction vessel, in which the metal salt suspension was present, and connected to the regulated power supply operating in galvanostatic mode. Current was turned on, to a predetermined value (1.25 – 6.25 mA cm\textsuperscript{-2}, with corresponding initial voltages of 18 – 25 V), and 9.1 mL of 0.37 M tetraoctylammonium triethylhydroborate was added dropwise over 20 minutes, via a septum covered sample port and using a glass syringe. Current was adjusted as necessary, and the remainder of the process was carried out as detailed above in the surfactant adsorption variant.

5.4 Heat treatment

In an effort to remove the protective colloidal shell, samples were heat treated under nitrogen in a stainless steel tubular reactor (Figure 5-6), designed and made in house.
The reactor body was created from a 300 mm long, 6 mm thick, 64 mm ID stainless steel pipe sealed at one end by a welded 6mm thick plate. A pre-manufactured pipe flange (Bartle and Gibson) was welded to the other end and covered with a 13 mm thick endplate. The endplate is secured to the flange by four 76 mm bolt and nut assemblies, 13 mm diameter. An airtight seal was created at the flange/endplate interface using a 2 mm thick graphite gasket (Durabla Manufacturing Co.). Samples were positioned within the reactor in 64 mm diameter watchglasses fitted on a sectioned piece of stainless steel sheet metal, as depicted in Figure 5-6.

Low pressure nitrogen (Praxair, industrial grade) was flushed in the tubular reactor through a 3 mm OD stainless steel tubing, secured to a threaded coupling, at sealed end of the reactor, by a bored through stainless steel Swagelok® fitting. An identical fitting, also connected to 3 mm OD stainless steel tubing, at the flange end of the reactor served as an outlet for the flowing nitrogen. Central to the nitrogen inlet and outlets was a third threaded coupling which served to hold a
standard 3 mm thermocouple. The reactor was heated by wrapping the outside of the reactor body with heating tape and fiberglass insulation. Temperature was maintained via the thermal couple and an automated temperature controller (OMEGA, model CN760000).

For thermal heat treatment, samples were loaded into the watchglass tray and the reactor was sealed. Nitrogen was flushed through the reactor at a slightly positive pressure (~ 5 – 10 psig) for approximately 30 minutes, and then the temperature controller was activated. Heat treatment was conducted for approximately 1 hour after the reactor reached the desired temperature, and then the temperature controller was switched off. The reactor was allowed to cool to 50 °C, under continuous nitrogen flow, and then it was disassembled and the heat treated samples were removed.

**5.5 Characterization of nano-particulate deposited catalyst**

The catalyst deposit was characterized by determining particle size, catalyst loading, and bulk catalyst composition (i.e. metal alloy ratios). Particle size was determined by electron microscope imaging and initial estimates of catalyst loading were made by mass difference. Loose fibres from the deposition and ethanol washing stages of catalyst preparation were collected and their mass was added to the experimental mass difference of the felt as described in Section 5.3.2. This is only reliable; however, when no additional matter (e.g. aggregated colloid or unreacted metal salts) are caught in the filter paper. Accurate measurements of catalyst loading and bulk composition were subsequently made using two separate techniques: Energy dispersive x-ray analysis (EDX) and inductively coupled plasma – optical emission spectroscopy (ICP-OES). Due to the relative cost difference EDX data was consistently collected for all samples; whereas ICP-OES was only collected on select samples. A correlation between catalyst loading by ICP-OES and EDX signal is given in Appendix B.

**5.5.1 Particle Size by Electron Microscopy**

Traditionally particle size information for fuel cell catalysts is collected using transmission electron microscopy (TEM), on catalyst particles deposited on carbon black, 10 – 90 nm in diameter. TEM, however, is limited by the thickness of the sample and in the case of three dimensional
supports it cannot be used without casting the sample in resin and cutting thin cross sections to be analysed.

For morphological analysis of the deposits on three dimensional substrates, high resolution scanning electron microscopy (HiRes SEM) was employed. HiRes SEM analysis was conducted at the BioImaging Laboratory housed at the University of British Columbia, using a Hitachi S4700 SEM capable of resolving 2.5 nm particles at a magnification of 500,000x.

Single carbon fibres were pulled from the sample and flush mounted on SEM stubs using carbon sticky. The samples were loaded into the system and images were generated using a beam voltage and current of 2.0 kV and 12 µA respectively, at a working distance of 2.8 mm. Images were collected at various locations on the fibre and were subsequently loaded into Adobe® Photoshop to estimate particle size by comparison to the image scale bar.

5.5.2 EDX

EDX is non-destructive method of analysis conducted in conjunction with scanning electron microscopy, a technique detailed in Section 5.5.1. In EDX analysis, an electron beam, in the energy range of 5 – 20 eV, strikes the surface of an electrically conductive material dislodging atomic electrons from the material. These electrons are quickly replaced by other electrons, and in the process, x-rays are emitted from the material. The energy of the x-ray emitted is characteristic of the element it is sourced from. An energy x-ray analyzer is used to measure the number and energies of the x-rays emitted. From this data, a spectrum of x-ray energy versus relative counts of the number of detected x-rays can be created and evaluated to determine the qualitative and quantitative properties of the sample, such as bulk metal alloy ratios. Since the electron beam penetrates the surface of a Pt particle by about 0.5 microns, EDX is not considered to be a surface analysis technique.

EDX analysis was conducted at the Electron Microscopy Laboratory, Department of Metals and Materials Engineering, the University of British Columbia, using a Hitachi S-3000N scanning electron microscope equipped with a Quartz XOne light-element, high-resolution x-ray detector. Approximately 1 cm² of deposited material was prepared with a 0.5 cm² step cut into it to expose the centre of the sample for analysis as depicted in Figure 5-7.
The felt sample was mounted on a SEM stub using a double sided carbon sticky tab (Fullam Inc., d = 8 mm). The sample was loaded into the microscope and magnification was adjusted to 600x. Area and spot EDX analysis was performed using a 20 keV electron beam over a period of 100 seconds. Three to five locations were analysed in each of the surface, and exposed centre areas of the sample.

5.5.3 ICP-OES

ICP-OES is frequently employed for analysis of all metallic and many non-metallic elements. The principle behind ICP-OES and other emission spectroscopy techniques is that many elements, when subjected to suitable excitation, will emit radiation of characteristic wavelengths. An optical sensor is used to collect the intensity of radiation at particular wavelengths, and from this spectrum, quantitative and qualitative analysis of the types of elements present can be made. ICP-OES uses a plasma excitation source, which is capable of inducing characteristic emissions from most metallic metals.

ICP-OES is a destructive method for measuring the bulk loading and composition of catalyst deposited on a support, as the metal must be stripped from the carbon surface into solution for
analysis. Analysis was outsourced to Vizon Scitec (Vancouver, Canada) and conducted using a Perkin Elmer Optima, model 3300DV instrument. The following is a brief synopsis of the method: a 1.0 cm² sample of catalyst substrate was weighed and subsequently digested in 4 mL of warm aqua regia (3:1v HCl:HNO₃ at 458 K) for approximately 3 hours, to strip the metal deposit from the substrate. Following digestion, the aqua regia solution was diluted to 10 mL and the quantity of metals in solution was determined by ICP-OES.

Warm aqua regia digestion is effective for Pt, although there is some indication that Sn and/or SnO may not completely dissolve (Schlecht and O'Connor, 2003). For these reasons the bulk metal alloy ratios determined by EDX where taken as accurate, and the Sn loading on the sample was calculated based on the Pt loading determined by ICP-OES. This often involved an upward adjustment in the Sn loading from that determined by ICP-OES, confirming that Sn may not readily dissolve in the aqua regia solution.

5.6 Half cell electrochemical testing

All half cell electrochemical test experiments were conducted in a 1 L CNC ASTM standard electrochemical cell (Figure 5-8), filled with a working solution volume of 450 mL. Two ¼ " glassy carbon rods were employed as counter electrodes with a total surface area of 20 cm² exposed to the solution. Hg/Hg₂SO₄ in saturated K₂SO₄ (0.64 V versus SHE and 0.40 V versus the Standard Calomel Electrode [SCE]) was used as the reference electrode, which was housed in an adjustable Luggin capillary.

The working solution electrolyte was 0.1 M H₂SO₄, made using A.C.S. certified sulphuric acid (Fisher Chemicals Inc.) and deionized (Ion X Changer 1506-35, Cole-Parmer Inc.) water. The same working electrolyte was used to fill the Luggin capillary.
Figure 5-8: 1L CNC ASTM electrochemical cell used in electrochemical half cell testing.
A catalyst sample with a geometric area of 1 cm by 2 cm was cut from the deposit sample for use as the working electrode. The material was mounted to a Pt/Ti feeder, constructed by spot welding a 1/16" titanium rod onto 1 cm$^2$ of Pt/Ti, 2 mm thick (Figure 5-9). Approximately 0.5 cm$^2$ of one end of the felt sample was adhered to the bottom of the feeder using an electrically conductive epoxy created by combining equal volumes of epoxy resin (RBC Industries Inc, RBC-2100), epoxy hardener (RBC industries Inc.), and 80 – 200 micron glassy spherical carbon powder (Alfa Aesar). The glued sample was allowed to cure overnight before using, and was inserted into the test cell so that only 1 cm$^2$ of working electrode substrate was exposed to the solution.

![Mounted working electrode for half cell testing.](image)

Electrochemical measurements of the assembled cell, were made using a computer controlled Princeton Applied Research Parstat potentiostat (model 2263) and the associated Power Suite software. Ambient conditions generally corresponded to a working temperature of approximately 293 K, higher temperature studies at 333 K and 353 K were conducted by immersing the test cell in a temperature controlled water bath (Blue M Electric Co., model MW-115255A-1), and monitoring the cell temperature with an inserted alcohol thermometer.
5.6.1 Chemical and electrochemical cleaning of deposited electrodes

Prior to testing, working electrodes were cleaned both chemically and electrochemically in two separate treatments. For the chemical treatment, a solution consisting of 50 %v 1 M H₂SO₄ and 50 %v 3%wt H₂O₂, was prepared. The working electrode was swirled in the solution for one minute and then rinsed with deionized water. The process was repeated three times.

Electrochemical pre-treatment was conducted in 0.5 M H₂SO₄. The working electrode was held at a half cell potential of 0.50 V versus the mercury/mercurous sulphate electrode (MSE) for 30 seconds, in order to oxidize any absorbed organic contaminants on the catalyst surface. Following the oxidation, the working electrode was held at a potential of -0.63 V MSE for 30 seconds, in order to reduce any metal oxides that may have formed at the higher potential. The oxidation/reduction steps were carried out three times and subsequently cyclic voltammetry was conducted between the potentials of -0.64 V MSE and 0.5 V MSE at a scan rate of 100 mV s⁻¹. The resulting voltammogram served to verify the electrode cleanness (Figure 5-10).

![Example of reference voltammogram used to verify the cleanness of Pt-Sn catalyst samples. Operation temperature: 20°C. Scan rate: 100 mVs. Electrolyte: 0.5 M H₂SO₄](image-url)
Following electrochemical treatment the electrode was rinsed with deionized water prior to further electrochemical testing using ethanol solutions. Chemical and electrochemical cleaning was conducted on all samples, and additionally prior to underpotential deposition studies, as outlined in Section 5.6.3.

5.6.2 Cyclic voltammetry

Cyclic voltammetry measurements were carried out using a start and switching potential of -0.64 V MSE and 0.50 V MSE, respectively. The scan rates were 5, 10, 50, 100 and 200 mV s\(^{-1}\). Data was subsequently recorded as a voltammogram plot of superficial current versus potential.

Following completion of all blank acid scans, anhydrous ethanol was added to the solution to create a 1 M ethanol in 0.1 M H\(_2\)SO\(_4\) solution. This was achieved by slowly adding 10.35 g of anhydrous ethanol over 3 minutes, while stirring, and maintaining the working electrode at a constant potential of -0.63 V MSE to avoid any electrochemical oxidation of ethanol during addition. After ethanol addition, the solution was allowed to come to rest and cyclic voltammetry was conducted using the potential range and scan rates given above. Once the 200 mV s\(^{-1}\) scan was completed; however, a second 5 mV s\(^{-1}\) scan was repeated to determine potential changes in the catalyst behaviour.

5.6.3 Chronopotentiometry

Chronopotentiometry was conducted in the same solution composition as the ethanol cyclic voltammetry runs, and for the most part was conducted immediately following cyclic voltammetry without refreshing the ethanol solution. In each chronopotentiometric scan, the current was initially set a 0.00 A for 10 seconds, and then adjusted to a specific value for 180 seconds (i.e. 2.5, 5 and 10 mA cm\(^{-2}\)). During the duration of the experiment, the half cell potential of the working electrode is recorded and plotted against time.
5.6.4 Chronoamperometry

Chronoamperometry was conducted in the same solution composition as the ethanol cyclic voltammetry and chronopotentiometry runs and for the most part immediately following chronopotentiometry. In each chronoamperometric scan, the half cell potential of the working electrode was held at 0.5 V MSE for 1 second to oxidize absorbed species on the surface, followed by a potential of 0 V MSE for 2 seconds, and then adjusted to specific values for 180 seconds (i.e. -0.35, -0.28, -0.23, -0.18, -0.13, and 0 V MSE). Chronoamperometry data is collected by plotting the cell current with time.

5.6.5 Determination of effective surface area by Cu underpotential deposition (Cu UPD) and stripping

Copper underpotential deposition was typically conducted on a sample after the electrochemical testing for ethanol activity was completed. Preceding the deposition; however, the sample was again cleaned electrochemically as indicated in Section 5.3.1. The setup was identical to those in the previous electrochemical methods (i.e. CV, CP and CA). Prior to use the glassware was cleaned thoroughly by rinsing it in chromic acid and deionized water.

The procedure began by verifying the potential at which Cu UPD occurs on both a pure Sn and Pt – Sn catalyst. Employing a 2 mM CuSO₄ in 0.1 M H₂SO₄ solution made from A.C.S. certified CuSO₄·5H₂O (Fisher Chemicals Inc.). Sn and Pt – Sn catalysts samples were subjected to cyclic voltammetry in the CuSO₄/H₂SO₄ solution, over an appropriate range and scan rate. The potentials at which Cu UPD and stripping occurred were observed from the voltammogram.

To begin the surface area determination procedure the blank activity of the sample in 0.1 M H₂SO₄ electrolyte was recorded by performing cyclic voltammetry over a range of -0.4 V MSE to 0.27 V MSE and a scan rate of 10 mV s⁻¹. It has been established by Green and Kucernak (2002) that this range is inclusive of both Cu underpotential deposition and stripping, and it was verified in the present work as well.

The blank electrolyte was subsequently replaced with 2 mM CuSO₄ solution in 0.1 M H₂SO₄ for deposition of the Cu UPD monolayer. Cu UPD was conducted with and without first
electrochemically oxidizing the catalyst monolayer to determine if Cu UPD would occur on oxidized Sn. It was previously determined that Cu UPD does not occur on oxidized Ru (Green and Kucernak, 2001). Oxidation was completed by maintaining a working electrode half cell potential of 0.500 V MSE for 300 s. Cu deposition was subsequently conducted for 300 s at a potential where Cu UPD was noted to occur on the preliminary scan described above.

Once the monolayer was deposited, the Cu was stripped from the sample by conducting a linear scan from -0.40 V MSE to 0.27 V MSE, at a scan rate of 10 mV s\(^{-1}\), and recording the current. The catalytically active surface area of the sample was then calculated using Simpson's Rule for integration as detailed in Section 2.4.

5.7 Full Cell Tests

5.7.1 MEA preparation

Membrane electrode assemblies for full fuel cell tests, of 5 cm\(^2\) effective geometric area, were prepared using a pre-assembled cathode half MEA (Fideris Inc., 4.0 mg cm\(^{-2}\) of Pt black). Prior to application of the 3-dimensional anode, the half MEA was protonated by soaking it in 1 L of 0.5 M \(\text{H}_2\text{SO}_4\) at 75 °C for approximately 1 hour.

To attach the anode, 1.0 mg cm\(^{-2}\) of Nafion® was deposited on the anode side of the membrane by distributing an even layer of 100 mg of 5 wt% solution of Nafion® in lower aliphatic alcohols and water (Sigma-Aldrich), using a micropipette and paint brush to ensure even application. The 5 cm\(^2\) three-dimensional catalyst anode was subsequently hot pressed to the liquid Nafion® layer by placing the assembly in a 120 °C vacuum oven (Fisher Scientific Co., Model 48), between two 80 x 80 x 8 mm stainless steel plates and weighted with a 2.4 kg stainless steel block atop for 45 minutes. This produced a compression pressure of 3.7 kPa.

5.7.2 Fuel cell tests

All fuel cell tests were conducted using a Fideris Inc. model MTK direct methanol fuel cell (Figure 5-11) test station, equipped with corrosion resistant fittings and gold plated end plates so that
flowing acid (0.5 M H₂SO₄) electrolyte could be used. The flow field was a simple serpentine as depicted in Figure 5-12.

Figure 5-11: Fideris Inc. model MTK direct methanol fuel cell test station
A 2 mm thick graphite gasket (Durabla Manufacturing Co.) was cut and coated with a thin layer of silicone sealant (Dow Corning, TT-S0001543A), to be fitted between the anode end plate and MEA. The three dimensional anode served also as a gas diffusion layer, hence no additional gas diffusion layer or backing layer was employed on the anode. Between the cathode end plate and catalyst layer; however, a $5 \text{ cm}^2$ Elat® carbon cloth (E-Tek Inc.) was employed. The entire cell (Figure 5-12) was held together with hand tightened bolts.

Dry medical grade oxygen (Praxair Inc.), at various pressures (i.e. 6.8 and 15 pisg), was fed to the cathode and a 0.5 M ethanol or 0.5 M ethanol and 0.5 M $\text{H}_2\text{SO}_4$ electrolyte solution was fed to the anode. Feed was through the bottom of the cell, and exit was through a side port, as depicted in Figure 5-13. Backpressure, required for system controls, was maintained with extra dry air (Praxair Inc.). A schematic depicting the fuel and oxidant handling systems present in the test station is given in Appendix F.
The fuel cell was operated using the associated FC Power® software. Parameters for oxygen flow rate, cathode pressure, fuel flow rate, cell temperature, and fuel temperature were adjusted.

Using desired conditions for oxygen flow rate, cathode pressure, and fuel flow rate, the system was heated to 40 °C and deionized water, or deionized water and electrolyte, was allowed to flow through the cell for approximately $2 \frac{1}{2}$ hours to hydrate the membrane. Following hydration, ethanol was added to the feed solution to create a 0.5 M ethanol concentration in the feed and the cell operation temperature was set (i.e. 40 or 60 °C). The fuel was allowed to flow for one to two hours until the open circuit potential had stabilized.

After stabilization, the open circuit potential was recorded and current was drawn from the fuel cell. The cell potential was measured after approximately 10 minutes of operation at a given current density. Increasing current loads were applied starting from 1 mA cm$^{-2}$ and progressing until the cell potential approached zero. A polarization curve was prepared by plotting cell potential versus current density, and a power density curve was prepared by plotting the product of cell potential and current density (cell power) against current density.
When all measurements were completed, the fuel cell system was flushed with deionized water for approximately 1 hour, changing the solution often, until the no potential registered on the cell and the pH of the water solution was neutral.
6.0 Results and Discussion

6.1 Bönnemann Colloidal Deposition on Graphite Felt

To investigate whether the Bönnemann colloidal method can be applied to produce nanoparticles of catalyst on three dimensional substrates (e.g. graphite felt), a Pt – Sn colloid catalyst was prepared using a 2:1 metal salt ratio and deposited on a 40 x 40 x 2 mm carbon felt substrate as detailed in Sections 5.3.1 and 5.3.2. Total deposition time was 20 hours.

Cyclic voltammetry results for the sample at a 5 mV s\(^{-1}\) scan rate and 20 °C are shown in Figure 6-1.

![Figure 6-1: Electro-oxidation of ethanol on Pt\(_2\)Sn catalyst, supported on graphite felt, prepared using the Bönnemann method. Operation temperature: 20°C. Scan rate: 5 mV/s. Electrolyte: 0.1 M H\(_2\)SO\(_4\) + 0.5 M EtOH](image-url)
Figure 6-1 depicts three curves, one in the blank 0.1 M H$_2$SO$_4$ solution and two successive scans in 0.5 M ethanol + 0.1 M H$_2$SO$_4$ solution. In the presence of ethanol, the catalyst clearly demonstrated activity indicated by increased current density relative to the scan in blank acid.

An onset of ethanol oxidation occurs at -0.23 and -0.16 V MSE in the first and second forward scans respectively. This is followed by a steady increase in current density which peaks at 2.5 mA cm$^{-2}$/0.22 V MSE for the first ethanol scan and 3.5 mA cm$^{-2}$/0.27 V MSE for the second. The potential was not increased beyond 0.50 V MSE in order to avoid the possible dissolution of any Sn catalyst. On the reverse scans respective peak current densities of 3.4 mA cm$^{-2}$/0.10 V MSE and 4.6 mA cm$^{-2}$/0.09 V MSE were observed.

The changes in cyclic voltammetry signals between the two successive scans may suggest that there are two different types of active sites on the catalyst (e.g. individual Pt and Sn deposits as well as Pt-Sn alloy deposits). In the second scan, the increase in the ethanol oxidation overpotential is likely due to changes in Pt-Sn catalyst structure (i.e. possible poisoning), brought on after the initial exposure to the ethanol solution, as only Pt-Sn alloy should be active at these potentials. The increase in magnitude for the current density peaks may indicate that the pure Pt catalyst surface is cleaner upon scanning over a range of reductive and oxidative potentials in the ethanol solution. In subsequent scans (i.e. third or forth scans) the activity is stable and compares well with the second scan. Hence, although the first scan at 5 mV s$^{-1}$ provides good information about fresh catalyst activity, the second scan is used to compare features at all scan rates.

Figure 6-2 shows the scan rate dependence of the voltammetric behaviour for the Bönnemann deposited catalyst at scan rates of 5, 10, 50, 100 and 200 mV s$^{-1}$. For simplicity, the blank acid scans are not included but can be found in Appendix C. It is observed that the same peak features are apparent at the 10 mV s$^{-1}$ scan rate, with a peak current density of 4.00 mA cm$^{-2}$ occurring on the forward scan at 0.28 V MSE, and a peak current density of 5.61 mA cm$^{-2}$ occurring on the reverse scan at 0.10 V MSE. The onset of oxidation at 10 mV s$^{-1}$ occurs at -0.16 V MSE. The location of these peaks in this sample compare favourably with data published in literature for Pt–Sn catalysts. In 0.5 M H$_2$SO$_4$ and 1 M ethanol for a Pt$_1$Sn$_1$ catalyst, Zhou et al. (2003) report forward and reverse peak current densities at 0.71 V and 0.46 V SCE (~ 0.31 V and 0.06 V MSE) respectively, in cyclic voltammetry at 10 mV s$^{-1}$.
At progressively higher scan rates, the forward peak current density becomes less predominant appearing as a "shoulder" of 5.86 mA cm$^{-2}$ at 0.32 V MSE for 50 mV s$^{-1}$, and nearly disappearing all together at 100 and 200 mV s$^{-1}$. The reverse peak shows a steady increase in magnitude with scan rate up to 100 mV s$^{-1}$. The potential at which the reverse peak occurs remained relatively constant at 0.1 V MSE with changing scan rate. The disappearance of the forward peak at high scan rates is indicative of slow oxidation kinetics. At high scan rates there is not enough time to cause the ethanol to reach diffusion control.

It has been reported in literature (Zhou et al, 2003), that there are two forward oxidation peaks for the electrooxidation of ethanol on Pt-Sn in cyclic voltammetry studies. This phenomenon
may again be the result of two different types of active sites. In this case, it is evident that we observe the first oxidation peak on the forward scan, and that the second, if it occurs at all, would occur at higher potentials where the binary catalyst is not necessarily stable.

Figure 6-3 shows the magnitude of both the forward and reverse peaks as a function of the square root of scan rate.

![Figure 6-3: Diffusion control in the forward and reverse peak of ethanol electro-oxidation by cyclic voltammetry on Pt₂Sn catalyst, supported on graphite felt, prepared using the Bönnemann method. Operation temperature: 20°C. Electrolyte: 0.1 M H₂SO₄ + 0.5 M EtOH](image)

Figure 6-3 shows that for the forward scan, the relationship is linear ($R^2 = 1.00$), indicating that the Randles-Sevcik equation for irreversible electro-oxidation applies (Equation 2-19b) and the forward peak is diffusion controlled. In the reverse peak, the relationship is linear ($R^2 = 1.00$) in the same range as the forward peak (5 to 50 mV s⁻¹), again suggesting diffusion control, after which it begins to level off. These observations suggest that the forward and reverse scan oxidation peaks are related. Coincident with the loss of peak on the forward scan, the peak on the reverse scan begins to
decay. One explanation for this phenomenon is that the species that are formed in forward scan peak are also oxidized in the reverse scan peak.

ICP-OES confirms a very low catalyst loading of 44 μg cm\(^{-2}\) for the Bönennemann colloidal deposition, which is visually verified by limited success in locating any appreciable deposit of catalyst on the substrate by HiRes SEM. This low loading explains the prevalence of low current densities observed in ethanol runs of cyclic voltammetry. On a mass basis activity; however, the catalyst performs quite well. The forward peak current density observed at a 10 mV s\(^{-1}\) scan rate, for instance, translates to a mass activity of 131 mA mg\(^{-1}\) Pt, which compares very favourably with literature values of 46 mA mg\(^{-1}\) Pt (Zhou et al, 2003). The results of these observations suggest that the Bönennemann method produces an active catalyst with a high utilization efficiency on the felt; however, modifications to the method are necessary in order to produce higher loadings on three dimensional substrates.

6.2 Electrochemically mediated colloidal metal deposition on 3-D substrates: Surfactant adsorption variant

6.2.1 Effect of applied current

Pt – Sn colloid catalysts were prepared using a bulk 2:1 Pt:Sn ratio and deposited on a 40 x 40 x 2 mm carbon felt substrate, in the presence of current, as detailed in Sections 5.3.1 and 5.3.3. Initially, current densities of 0, 1.25, 2.50, 6.25 mA cm\(^{-2}\) were applied, for a total deposition time of 7 hours, and with a 10 minute delay between the application of the electric field and the dropwise introduction of the salt suspension. This delay allows for the electrosoption/adsorption of tetraoctylammonium triethylhydroborate on the cathode graphite felt.

Cyclic voltammetry results for the samples at a 5 mV s\(^{-1}\) scan rate (second scan) and 20 °C are shown in Figure 6-4. For simplicity, the reverse scans are not included but can be found in appendix C. The sample Pt:Sn ratios on the surface and in the interior of the substrate, as determined by EDX analysis, and estimated mass loadings (Appendix B) are presented in Table 6-1.
Figure 6-4: Electro-oxidation of ethanol by cyclic voltammetry on Pt$_2$Sn catalyst supported on graphite felt using electrochemically mediated colloidal metal deposition (surfactant adsorption variant) at various applied current densities. Operation temperature: 20°C. Scan rate: 5 mV s$^{-1}$. Electrolyte: 0.1 M H$_2$SO$_4$ + 0.5 M EtOH

Table 6-1: Deposited Pt:Sn ratios, determined by EDX, and estimated loadings (Appendix B) on catalysts prepared using electrochemically mediated colloidal metal deposition (surfactant adsorption variant, 2:1 bulk Pt:Sn ratio) at various applied current densities.

<table>
<thead>
<tr>
<th>Deposition Current Density (mA cm$^{-2}$)</th>
<th>Exterior Pt:Sn ratio</th>
<th>Interior Pt:Sn ratio</th>
<th>Estimated loading (mg cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.1:1</td>
<td>2.2:1</td>
<td>4.4E-2</td>
</tr>
<tr>
<td>1.25</td>
<td>2.6:1</td>
<td>2.2:1</td>
<td>6.9E-2</td>
</tr>
<tr>
<td>2.50</td>
<td>4.7:1</td>
<td>2.9:1</td>
<td>0.11</td>
</tr>
<tr>
<td>6.25</td>
<td>8.9:1</td>
<td>2.7:1</td>
<td>0.18</td>
</tr>
</tbody>
</table>

The results in Table 6-1 suggest that as the deposition current applied is increased, a higher loading is obtained; however, the Pt:Sn catalyst ratio on the exterior and interior of the substrate increases from the bulk solution ratio of 2:1. This is more pronounced on the exterior of the sample where the ratio increases up to 8.9:1 at a deposition current density of 6.25 mA cm$^{-2}$. It is shown in
appendix D that the limiting current density for electrodeposition of Pt is substantially greater than that of Sn, due to the lower concentration of Sn$^{2+}$, indicating that in pure electrodeposition the catalyst would be Pt rich. These results may indicate that at higher applied current densities, electrodeposition competes with colloidal deposition, and occurs on the exterior of the substrate, and to some extent in the substrate interior.

Figure 6-4 suggests that at higher applied deposition current densities, the performance of the catalyst is better at lower potentials. It is not known; however, if these changes in performance are attributed to a change in catalyst composition or overall catalyst loading (Table 6-1). Also as indicted in Table 6-1, the distribution of the catalyst composition becomes less uniform across the three-dimensional matrix with an increase of the deposition current density. In light of both of these observations, an applied current density of 1.25 mA cm$^{-2}$, was chosen as the appropriate current density for further deposition experiments. At this current density there is increased catalyst activity, versus the zero current (i.e. Bönnemann) sample, the Pt:Sn ratio is maintained close to bulk conditions, and composition distribution across the catalyst substrate is more uniform. Once Pt:Sn ratios are altered, and a preferred ratio is determined, the effects of applied deposition current will be revisited.

**6.2.2 Effect of deposition time on catalyst activity**

Using a deposition current density of 1.25 mA cm$^{-2}$, Pt – Sn colloid catalyst was prepared with a bulk 2:1 Pt:Sn ratio and deposited on a 40 x 40 x 2 mm carbon felt substrate for 7 and 14 hours respectively. There was a 10 minute delay between the application of the electric field and the dropwise introduction of the salt suspension to afford the surfactant adsorption on the felt.

The deposited catalyst Pt:Sn ratios on the exterior and in the interior of the substrate, as determined by EDX analysis, are presented in Table 6-2.
Table 6-2: Deposited Pt:Sn ratios, determined by EDX, and estimated loadings (Appendix B) on catalysts prepared using electrochemically mediated colloidal metal deposition (surfactant adsorption variant, 2:1 bulk Pt:Sn ratio, 1.25 mA cm\(^{-2}\) applied current) at various deposition times.

<table>
<thead>
<tr>
<th>Deposition time (h)</th>
<th>Exterior Pt:Sn ratio</th>
<th>Interior Pt:Sn ratio</th>
<th>Estimated loading (mg cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>2.6</td>
<td>2.2</td>
<td>6.9E-2</td>
</tr>
<tr>
<td>14</td>
<td>4.5</td>
<td>2.2</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Table 6-2 indicates that for the 14 hour deposition, the exterior of the sample is Pt enriched, versus the interior which remains closer to the bulk Pt:Sn ratio used. This again may indicate the effect of electrodeposition competing with chemical reduction and purely colloidal adsorption.

Figure 6-5: Electro-oxidation of ethanol by cyclic voltammetry on Pt-Sn catalyst supported on graphite felt using electrochemically mediated colloidal metal deposition with 1.25 mA cm\(^{-2}\) applied current (bulk 2:1 Pt:Sn ratio) and various deposition times. Operation temperature: 20°C. Scan rate: 5 mV s\(^{-1}\). Electrolyte: 0.1 M H\(_2\)SO\(_4\) + 0.5 M EtOH
Interestingly, despite a higher loading, the activity of the sample prepared by a 14 hour deposition (Figure 6-5) was inferior. While, the decrease in activity for the 14 hour deposition may be a result of the changes in catalyst composition (Table 6-2), the late onset of oxidation contrasts that of the 2.50 mA cm\(^{-2}\) deposition in Figure 6-4 that has a similar composition. A more probable explanation would be that after 7 hours, all the active deposition sites of the catalyst substrate are occupied by colloidal deposit and deposition only continues by growth of the initial deposits by electrodeposition, mostly of Pt. This would account for the increased loading estimate (Table 6-2) and these larger particles will subsequently be less active.

**6.2.3 Proposed mechanism**

Although at higher applied deposition current densities and longer deposit times there is some indication that significant electrodeposition may occur, it is also evident that at shorter deposit times, and lower applied deposition current densities (i.e. 1.25 mA cm\(^{-2}\)), the deposit is largely colloidal (i.e. chemical reduction). This is evident in Table 6-1 as the catalyst composition on the both the exterior and interior of the substrate remains close to that found in the bulk solution. Additionally, by HiRes SEM it can be seen that the majority of catalyst deposits are in the 3 – 5 nm size range that would be expected by Bönnemann colloidal deposition (Figure 6-6). Due to the substantial increase in activity brought about by electrochemically mediated method, versus the same deposition with no applied current (Figure 6-4), it can be inferred that low applied deposition currents assist colloidal deposit onto the substrate surface.
Figure 6-6: Particle size by HiRes Scanning Electron Microscope for the surfactant adsorption variant of electrochemically mediated colloidal metal deposition on graphite felt using 1.25 mA cm$^2$ applied current.

Figure 6-7 compares catalyst activity in two samples prepared using an applied deposition current density of 1.25 mA cm$^2$. The first is the 7 hour deposition, already discussed, in which a 10 minute delay time is allowed between the time when the deposition current is applied and the addition of the metal salt suspension is commenced. During this delay time only tetroctylammonium triethylhydroyborate is present in the system. The second allows no delay time (i.e. the application of current and addition of metal salt occur at the same time). The deposit obtained without current is added for reference.
Figure 6-7: Effect of time delay between the application of deposition current and the addition of metal salt on the activity of Pt-Sn catalyst, supported on graphite felt using electrochemically mediated colloidal metal deposition.
Operation temperature: 20°C. Scan rate: 5 mV s⁻¹. Electrolyte: 0.1 M H₂SO₄ + 0.5 M EtOH

Figure 6-7 shows that when no delay time is allowed, current actually inhibits the electrochemically mediated deposit, whereas a delay time of 10 minutes substantially improves deposit. It is hypothesized that under the action of the electric field, two competing scenarios are occurring: the first is that tetraoctylammonium hydroborate is consumed by oxidation reactions at the anode, which are parasitic and do not assist in colloidal deposition. The second is that the electric field has an electrophoretic affect, causing migration of the positively charged portion of the tetraoctylammonium hydroborate molecules (i.e. the tetraoctylammonium salt) towards the cathode where they absorb (Figure 6-8). This mechanism aligns with that proposed by Reetz and Helbig (1994), and outlined in Section 4.2.5, in which tetraoctylammonium bromide is found to migrate towards a negatively charged electrode.
Figure 6-8: Schematic of electrochemically mediated colloidal metal formation and deposition. (a) electrophoretic surfactant \([\text{N(octyl)}_4\text{Et}_3\text{BH}]\) adsorption and (b) colloidal metal formation.

When the 10 minute delay time is allowed, an opportunity exists for tetraoctylammonium hydroborate to migrate towards the carbon substrate cathode and, although some of the molecules may still be consumed, the cationic surfactant will exist in large quantities in the vicinity of the cathode. When the delay time is not allowed, the colloidal reaction proceeds quickly in the bulk solution consuming the tetraoctylammonium hydroborate before it reaches the carbon substrate surface.

This hypothesis is supported by visual observations. In the case of the 10 minute delay time, when metal salt solution is introduced a large amount of gas evolution becomes evident on the surface of the carbon substrate. This gas evolution is likely hydrogen and trithethylborate, both of which are byproducts of the colloidal reaction, indicating colloidal formation and metal reduction on the felt surface. The gas evolution continues while approximately 20% of the metal salt suspension is added after which it becomes less evident, and the bulk solution darkens, indicating colloidal reaction in the bulk solution.

In the case of no time delay, gas evolution on the felt substrate is less apparent and the solution darkened in less than half the time. Both these observations are indications that less tetraoctylammonium triethylhydroborate is present in the vicinity of carbon substrate, and more is
present in the bulk solution. The hypothesis of this mechanism is further demonstrated after experiments involving changes in catalyst Pt:Sn ratios are explored.

### 6.2.4 Modification of the Pt:Sn ratio

Using a deposition current density of 1.25 mA cm\(^{-2}\), Pt – Sn colloid catalysts were prepared with metal salt suspensions produced in 0.5:1, 1:1, 9:1 and 25:1 Pt:Sn ratios and compared against the sample already produced using a 2:1 Pt:Sn ratio. In each deposition, the concentration of PtCl\(_2\) in the suspension was held constant and only the concentration of SnCl\(_2\) was adjusted. The total volume of THF was maintained at 105 mL. Coincident with changes in the amount of SnCl\(_2\) used, appropriate changes were made in the concentration of tetraoctylammonium bromide stabilizer, and the volume of 0.37 M tetraoctylammonium triethyl hydroborate used. To complete the data set pure Pt and Sn catalyst samples, respectively, were also made. The concentration of SnCl\(_2\) employed in the pure Sn catalyst sample was the molar equivalent of the PtCl\(_2\) amount used in all other samples. The quantities of each material required in creating the suspensions, as detailed above, are given in Table 6-3.

<table>
<thead>
<tr>
<th>Bulk Pt:Sn ratio</th>
<th>PtCl(_2) (mM)</th>
<th>SnCl(_2) (mM)</th>
<th>N(oct)(_4)Br (mM)</th>
<th>0.37 M N(oct)(_4)BEt(_3)H (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5:1</td>
<td>7.4</td>
<td>14.8</td>
<td>67.2</td>
<td>19.1</td>
</tr>
<tr>
<td>1:1</td>
<td>7.4</td>
<td>7.4</td>
<td>44.9</td>
<td>12.7</td>
</tr>
<tr>
<td>2:1</td>
<td>7.4</td>
<td>3.7</td>
<td>33.6</td>
<td>9.1</td>
</tr>
<tr>
<td>9:1</td>
<td>7.4</td>
<td>0.8</td>
<td>24.9</td>
<td>7.1</td>
</tr>
<tr>
<td>25:1</td>
<td>7.4</td>
<td>0.3</td>
<td>23.3</td>
<td>6.6</td>
</tr>
<tr>
<td>Pure Pt</td>
<td>7.4</td>
<td>-</td>
<td>22.4</td>
<td>6.4</td>
</tr>
<tr>
<td>Pure Sn</td>
<td>-</td>
<td>7.4</td>
<td>22.4</td>
<td>6.4</td>
</tr>
</tbody>
</table>

Catalysts were deposited on a 40 x 40 x 2 mm graphite felt substrate as detailed in Sections 5.3.1 and 5.3.3, using a 10 minute delay between the application of the electric field and the dropwise introduction of the salt suspension, and a total deposition time of 7 hours.

Figure 6-9 depicts cyclic voltammograms at a 5 mV s\(^{-1}\) scan rate (second scan) for the catalysts created using the given bulk Pt:Sn ratios in the metal salt suspensions.
Figure 6-9 suggests that, for the most part, the addition of Sn to the catalyst composition improves the onset of ethanol oxidation, and causes both a shift in potential and magnitude of the forward scan peak current density versus the pure Pt sample. The pure Sn sample had no activity for the electro-oxidation of ethanol. For comparative purposes the quantitative features of each forward ethanol scan are included in Table 6-4. Approximate values for the ‘shoulder’ peak in the bulk 9:1 Pt:Sn sample are also included.
Table 6-4: Quantitative features of cyclic voltammetry forward scans featured in Figure 6-9.

<table>
<thead>
<tr>
<th>Bulk Colloid Pt:Sn ratio</th>
<th>Onset of EtOH oxidation (V MSE)</th>
<th>Peak Ethanol Oxidation i (mA cm⁻²)</th>
<th>Potential (V MSE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>-0.49</td>
<td>7.0</td>
<td>0.22</td>
</tr>
<tr>
<td>1</td>
<td>-0.36</td>
<td>13.5</td>
<td>0.27</td>
</tr>
<tr>
<td>2</td>
<td>-0.31</td>
<td>17.9</td>
<td>0.26</td>
</tr>
<tr>
<td>9</td>
<td>-0.45</td>
<td>9.3/30.3</td>
<td>0.05/0.47</td>
</tr>
<tr>
<td>25</td>
<td>-0.25</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pure Pt</td>
<td>-0.14</td>
<td>20.3</td>
<td>0.39</td>
</tr>
</tbody>
</table>

Both Figure 6-9 and Table 6-4 clearly demonstrate the bifunctional mechanism of Pt – Sn catalysts discussed in Section 4.1. The improvement in the onset of ethanol oxidation, and the potential at which ethanol oxidation peaks, by the inclusion of Sn is the result of the ability of Sn to activate water molecules at low potentials and prevent Pt poisoning at these potentials. At higher potentials where Pt is less readily poisoned; however, the inclusion of Sn may be inhibiting in that it reduces the Pt catalyst’s ability to adsorb ethanol and ethanol oxidation derivatives by modifying the electronic structure of the Pt catalyst (see also Section 4.1 – Ethanol Electro-oxidation). With two competing factors in performance; however, there must exist an optimum range of Pt:Sn ratios in which catalyst performance is improved at all potentials relative to pure Pt. Clearly the catalyst produced by a bulk 9:1 Pt:Sn ratio produced the best result.

It is noted from Figure 6-9 and Table 6-4; however, that although the bulk 9:1 Pt:Sn ratio catalyst provides superior performance at most potentials, the potential at which current density peaks is higher than even the pure Pt sample. An understanding to this is gained by considering the first 5 mV s⁻¹ cyclic voltammogram (Figure 6-10) for the catalyst, in which additional features of the voltammogram (i.e. the shoulder feature in Figure 6-9 and reverse peaks) are more clearly defined.
Figure 6-10: Electro-oxidation of ethanol by cyclic voltammetry (first scan) on Pt-Sn catalyst supported on graphite felt using electrochemically mediated colloidal metal deposition (9:1 bulk Pt:Sn ratio).
Operation temperature: 20°C. Scan rate: 5 mV s\(^{-1}\). Electrolyte: 0.1 M H\(_2\)SO\(_4\) + 0.5 M EtOH

Figure 6-10 shows that two ethanol oxidation peaks are present in the forward scan, one at 0.13 V MSE of magnitude 24.3 mA cm\(^{-2}\), and a second, also present in Figure 6-9, at 0.44 V MSE of magnitude 31.0 mA cm\(^{-2}\). As noted in Section 6.1, two ethanol oxidation peaks are possible and the fact that they both occur in this lower potential range (i.e. before 0.5 V MSE) suggests a highly active catalyst for ethanol oxidation. An additional observation in Figure 6-10 is that along with two forward scan peaks, two reverse scan peaks are formed, confirming that the forward and reverse scan peaks are related as discussed in Section 6.1. In this case the shape of the reverse scan peaks indicate that the species being electrooxidized are adsorbed to the surface of the catalyst.

Figure 6-11 correlates the bulk Pt:Sn ratio with the catalyst composition measured by EDX on the exterior and interior surfaces of the sample.
Figure 6-11: Relationship between Pt:Sn ratios in the catalyst deposit versus those used in the bulk conditions for electrochemically mediated colloidal metal catalyst deposits on graphite felt.

The data presented in Figure 6-11 shows a reasonable linear correlation between the Pt:Sn ratio of the catalyst, as measured by EDX, and the Pt:Sn ratio of the bulk metal solution used to prepare the catalyst (exterior: $R^2 = 0.98$, interior: $R^2 = 0.96$). From these relationships, the relative ratio of Pt:Sn on the substrate exterior/interior can be easily controlled by setting the bulk concentration ratio of metal salts. The average catalyst Pt:Sn ratio for the best performing sample (prepared with the bulk 9:1 Pt:Sn ratio) is 3.1:1 (i.e. 3.6:1 on the exterior, 2.5:1 on the interior).

The data in Figure 6-11 indicates that the catalyst is Pt enriched, relative to the bulk solution, for Pt:Sn ratios of 0.5:1, 1:1, and 2:1 and becomes Sn enriched for the higher Pt:Sn ratios of 9:1 and 25:1. The same trends are visible on both the exterior and interior of the substrate, albeit they are more pronounced on the exterior. For pure faradaic reduction of Sn$^{2+}$ and Pt$^{2+}$, it is shown in appendix D, that as Sn$^{2+}$ concentration in the solution decreases, the limiting current density for Sn$^{2+}$ reduction also decreases and less Sn$^{0}$ will deposit faradaically. The same trend would be apparent
for any colloids formed electrochemically by the method set out by Reetz and Helbig (1994). Thus faradaic deposition and/or faradaic colloid formation alone, does not explain the trends in Figure 6-11. When the competing effects of Bönnemann colloidal deposition are considered; however, an explanation on the trend can be hypothesized.

At the lower Sn concentrations, less Sn$^{2+}$ is reduced faradaically and thus more Sn$^{2+}$ will be available for deposit by Bönnemann colloidal deposition. It maybe this increased Bönnemann deposition that causes the Sn enriched catalyst. Yet to be explained; however, is why large amounts of Sn deposit by faradic means (i.e. electrodeposition and electrochemical colloid formation) are not prevalent on the substrate at the higher Sn concentrations.

One explanation for this may be that although Sn$^{2+}$ is more readily reduced by the method of Reetz and Helbig at higher concentrations, Sn produced by this means may not adhere as well to the catalyst surface as the Bönnemann colloid; but rather remains in solution or easily washes away. By comparison, in the case of Pt, the PtCl$_2$ concentration remained constant throughout all the depositions so it not expected that the relative amounts of faradic reduction of Pt$^{2+}$ and Bönnemann reduction of Pt$^{2+}$ change as the Pt:Sn ratio is altered. This hypothesis is supported by examining the filtrate from the colloid of the 1:1 bulk Pt:Sn prepared sample. The filtrate from this sample, as well as the 0.5:1 bulk ratio sample, contained a crystalline substance not readily observed on colloidal filtrates of the higher Pt:Sn ratios. It is not expected that the Bönnemann colloid would be crystalline, but rather a waxy residue, and any Bönnemann colloid would likely be small enough to pass through the filter. It is expected; however, that colloids produced by the method of Reetz and Helbig, and stabilized by tetraoctylammonium bromide salt, would be crystalline. EDX analysis of the crystalline substance indicated that it was largely Pt and Sn in a 0.7:1 ratio. The finding of colloids produced by the method of Reetz and Helbig, rich in Sn, and remaining in the solution to be captured by filtration, supports the hypothesis outlined above.

In the case of the 9:1 bulk Pt:Sn ratio sample detailed in Section 6.2.4, the net catalyst loading was calculated by mass difference to be 0.44 mg cm$^{-2}$ substrate. This result is in good agreement with that determined by ICP-OES which is also 0.44 mg cm$^{-2}$ (Table 6-5). The remainder of the mass loadings in Table 6-5 are estimated using the EDX-ICP correlation given in Appendix B.
Table 6-5: Estimated loadings (Appendix B) on catalysts prepared using electrochemically mediated colloidal metal deposition (surfactant adsorption) with various bulk Pt:Sn ratios.

<table>
<thead>
<tr>
<th>Bulk Colloid Pt:Sn ratio</th>
<th>Estimated loading (mg cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>8.7E-2</td>
</tr>
<tr>
<td>1</td>
<td>9.7E-2</td>
</tr>
<tr>
<td>2</td>
<td>6.9E-2</td>
</tr>
<tr>
<td>9</td>
<td>0.44</td>
</tr>
<tr>
<td>25</td>
<td>0.33</td>
</tr>
<tr>
<td>Pure Pt</td>
<td>0.23</td>
</tr>
</tbody>
</table>

Table 6-5 shows estimated loadings (Appendix B) for each bulk Pt:Sn ratio. The values further reflect a competing electrochemical formation of Sn colloids by the method of Reetz and Helbig (1994), in that the Sn²⁺ quantity in solution affects the amount of Bönemann colloidal formed and thus the overall catalyst loading. The higher catalyst loading achieved for the bulk 9:1 Pt:Sn sample is at least partially responsible for its promising levels of activity.

### 6.2.5 Reduction of reactor scale

Should the mechanism proposed in Section 6.2.3 prove to be accurate, one problem associated with electrochemically mediated colloidal metal depositions is that once colloidal formation begins in the bulk metal solution, and not in the vicinity of the substrate, the colloid is less likely deposited on the substrate and is effectively lost. One method of overcoming this loss would be to reduce the size of the reaction vessel and thus increase the geometric surface area of the felt cathode per reactor volume ratio of the setup.

For the scale reduction experiment, a 43% reduction was made in reactor volume along with a 20% increase in felt substrate geometric surface area. This produces a geometric surface area of the felt cathode per reactor volume ratio 3.3 times that of the original experiment (0.10 versus 0.03 cm² graphite felt/cm³ reactor volume). The same setup, conditions, and reactant concentrations detailed in Section 5.3.3 were retained; however, the total deposition current employed was adjusted upwards by 20% to maintain the applied deposition current density.
Figure 6-12 shows the cyclic voltammograms at 5 mV s\(^{-1}\) (second scan) from samples produced by both the original scale and the reduced scale with increased substrate surface area.

![Cyclic Voltammogram](image)

**Figure 6-12:** Electro-oxidation of ethanol by cyclic voltammetry on Pt-Sn catalyst supported on graphite felt using electrochemically mediated colloidal metal formation (surfactant adsorption, 9:1 bulk Pt:Sn ratio) at various experimental scales.

Operation temperature: 20°C. Scan rate: 5 mV s\(^{-1}\). Electrolyte: 0.1 M H\(_2\)SO\(_4\) + 0.5 M EtOH

Figure 6-12 suggests that, in this situation, not only is reproducibility between the two scales very good, but the reduced scale may be actually produce a slightly better catalyst. This increase in deposit activity maybe the result of the narrowing of the interelectrode gap that is associated with the scale down.

Unless otherwise noted, the remainder of catalyst deposits in this report are created with the scaled down experiment.
6.2.6 Revisiting the effects of current density for bulk Pt:Sn ratio of 9:1

In Section 6.2.1, an applied current density of 1.25 mA cm$^{-2}$ was chosen for electrochemically mediated colloidal metal depositions as the effects of electrodeposition were minimal. The effects of altering the Pt:Sn ratio in Section 6.2.4; however, tell a slightly different story in that at higher Pt:Sn ratios, a deposition current density of 1.25 mA cm$^{-2}$ has some significant affect on the actual catalyst composition. As a result, the effects of current were revisited on the 9:1 bulk Pt:Sn ratio. Cyclic voltammograms at 5 mV s$^{-1}$ (second scan) for this study are included in Figure 6-13.

![Cyclic voltammogram](image)

**Figure 6-13:** Electro-oxidation of ethanol by cyclic voltammetry on Pt-Sn catalyst supported on graphite felt using electrochemically mediated colloidal metal deposition (surfactant adsorption, 9:1 bulk Pt:Sn ratio) and various deposition current densities. Operation temperature: 20°C. Scan rate: 5 mV s$^{-1}$. Electrolyte: 0.1 M H$_2$SO$_4$ + 0.5 M EtOH
Figure 6-13 suggests that, for the 9:1 bulk Pt:Sn ratio, the 1.25 mA cm\(^{-2}\) current density is preferred to the higher 6.25 mA cm\(^{-2}\) deposition current density. At the 1.25 mA cm\(^{-2}\) deposition current density the onset of ethanol oxidation (-0.45 V MSE) is much earlier than that at the 6.25 mA cm\(^{-2}\) deposition current density (-0.12 V MSE), and the overall current densities of the later sample are much lower over the whole potential range. Furthermore, the features of the sample prepared at 6.25 mA cm\(^{-2}\) compare with that of pure Pt, in that the onset of oxidation is similar (-0.12 V MSE versus -0.14 V MSE) and additionally the peak current density is similar (17.1 mA cm\(^{-2}\) at 0.38 V MSE versus 20.3 mA cm\(^{-2}\) at 0.39 V MSE). This indicates that the trend of creating a Pt rich sample with higher applied current densities is still as evident at the 9:1 bulk ratio as it was for the 2:1 bulk ratio in Section 6.2.1.

**6.2.7 Ternary metal systems**

Pt – Ru based ternary metal systems have been widely explored for electro-catalysis of methanol oxidation and have shown some promising results (Lamy et al, 2002). On this basis, and as discussed in Section 4.1, Pt – Ru based ternary metal systems have also been considered for ethanol electro-oxidation, although none of them have shown any promise above that of Pt – Sn binary systems. Pt – Sn based ternary systems are not frequently reported. As detailed in Section 4.1, studies of only two Pt – Sn based ternary systems, notably Pt – Ru – Sn (Zhou et al, 2003) and Pt – Sn – Ni (Spinacé et al, 2005) could be found.

In attempt to improve upon the bulk 9:1 Pt:Sn metal salt ratio, a third metal was added to the metal salt suspension for electrochemically mediated colloidal depositions. The metals chosen were Pd, Ir, Mo and Ni, with metal salt precursors being PdCl\(_2\), IrCl\(_3\), MoCl\(_3\) and NiBr\(_2\) respectively. The concentrations of PtCl\(_2\) (7.4 mM) and SnCl\(_2\) (0.8 mM) were not changed from the original deposition experiment and PdCl\(_2\), IrCl\(_3\) and MoCl\(_3\) were each added at a concentration of 0.35 mM to contribute as 4.0 molar % of the bulk metal salt solution. Ni on the other hand, was added to the bulk metal salt solution in a concentration of 0.8 mM in order to produce a bulk Pt:Sn:Ni ratio of 9:1:1, as it has been previously established by Spinacé et al (2005) that a significant Ni contribution may improve upon the Pt:Sn binary system. With the metal salt concentration increase brought on by addition of the third metal, an increase in concentration of tetraoctylammonium bromide stabilizer (25.9 mM for
Pd, Ir and Mo, 27.5 mM for Ni) and volume of 0.37 M tetraoctylammonium triethyl hydroborate (7.4 mL for Pd, Ir and Mo, 7.9 mL for Ni) was made accordingly. All experiments were conducted in 105 mL of THF.

Figure 6-14 depicts the cyclic voltammograms at 5 mV s$^{-1}$ (second scan) for the ternary catalysts in contrast to both the 9:1 bulk Pt:Sn ratio catalyst and the pure Pt catalyst. Table 6-6 details the ternary catalyst ratios, as determined by EDX, for both the exterior and interior of the substrate.

![Figure 6-14: Electro-oxidation of ethanol by cyclic voltammetry on ternary catalysts supported on graphite felt using electrochemically mediated colloidal metal deposition (surfactant adsorption). Operation temperature: 20°C. Scan rate: 5 mV s$^{-1}$. Electrolyte: 0.1 M H$_2$SO$_4$ + 0.5 M EtOH](image-url)
Table 6-6: Deposited ternary catalyst ratios determined by EDX on catalysts deposited on graphite felt using electrochemically mediated colloidal metal deposition (surfactant adsorption) with 1.25 mA cm\(^2\) applied current.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Bulk colloid ratio</th>
<th>Exterior Pt:Sn:X ratio</th>
<th>Interior Pt:Sn:X ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt – Sn</td>
<td>9:1</td>
<td>3.6:1</td>
<td>2.5:1</td>
</tr>
<tr>
<td>Pt – Sn – Mo</td>
<td>9:1:0.4</td>
<td>3.5:1:0.9</td>
<td>3.0:1:0.9</td>
</tr>
<tr>
<td>Pt – Sn – Ir</td>
<td>9:1:0.4</td>
<td>3.7:1:0.7</td>
<td>3.4:1:0.2</td>
</tr>
<tr>
<td>Pt – Sn – Pd</td>
<td>9:1:0.4</td>
<td>6.4:1:0.0</td>
<td>4.3:1:0.2</td>
</tr>
<tr>
<td>Pt – Sn – Ni</td>
<td>9:1:1</td>
<td>18.9:1:1.0</td>
<td>3.9:1:1.7</td>
</tr>
</tbody>
</table>

The ratios given in Table 6-6 suggest that the addition of Mo or Ir to the Pt – Sn system does not significantly affect the relative Pt:Sn deposition ratio, on the exterior of the substrate, whereas the addition of Pd or Ni enriches the Pt content of the catalyst, most likely by creating selective nucleation sites.

Figure 6-14 suggests that Mo and Ir had a negative effect on the overall performance for ethanol electro-oxidation. In the case of these two ternary alloy systems, it maybe that the third metal negatively effects the Pt catalyst structure, not allowing it to absorb ethanol or ethanol intermediates as easily. Additionally the performance of the Pt-Sn-Ni catalyst, in the ratio studied, appears to significantly reduce the catalyst performance. This is most likely due to the change in the Pt:Sn ratio of the deposit, at least on the surface of the substrate, as indicated in Table 6-6. Altering the Ni content in this catalyst may produce more favorable results.

Despite an apparent difference in the Pt:Sn ratio for the Pt-Sn-Pd catalyst, versus the Pt - Sn binary catalyst, the sample appears to perform equivalently to the Pt-Sn catalyst, if not slightly better at lower potentials. One indication for this is that the Pd deposit is sporadic, not detected on the exterior and only detected in one of three EDX readings in the interior of the substrate. This would suggest that Pd is not readily deposited in the catalyst by this method, but its presence influences the deposition of the Pt:Sn ratio.

Due to limited improvements in activity, ternary formulations are not used in the remainder of this study.
6.2.8 Electrodeposition versus Electrophoresis

As established in Sections 6.2.4 and 6.2.6, it is evident that electrodeposition may compete with the electrophoretic colloidal mechanism outlined in 6.2.3, in which the metal salts are reduced chemically by triethyl hydroborate. The extent to which competing electrodeposition occurs is determined experimentally in this section.

To evaluate the effect of the chemical reductant portion of the tetraoctylammonium triethyl hydroborate molecule (i.e. triethyl hydroborate) in creating the electrochemically mediated colloidal metal depositions, a sample was prepared without it. In place of the tetraoctylammonium triethyl hydroborate in this experiment, a 0.37 M solution of tetraoctylammonium bromide in THF was prepared and delivered to the felt suspension in the same matter as the tetraoctylammonium trithyl hydroborate. All other parameters remained the same, and the sample was created using a bulk 9:1 Pt:Sn metal salt ratio in the scaled down 50 mL jacketed vessel.

As evident in Figure 6-15, the catalyst sample created without the chemical reductant shows very little activity in ethanol relative to that of the blank acid electrolyte solution, comparable to pure Sn. This suggests that, although electrodeposition may have a role; it does not act independently of colloidal formation. This is further supported by the calculations given in appendix D, which would suggest that under pure electrodeposition (assuming 100% current efficiency) all the metal in solution would deposit within the time allowed. This is obviously not occurring as already confirmed by ICP-OES and sample mass difference. EDX analysis for this sample also shows a low Pt:Sn ratio for this sample (exterior 0.8:1, interior: 1.0:1), indicating a Sn enriched catalyst. Therefore, electrodeposition in the absence of reductant, maybe occurring primarily for Sn. One possible explanation for this is that SnCl₂ is fully soluble in THF where as PtCl₂ is only slightly soluble and therefore much more Sn²⁺ ions will exist in solution.

Since appreciable electrodeposition does not appear to be occurring independently of Bönne mann colloid formation, the electrophoretic mechanism outlined in Section 6.2.3 is considered operative. Additionally the electrochemical formation of Sn colloids appears to be occurring and may be responsible for the deposit Pt:Sn ratios observed in Section 6.2.4
Figure 6-15: Electro-oxidation of ethanol by cyclic voltammetry on Pt-Sn catalyst supported on graphite felt using electrodeposition in organic media (9:1 bulk Pt:Sn ratio) in the absence of hydroborate reductant. Operation temperature: 20°C. Scan rate: 5 mV s⁻¹. Electrolyte: 0.1 M H₂SO₄ + 0.5 M EtOH

6.3 Improving the catalyst load

Although vast improvements in catalyst loading have been made by electrochemically mediated colloidal metal salt depositions over the traditional Bönnemann method (0.44 versus 0.044 mg cm⁻²), the loading still remains low compared to most conventionally produced direct alcohol fuel cell anodes (~1-4 mg cm⁻²). Therefore, several further attempts were made to improve the catalyst loading, and are described herein.
6.3.1 Pd nucleation

Deposits were attempted on Pd nucleated graphite felt (Section 5.2.1) using the electrochemically mediated colloidal metal deposition method with and without applied deposition current.

Cyclic voltammograms at 5 mV s$^{-1}$ (second scan) for the Pd nucleated catalysts, in contrast to the same methods on untreated substrate, are given in Figure 6-16. Composition data, as determined by EDX, is included in Table 6-7. In this study a bulk Pt:Sn ratio of 2:1 was utilized and current assisted depositions were conducted at 1.25 mA cm$^{-2}$ for 7 hours with a 10 minute delay between the application of electric field and the introduction of metal salt.

![Figure 6-16: Electro-oxidation of ethanol by cyclic voltammetry on Pt-Sn catalyst supported on graphite felt using electrochemically mediated colloidal metal deposition (surfactant adsorption, 2:1 bulk Pt:Sn ratio), and the same without current, on Pd nucleated felt. Operation temperature: 20°C. Scan rate: 5 mV s$^{-1}$. Electrolyte: 0.1 M H$_2$SO$_4$ + 0.5 M EtOH](image-url)
Table 6-7: Deposited Pt:Sn ratios determined by EDX on catalysts prepared using electrochemically mediated colloidal deposition (2:1 bulk Pt:Sn ratio) on Pd nucleated graphite felt.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>No current</td>
<td>2.1:1</td>
<td>2.2:1</td>
</tr>
<tr>
<td>No current/Pd nucleation</td>
<td>0.6:1:8.3</td>
<td>1.3:1:0.1</td>
</tr>
<tr>
<td>1.25 mA cm$^{-2}$ current</td>
<td>2.6:1</td>
<td>2.2:1</td>
</tr>
<tr>
<td>1.25 mA cm$^{-2}$ current/Pd nucleation</td>
<td>2.2:1:1.1</td>
<td>2.7:1:0</td>
</tr>
</tbody>
</table>

Figure 6-16 shows that the Pd nucleated felt increases catalyst activity for samples prepared in the absence of applied current, but reduces the catalyst activity in the presence of 1.25 mA cm$^{-2}$ of applied current density. The increase in activity of the Pd nucleated sample for the traditional Bönnemann method may be attributed to two things: The first is an increased loading (0.14 versus 4.4E-2 mg cm$^{-2}$ as measured by ICP-OES) brought about by increased deposition sites; and the second is the potential catalytic properties of deposited Pd itself. It is noted, in Table 6-7, that a substantial amount of Pd is detected on the outer surfaces of the catalyst substrate. The ratios in Table 6-7 also suggest that Pd nucleation sites have a preference for Sn deposition, and although it is suspected that this Pt:Sn ratio is not especially active for ethanol oxidation, the presence of Pd and increased load still improve the overall catalyst activity.

In considering the current assisted method, Table 6-7 shows there is less of a shift in the Pt:Sn ratio versus the untreated sample. This may suggest that the decrease in activity, shown in Figure 6-16, for the Pd nucleated sample may be the result of a decrease in catalyst loading brought about by the catalytic activity of the Pd nucleated sites towards hydroborate decomposition. This assumption is supported by visual observations. During surfactant electroadsorption there is a large amount of gas evolution on the graphite felt substrate throughout the 10 minutes that tetraoctylammonium triethylhydroborate is left under the action of an electric field. The gas evolution is likely an indication that the organic hydroborate is decomposing (i.e. evolving BE$_3$ and H$_2$ gas). The lower Pd:Pt ratio evident on the catalyst prepared with assisted current is attributed to the fact that the total Pd content between the two samples has not changed; however, the Pt-Sn catalyst loading is higher for the current assisted method.
6.3.2 Sn sensitization

As it was hypothesized in Section 6.3.2 that the presence of Pd nucleated sites may hinder electrochemically mediated colloidal metal deposition by enhancing the oxidation of tetraoctylammonium triethyl hydroborate, an attempt was made to treat the graphite felt with only the first step of the nucleation process: Sn sensitization.

Sn sensitization was performed in a matter identical to that of Pd nucleation outlined in Section 5.1.1, only PdCl₂ was omitted from the treatment solution. Cyclic voltammograms at 5 mV
s⁻¹ (second scan) for the Sn sensitized catalyst, in contrast to the same method on untreated substrate, are given in Figure 6-17. In this instance a deposition current density of 1.25 mA cm⁻² was used with a 10 minute delay between the application of electric field and the introduction of metal salt.

As shown by Figure 6-17, Sn sensitization alone does not have a positive affect on catalyst activity. The visual observations made during this deposition also indicate that deposition may be hindered by increased degradation of tetraoctylammonium triethyl hydroborate brought about by the presence of adsorbed Sn²⁺ on the substrate surface.

6.3.3 Nitric acid wash

Deposits were attempted on nitric acid oxidized graphite felt (Section 5.2.2) using the electrochemically mediated method with a deposition current density of 1.25 mA cm⁻².

![Figure 6-18: Electro-oxidation of ethanol by cyclic voltammetry on Pt-Sn catalyst supported on nitric acid treated graphite felt using electrochemically mediated colloidal metal deposition (surfactant adsorption, 9:1 bulk Pt:Sn ratio). Operation temperature: 20°C. Scan rate: 5 mV s⁻¹. Electrolyte: 0.1 M H₂SO₄ + 0.5 M EtOH](image)
As shown by Figure 6-18, nitric acid pretreatment of the substrate does not have a positive affect on catalyst activity. The visual observations made during this deposition again indicate that deposition may be hindered by increased degradation of tetraoctylammonium triethylhydroborate brought about by nitric acid induced oxidation of the substrate surface.

6.3.4 Tetraoctylammonium triethyl hydroborate charging time

As suggested in Section 6.2.3, a 10 minute time delay between the application of the electric field and introduction of metal salt appears to significantly enhance catalyst activity and deposit for electrochemically mediated colloidal metal depositions. In this instance, a longer delay time of 60 minutes is allowed in order to determine if more tetraoctylammonium triethyl hydroborate will migrate towards the cathode under this increased amount of time. This sample was also prepared using the bulk 9:1 Pt:Sn metal salt ratio and conditions identical to the previous section. The 5 mV s$^{-1}$ cyclic voltammogram (second scan) of these results is shown in Figure 6-19, and contrasted against the same sample prepared with the original 10 minute time delay.

It is suggested in Figure 6-19 that after 60 minutes of delay, in which the cathode is presumably charged with the tetraoctylammonium triethyl hydroborate molecule, the activity of the sample produced is significantly reduced at all potentials in the CV scan. This may suggest that the tetraoctylammonium triethyl hydroborate is being oxidized at the anode, as hypothesized in Section 6.2.3, and the delay time required must be short enough to limit electrochemical decay of the molecule, yet long enough to allow electrophoretic migration. In this instance, 60 minutes is too long of a delay time.
Figure 6-19: Electro-oxidation of ethanol by cyclic voltammetry on Pt-Sn catalyst supported on graphite felt using electrochemically mediated colloidal metal deposition (surfactant adsorption, 9:1 bulk Pt:Sn ratio) and a varying delay time between the application of electric field and the introduction of metal salt suspension.
Operation temperature: 20°C. Scan rate: 5 mV s\(^{-1}\). Electrolyte: 0.1 M H\(_2\)SO\(_4\) + 0.5 M EtOH

6.4 Electrochemically mediated colloidal metal deposition on 3-D substrates: Metal adsorption

6.4.1 A Comparison to Surfactant Adsorption

As detailed in Section 5.3.3, a variant of the electrochemically mediated technique was also investigated in which the order of the two key reaction components, namely the tetraoctylammonium triethylhydroborate reductant and the metal salt suspension, are introduced in reverse order. More specifically, in this variant the metal salt is present in the reactor initially and tetraoctylammonium
triethylhydroborate is added dropwise under the action of the electric field. It is hypothesized that, in this variant, the metal salts/ions will initially adsorb to the three-dimensional substrate.

This variant is first trialed with a bulk Pt:Sn ratio of 9:1 and 1.25 mA cm$^{-2}$ of applied current for 7 hours. For this order of reactant addition, there was no delay between the application of electric field and the addition of the second compound (i.e. tetraocylammonium triethylhydroborate). This was due to the fact that the metal salt suspension on its own on did not have enough conductivity to maintain the applied current density. The 5 mV s$^{-1}$ cyclic voltammogram (second scan) of these results are shown in Figure 6-20, contrasted against the same 9:1 ratio sample prepared with the original order of reactant addition (i.e. surfactant adsorption) conducted in Section 6.2.

Figure 6-20: Electro-oxidation of ethanol by cyclic voltammetry on Pt-Sn catalyst supported on graphite felt using surfactant and metal adsorption variants of electrochemically mediated colloidal metal deposition (9:1 bulk Pt:Sn ratio).
Operation temperature: 20°C. Scan rate: 5 mV s$^{-1}$. Electrolyte: 0.1 M H$_2$SO$_4$ + 0.5 M EtOH
From Figure 6-20 it is difficult to determine whether or not the metal adsorption variant produces a better performing catalyst than the surfactant adsorption variant. Based on Figure 6-20 the surfactant adsorption variant produces higher current densities than the metal adsorption variant throughout the higher potential range; however, there is an improvement in current density at lower potentials as well as the onset of ethanol oxidation (-0.53 versus -0.45 V MSE), for the metal adsorption variant.

Additional electrochemical testing was required in order to better differentiate between the two samples and chronopotentiometry results conducted at 20 °C are shown in Figure 6-21.

![Figure 6-21: Electro-oxidation of ethanol by chronopotentiometry on Pt-Sn catalyst supported on graphite felt using surfactant and metal adsorption variants of electrochemically mediated colloidal metal deposition (9:1 bulk Pt:Sn ratio). Operation temperature: 20°C. Electrolyte: 0.1 M H₂SO₄ + 0.5 M EtOH](image)

As depicted in Figure 6-21, under the same applied current densities, the half cell potential for metal adsorption variant is consistently lower than the surfactant adsorption variant. This
suggests that the metal adsorption variant produces better performing catalysts, at least in the low potential range that is of interest for the direct ethanol fuel cell. Several factors could contribute to this difference in performance, the first is a composition difference between the two samples, as determined by EDX, detailed in Table 6-8.

<table>
<thead>
<tr>
<th>Preparation Method</th>
<th>Exterior Pt:Sn ratio</th>
<th>Interior Pt:Sn ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surfactant adsorption</td>
<td>3.6</td>
<td>2.5</td>
</tr>
<tr>
<td>Metal salt adsorption</td>
<td>3.8</td>
<td>4.0</td>
</tr>
</tbody>
</table>

As suggested in Table 6-8, the Pt:Sn ratio obtained for the metal adsorption variant on the exterior of the substrate does not change substantially from the surfactant adsorption variant. However, the ratio within the interior of the substrate has increased substantially for the metal salt adsorption variant. With the increase in Pt:Sn ratio for the interior of the sample, Pt:Sn ratio distribution across the catalyst, for the metal adsorption variant, is more uniform. This may be an indication that the early exposure of the felt substrate to a high concentration of metal salt, under an applied current, favours a more uniform adsorption and nucleation of metal sites across the thickness of the felt.

Figure 6-22 shows the particle sizes achieved for the metal adsorption variant of the electrochemically mediated colloidal metal deposition on graphite felt. When contrasted against the surfactant adsorption technique (Figure 6-6), there is a clear indication that the metal adsorption variant produces larger particles. It should be noted; however, that two distinct ranges of particle size exist within this deposit; those in the 3 - 10 nm range and those in the 30 - 50 nm range. This could be a possible indication that the effects of electrodeposition and colloidal deposition are acting more independently than observed by the surfactant adsorption variant in Section 6.2.

As in the surfactant adsorption variant, a good indication of sample loading could be determined for this sample by weight difference. This was determined to be approximately 1.1 mg cm\(^{-2}\) also coinciding well with the value of 0.96 mg cm\(^{-2}\) determined by ICP-OES. This substantial increase, compared to the surfactant adsorption variant (0.44 mg cm\(^{-2}\)), is responsible for the improved activity shown by chronopotentiometry (Figure 6-21).
6.4.2 Effect of current density and Pt:Sn ratio

In order to evaluate effects of deposition current density and bulk Pt:Sn ratio, two additional deposits were performed for the metal adsorption variant, one with an increase in applied current density (2.50 mA cm$^{-2}$) and a second with a change in the bulk metal salt composition (2:1 Pt:Sn).
Figure 6-23: Electro-oxidation of ethanol by cyclic voltammetry on Pt-Sn catalyst supported on graphite felt using the metal adsorption variant of the electrochemically mediated colloidal metal deposition method at varying conditions. Operation temperature: 20°C. Scan rate: 5 mV s\(^{-1}\). Electrolyte: 0.1 M H\(_2\)SO\(_4\) + 0.5 M EtOH

Figure 6-23 depicts the 5 mV s\(^{-1}\) cyclic voltammogram (second scan) showing the effect of deposition current density and bulk Pt:Sn ratio on the metal adsorption variant. It is confirmed in these plots that the 2:1 bulk Pt:Sn ratio is again a poorer performer than the 9:1 bulk Pt:Sn ratio, showing much lower onset of oxidation (-0.31 versus -0.53 V MSE) and overall lower current density. This reflects the results obtained for the surfactant adsorption variant.

The higher applied current density results in a lower onset of ethanol oxidation (-0.47 versus -0.53 V MSE) and apparent improvements in catalyst activity at higher potentials. However, it is noted that these improvements are still within the variation of the two replicate samples that will be compared for the metal adsorption variant in the following section.
Figure 6-24: Electro-oxidation of ethanol by chronopotentiometry on Pt-Sn catalyst supported on graphite felt using the metal adsorption variant of the electrochemically mediated colloidal metal deposition (9:1 bulk Pt:Sn ratio) with varying deposition current densities. Operation temperature: 20°C. Electrolyte: 0.1 M H₂SO₄ + 0.5 M EtOH

Figure 6-24 depicts chronopotentiometry results from catalysts produced by the metal adsorption variant using both 1.25 and 2.50 mA cm⁻² deposition current densities. The results in these plots confirm that the effect of deposition current density will need to be further investigated before its influence on catalyst activity can be assessed.

6.5 Reproducibility

Before processes developed in Sections 6.2 and 6.4 are used to create fuel cell catalysts, it is necessary to determine that the activity of the electrochemically mediated colloidal metal deposits is relatively reproducible.
Figure 6-25 depicts the 5 mV s\(^{-1}\) cyclic voltammogram (second scan) of three catalysts prepared using the surfactant adsorption variant with standard conditions and a 9:1 bulk Pt:Sn ratio. Two of these samples were prepared at the original experiment scale, and one at the reduced scale.

Figure 6-25 suggests that, particularly at lower potentials of interest in the direct alcohol fuel cell, reproducibility is good for the surfactant adsorption variant. The slightly better current density associated with lower potentials for the reduced scale can again be associated with a smaller interelectrode gap as indicated in Section 6.2.5.

Considering now the metal adsorption variant, repeats of the sample created in Section 6.4 was completed. Figure 6-26 depicts the 5 mV s\(^{-1}\) cyclic voltammogram (second scan) of three catalysts prepared at the reduced scale with standard conditions and a 9:1 bulk Pt:Sn ratio.
Figure 6-26: Demonstration of reproducibility in electro-oxidation of ethanol by cyclic voltammetry on Pt-Sn catalyst supported on graphite felt using the metal adsorption variant of electrochemically mediated colloidal metal deposition (9:1 bulk Pt:Sn ratio). Operation temperature: 20°C. Scan rate: 5 mV s⁻¹ Electrolyte: 0.1 M H₂SO₄ + 0.5 M EtOH

Figure 6-25 expresses acceptable reproducibility for the metal adsorption variant as well.

6.6 **Sample Heat Treatment**

As indicated in Section 4.2.5 – Protective Shell Colloids, it has been widely published that heat treatment of Bönnemann colloidal prepared catalyst is necessary to remove the protective shell before any catalytic activity is obtained. In the studies detailed in Sections 6.2 through 6.5 no heat treatment has been performed; however, the catalysts have displayed good activity. Furthermore, evidence of Pt and Sn oxidative and reductive features in blank acid solutions have been clearly visible during cyclic voltammetry, particularly at higher loadings (Appendix C). This may be an
indication that, under the modified methods, heat treatment is not necessary and that the ethanol washes followed by chemical and electrochemical cleaning are sufficient.

To test the effect of heat treatment both the surfactant and metal adsorption variants of the electrochemically mediated colloidal metal depositions were subjected to heat treatments for 1 hour, at 200 °C (See also Section 5.4). Temperatures above 200 °C could not be explored due to the low melting point of tin (232.0 °C). Figure 6-27 shows the 5 mV s$^{-1}$ cyclic voltammogram (second scan) of the variants produced with a 9:1 bulk Pt:Sn ratio, with and without heat treatment.

![Figure 6-27: Electro-oxidation of ethanol by cyclic voltammetry on Pt-Sn catalyst supported on graphite felt using the surfactant and metal adsorption variants of the electrochemically mediated colloidal metal deposition technique (9:1 bulk Pt:Sn ratio), with and without heat treatment under N$_2$ gas at 200 °C for 1 hour. Operation temperature: 20°C. Scan rate: 5 mV s$^{-1}$. Electrolyte: 0.1 M H$_2$SO$_4$ + 0.5 M EtOH](image)

Figure 6-27 demonstrates that, although heat treatment at 200 °C has little or no effect on the surfactant adsorption variant, it causes a substantial decrease in catalytic activity for the metal.
adsorption variant. Although it is expected that the smaller catalyst particles evident in the surfactant adsorption variant be more prone to melting and agglomeration under these conditions, it is also noted that the particles are more widely dispersed (Figure 6-6) than in the metal adsorption variant (Figure 6-22). It may be that the higher loading and increased proximity of particles in the metal adsorption variant contributes more to particle agglomeration during heat treatment and causes this apparent reduction in activity.

Since no improvements with heat treatment are noted on either electrochemically mediated colloidal metal deposition, heat treatment was not applied on the remainder of the samples prepared in this study.

6.7 Pt-Sn effective surface area by Cu UPD and stripping

Since it is not clear if Cu UPD deposition occurs on Sn in the study of Boucher and Alonso-Vante (2003), its application on Pt – Sn catalysts was first determined experimentally. This was accomplished by analyzing cyclic voltammograms of Sn and Pt – Sn based catalysts in Cu^{2+} solutions (See also Experimental Methods, Section 5.6.5). Once applicability was verified, effective surface area could be determined as has previously been accomplished for Pt – Ru based alloys (Green and Kucernak, 2002).

6.7.1 Cu UPD and stripping on Sn

In order to assess the applicability of Cu UPD on Sn deposits, the Sn catalyst sample created by electrochemically mediated colloidal metal deposition (surfactant absorption variant, Section 6.2.4) was subjected to cyclic voltammetry (Figure 6-28) over the range of 0.4 to -0.5 V MSE, and a scan rate of 2 mV s^{-1}, in a 0.1 M H_{2}SO_{4} and 2 mM CuSO_{4} solution (see also Experimental Methods, Section 5.6.5).
Figure 6-28: Demonstration of Cu UPD and bulk deposition by cyclic voltammetry on Sn catalyst supported on graphite felt using electrochemically mediated colloidal metal deposition (surfactant adsorption variant).
Operation temperature: 20°C. Scan rate: 0.5 mV s^{-1}. Electrolyte: 0.1 M H_2SO_4 + 2 mM CuSO_4

Figure 6-28 shows that in the forward scan, from 0.4 to -0.5 V MSE, the underpotential deposition of Cu^{2+} (I) begins at -0.27 V MSE and progresses until -0.45 V MSE when bulk deposition (II) commences. The potential at which bulk deposition of Cu^{2+} commences experimentally corresponds closely with the theoretical value as determined by the Nernst equation (Equation 6-1).

\[
Cu^{2+} + 2e^- \rightarrow Cu^0 \quad E_o = -0.42 \text{ V MSE}
\] (Eq. 6-1)

The anodic (return) portion of the scan shows the generation of current associated with the oxidation and stripping of Cu (III) from the surface of the Sn deposit between -0.41 and -0.34 V MSE.
In order to investigate the underpotential deposition region only, cyclic voltammetry scans were completed over the range of 0 to -0.45 V MSE. The Cu UPD stripping was apparent on the anodic portion of the scan at 0.5 mV s^{-1} between the potentials of -0.40 and -0.36 V MSE (Figure 6-29). It was not observed at higher scan rates.

![Voltammetric Cu UPD stripping from Sn catalyst supported on graphite felt using electrochemically mediated colloidal metal deposition (surfactant adsorption variant)](image)

*Figure 6-29: Voltammetric Cu UPD stripping from Sn catalyst supported on graphite felt using electrochemically mediated colloidal metal deposition (surfactant adsorption variant)*

*Operation temperature: 20°C. Scan rate: 0.5 mV s^{-1}. Electrolyte: 0.1 M H_{2}SO_{4} + 2 mM CuSO_{4}*

Considering again the Copper UPD in the cathodic scan, it is suggested that the UPD process begins at -0.26 V MSE, as already indicated, but continues until -0.45 V MSE after which the onset of bulk deposition occurs. From this information, deposition between -0.26 and -0.45 V MSE would likely produce only underpotential deposited Cu on the Sn catalyst.
6.7.2 Cu UPD deposition on Pt – Sn and surface area determination

The bulk 9:1 Pt:Sn catalyst sample created using electrochemically mediated colloidal metal deposition (surfactant adsorption variant, Section 6.2.4) was next subjected to cyclic voltammetry (Figure 6-31) over the range of 0.4 to -0.5 V MSE, at a scan rate of 10 mV s\(^{-1}\), in a 0.1 M H\(_2\)SO\(_4\) and 2 mM CuSO\(_4\) solution.

![Cyclic Voltammetry Graph](image)

*Figure 6-30: Demonstration of Cu UPD and Cu bulk deposition by cyclic voltammetry on Pt-Sn catalyst supported on graphite felt using electrochemically mediated colloidal metal deposition (surfactant adsorption variant, 9:1 bulk Pt:Sn ratio). Operation temperature: 20°C. Scan rate: 10 mV s\(^{-1}\). Electrolyte: 0.1 M H\(_2\)SO\(_4\) + 2 mM CuSO\(_4\).*

Figure 6-30 shows that both UPD (I) and bulk (II) Cu deposition occur on the Pt-Sn catalyst at potentials of -0.33 and -0.61 V MSE, respectively. The potentials are in good agreement with what has been determined by Green and Kucernak (2002) for pure Pt. Based on Figure 6-30, deposition between -0.33 and -0.41 V MSE would likely produce only underpotential deposited Cu
monolayer on the Pt – Sn alloy. On the anodic scan there are two Cu stripping peaks, occurring at potentials of -0.26 and +0.02 V MSE. These can be attributed to the bulk stripping (III) and UPD stripping (IV) of Cu from the Pt-Sn surface respectively.

Figure 6-31 shows the Cu UPD stripping curves associated only with the under potential deposition of Cu at -0.4 V MSE on the bulk 9:1 Pt:Sn catalyst (surfactant adsorption variant). It is observed that with and without prior oxidation of the sample at 0.5 V MSE (see also Section 5.6.5), the signal remains the same, indicating there is no reduced affinity of the underpotential deposited Cu for SnO as there is with RuO. However, it can be seen that with oxidation, the Cu UPD stripping peaks are more pronounced, and it is this data that is used for surface area determinations.

Figure 6-31: Cu UPD stripping by cyclic voltammetry from Pt-Sn catalyst supported on graphite felt using electrochemically mediated colloidal metal deposition (surfactant adsorption variant, 9:1 bulk Pt:Sn ratio). Oxidation at 0.5 V MSE for 180 s. Operation temperature: 20°C. Scan rate: 10 mV s⁻¹. Electrolyte: 0.1 M H₂SO₄ + 2 mM CuSO₄
It is proposed that the first peak in Figure 6-31 at -0.22 V MSE is the result of Cu UPD stripping from Sn, and the second at +0.04 V MSE is that from Pt. This first peak is not in the range of Cu UPD stripping from Pt (Green and Kucernak, 2002) and the applied Cu deposition potential (-0.4 V MSE) is too high for the peak to result from bulk deposition and stripping of Cu from Pt (Figure 6-30).

Taking the area between the Cu UPD curve (with oxidation) and the scan in the absence of Cu\(^{2+}\), the total catalyst area was calculated, as detailed in Section 5.6.5, to be 98.0 cm\(^2\) geometric area or 233.3 cm\(^2\) mg\(^{-1}\) of catalyst, when using the mass loading determined by ICP-OES. An estimation of the active catalyst surface ratio of Pt:Sn can be determined by approximating the current stripping effects from -0.33 to -0.15 V MSE to be sourced from Sn Cu UPD stripping, and that from -0.15 to +0.27 V MSE, to be sourced from Pt Cu UPD stripping. This gives an active surface area ratio of 3.5:1, which corresponds nicely with the average values taken by EDX (3.1:1). The value determined by EDX, being slightly lower, indicates some segregation of Pt on the surface of the catalyst.

Similarly Figure 6-32, depicts the Cu UPD stripping curve associated with the metal adsorption variant produced with a bulk 9:1 Pt:Sn ratio (Section 6.4). The sample was again oxidized at 0.5 V MSE prior to the Cu UPD. The total area calculated from Figure 6-32 was 73.2 cm\(^2\) geometric area or 76.3 cm\(^2\) mg\(^{-1}\) of catalyst. This reduction in catalyst specific area reflects the increase in catalyst particle size depicted in Figure 6-22.

As with the surfactant adsorption variant, two distinct stripping peaks are observed in Figure 6-32, and the corresponding Pt and Sn areas can be approximated in order to determine the active catalyst surface ratio of Pt:Sn. Thus, a Pt:Sn active catalyst surface ratio of 7.7:1 was found. This is both substantially higher than that determined by the same method for the surfactant adsorption variant (3.5:1), and for that determined by EDX for bulk composition (3.9:1) of this variant. This indicates that Pt is covering the Sn content of the catalyst.
2.0

-0.6 -0.4 -0.2 0.0 0.2 0.4

Potential (V MSE)

-0.5 0.0 0.5 1.0 1.5 2.0

0.1 M H₂SO₄

0.1 M H₂SO₄ + 2 mM CuSO₄

Pt signal

Sn signal

6.8 Effect of temperature on catalyst activity

To evaluate the effect of temperature on catalyst activity and stability, cyclic voltammetry and chronopotentiometry were conducted at elevated temperatures on both surfactant and metal adsorption variants of the electrochemically mediated colloidal metal deposition technique (9:1 bulk Pt:Sn ratio), as these are the best performing catalysts prepared in this study. Figure 6-33 shows cyclic voltammetry data (5 mV s⁻¹, second scan) for the surfactant adsorption variant at 20, 60 and 80 °C.
It is noted in Figure 6-33 that at the elevated temperatures the peak in ethanol oxidation is not observed; however, an overall increase in catalyst activity is apparent. It is probable that the peak at 20 °C is due to poisoning and therefore not visible at higher temperatures where the surface is cleared.

Figure 6-34 summarizes the chronopotentiometry results of the same sample at both 20 and 80 °C. Again the increase in activity at lower potentials is noted.
Figure 6-34: Electro-oxidation of ethanol by chronopotentiometry on Pt-Sn catalyst supported on graphite felt using electrochemically mediated colloidal metal deposition (surfactant adsorption variant, 9:1 bulk Pt:Sn ratio). Electrolyte: 0.1 M H₂SO₄ + 0.5 M EtOH

For the metal adsorption variant, a similar increase in activity at low potentials was prevalent from 20 to 60 °C; however, at 80 °C the catalyst appeared to lose activity and a noisy signal was produced for a current response. Subsequent to experiments at 80 °C, the lost activity of the catalyst was unrecoverable, even following additional electrochemical cleaning and heat treatments. This suggests that the catalyst is not stable at these elevated temperatures. Figure 6-35 summarizes chronopotentiometry results for the metal adsorption variant at 20 and 60 °C. It is already noted in the last chronopotentiometry scan at 60 °C (5 mA cm⁻²) that activity and stability in the catalyst is beginning to be lost.
Chronoamperometry was conducted for both the surfactant and metal adsorption variants of the electrochemically mediated colloidal metal deposit prepared with a 9:1 bulk Pt:Sn ratio. The procedure was carried out as detailed in Section 5.6.4 under six applied potentials, namely: -0.35, -0.28, -0.23, -0.18, -0.13 and 0 V MSE. As described in Section 2.3.4 – Theoretical Principles, the technique provides a good opportunity to study catalyst poisoning and it can be used to calculate Tafel slopes, providing diffusion limitation can be ruled out.

Figure 6-36 depicts chronoamperometry results for the surfactant adsorption variant at 20 °C.
Figure 6-36: Electro-oxidation of ethanol by chronoamperometry on Pt-Sn catalyst supported on graphite felt using electrochemically mediated colloidal metal deposition (9:1 bulk Pt:Sn ratio). Operation temperature: 20°C. Electrolyte: 0.1 M H₂SO₄ + 0.5 M EtOH

Figure 6-36 indicates that at lower applied potentials the current remains relatively constant over time; however, at higher applied potentials (i.e. 0 V MSE) there begins to be a downward drift over time. This may indicate that at higher potentials some catalytic poisoning is occurring.

As established by the Cottrel Equation (Equation 2-20) in Appendix E, diffusion control is not prevalent for the surfactant adsorbed variant at both 20 and 80 °C. Thus Figure 6-37 depicts a Tafel plot of anodic half cell potential versus the logarithm of current density taken from Figure 6-36 at 180 seconds. A second curve is also shown in Figure 6-37 for the same system at 80 °C.
At both temperatures depicted in Figure 6-37 there is an apparent shift in the slope of the plot between the lower and higher potentials (Table 6-9). The exchange current density was calculated for the lower potential range by determining the current density at $E_e$, calculated using the Nernst equation (Equation 2-5), and adjusted for temperature using Equation 2-7.

Table 6-9: Tafel slope and exchange current densities for Pt-Sn catalyst supported on graphite felt using electrochemically mediated colloidal metal deposition (surfactant adsorption). Electrolyte: 0.1 M H$_2$SO$_4$ + 0.5 M EtOH

<table>
<thead>
<tr>
<th>Temperature/Region</th>
<th>Tafel Slope (mV/dec)</th>
<th>$i_0$ (mA cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 °C/ $E \leq -230$ mV MSE</td>
<td>98</td>
<td>2.5 E-5</td>
</tr>
<tr>
<td>20 °C/ $E \geq -230$ mV MSE</td>
<td>363</td>
<td>-</td>
</tr>
<tr>
<td>80 °C/ $E \leq -220$ mV MSE</td>
<td>257</td>
<td>9.5E-2</td>
</tr>
<tr>
<td>80 °C/ $E \geq -220$ mV MSE</td>
<td>645</td>
<td>-</td>
</tr>
</tbody>
</table>
Although no Tafel parameters have been reported for ethanol on Pt based catalyst, the existence of a shift in Tafel slope has been reported for methanol oxidation. Jiang and Kucernak (2003) reported a shift in Tafel slope for methanol oxidation at 60 °C on Pt-Ru at -0.21 V MSE, which compares to the half cell potentials in which the shift is observed for ethanol oxidation at 20 °C and 80°C on Pt-Sn (-0.23 and -0.22 V MSE respectively). It is proposed by Jiang and Kucernak that the Tafel slope in the lower potential range represents an irreversible one electron process (i.e. splitting of the C – H bond), and that a combination of more complex reactions occur at the higher potentials.

Figure 6-38 depicts chronoamperometry at 20 °C for the metal adsorption variant catalyst prepared using the same 9:1 bulk Pt:Sn ratio. It is demonstrated in Appendix E, by the Cottrell Equation, that diffusion control is not prevalent in this sample and thus a Tafel slope plot is given in Figure 6-39. Values at 80 °C could not be obtained due to the inherent instability of the catalyst at this temperature. The resultant Tafel slopes and calculated exchange current density are shown in Table 6-10.

In Figure 6-39 the shift in Tafel slope is again seen in the same potential range (-0.22 V MSE) as reported by Jiang and Kucernak for methanol. The Tafel slope and exchange current densities for the metal adsorption variant are both larger than those obtained for the surfactant adsorption variant (Table 6-10) at the same temperature. The effect of both of these changes are competing, and while the increase in Tafel slope will serve to increase overpotential, the increase in exchange current density will reduce overpotential. It should be noted; however, that in the metal adsorption variant calculated overpotentials are consistently lower in the same range of current densities, suggesting that the increase in exchange current density has a more dramatic effect. This may also help explain the increase in catalyst activity for the metal adsorption variant particularly at lower potentials, where there is nearly a three order increase in \( i_o \), and the increase in Tafel slope is only slightly more than two fold.
Figure 6-38: Electro-oxidation of ethanol by chronoamperometry on Pt-Sn catalyst supported on graphite felt using electrochemically mediated colloidal metal deposition (metal adsorption variant, 9:1 bulk Pt:Sn ratio).
Operation temperature: 20°C. Electrolyte: 0.1 M H₂SO₄ + 0.5 M EtOH

Table 6-10: Tafel slope and exchange current densities for Pt-Sn catalyst, supported on graphite felt using electrochemically mediated colloidal metal deposition (metal adsorption variant, 9:1 bulk Pt:Sn ratio). Electrolyte: 0.1 M H₂SO₄ + 0.5 M EtOH.

<table>
<thead>
<tr>
<th>Temperature/Region</th>
<th>Tafel Slope (mV/dec)</th>
<th>i₀ (mA cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 °C/E ≤ -220 mV MSE</td>
<td>216</td>
<td>1.9E-2</td>
</tr>
<tr>
<td>20 °C/E ≤ -220 mV MSE</td>
<td>546</td>
<td></td>
</tr>
</tbody>
</table>
Figure 6-39: Tafel plot of overpotential versus the logarithm of current density for Pt-Sn catalyst supported on graphite felt using electrochemically mediated colloidal metal deposition (metal adsorption variant, 9:1 bulk Pt:Sn ratio).
Operation temperature: 20 °C. Electrolyte: 0.1 M H₂SO₄ + 0.5 M EtOH

6.10 The Effect of Substrate on Pt-Sn Deposition

By employing the metal adsorption electrochemically mediated colloidal metal deposit variant in a 9:1 bulk Pt:Sn ratio, catalyst samples were created on two other substrates discussed in Section 3.0, namely compressed carbon felt (Electrolytica GF-S3) and carbon cloth (Electrolytica GC-10) (See also Figure 3-2). Cyclic voltammetry for ethanol oxidation using these substrates is detailed in Figures 6-40. The graphite felt substrate is included for comparison.
Figure 6-40 suggests that adherence of the colloidal catalyst to compressed graphite felt is poor by this method, with current densities not exceeding 0.5 mA cm\(^{-2}\) over the entire potential range. The activity of the deposit on carbon cloth compares more favourably; however, the deposit on carbon cloth is still somewhat less active compared to graphite felt. An additional comparison between the carbon cloth and graphite felt deposit was conducted using chronopotentiometry (Figure 6-41).
The results of chronopotentiometry studies confirm the lower activity of the carbon cloth sample. It is not known how different pretreatment methods would have affected the deposition on the cloth or compressed felt substrate. Therefore uncompressed graphite felt was retained for fuel cell tests.

6.11 Fuel Cell Tests

Catalyst samples, supported on graphite felt, prepared with both the surfactant and metal adsorption electrochemically mediated colloidal metal deposition variants were subjected to fuel cell tests by preparing membrane electrode assemblies as detailed in Section 5.7.1. Catalysts were not heat treated, but were subject to chemical and electrochemical cleaning and dried prior to MEA
preparation, as discussed in Section 5.6.1. 1 M ethanol was employed at a feed rate of 5 mL min\(^{-1}\). Initially no supporting electrolyte was used in order to evaluate the ionic conductivity of the Nafion® bonded three dimensional anode, with only flowing ethanol, at various temperatures. Two different oxygen flow rates were used at the cathode, 100 and 550 mL min\(^{-1}\), and the corresponding cathodic absolute pressures were 148 kPa and 205 kPa. These scenarios yield \(\text{O}_2:\text{C}_2\text{H}_5\text{OH}\) stoichiometric ratios of 1.3 and 9.9, respectively. Using these feed conditions, cell performance was evaluated at both 40 and 60 °C.

Figures 6-42 and 6-43 show polarization and power density curves associated with the MEAs produced using both the surfactant adsorption (6-42) and metal salt adsorption (6-43) deposition variants prepared with a 9:1 bulk Pt:Sn ratio.

![Figure 6-42: Performance of single direct ethanol fuel cell with a 3-dimensional anode prepared using electrochemically mediated colloidal metal deposition (surfactant adsorption variant, 9:1 bulk Pt:Sn ratio). Anode: loading 0.44 mg Pt-Sn cm\(^{-2}\), aqueous 1.0 M EtOH solution with flow rate of 5 mL min\(^{-1}\) at atmospheric pressure. Cathode: loading 4.0 mg Pt cm\(^{-2}\), dry O\(_2\) feed at various pressures and flow rates. Closed symbols denote cell potential (E), open symbols denote cell power density (P).]
Figure 6-43: Performance of single direct ethanol fuel cell with a 3-dimensional anode prepared using electrochemically mediated colloidal metal deposition (metal adsorption variant, 9:1 bulk Pt:Sn ratio). Anode: loading 0.96 mg Pt-Sn cm\(^{-2}\), aqueous 1.0 M ethanol solution with flow rate of 5 mL min\(^{-1}\) at atmospheric pressure. Cathode: loading 4.0 mg Pt cm\(^{-2}\), dry O\(_2\) feed at 100 mL min\(^{-1}\) and 148 kN m\(^{-2}\) absolute pressure. Closed symbols denote cell potential (E), open symbols denote cell power density (P).

Figures 6-42 and 6-43 show, as expected, that cell performance is better at 60°C than at 40°C for both the surfactant and metal adsorption variants. The influence of oxygen flow rate, and subsequently cathodic pressure, in either case was not very significant. However, a higher cathodic pressure produces a slightly better result in the surfactant adsorption variant (Figure 6-42), indicating that ethanol crossover may be of concern due to the lower loading. In both catalysts, the performance is limited by the ionic conductivity across the felt anode as shown by the low superficial current density.

By employing the preferred conditions for each catalyst (i.e. 60 °C, 100 mL min\(^{-1}\) O\(_2\) feed for the metal adsorption variant and 60 °C, 550 mL min\(^{-1}\) O\(_2\) feed for the surfactant adsorption variant),
protonic conductivity was established in the three-dimensional anodes by including 0.5 M H₂SO₄ in the fuel feed. The fuel cell results from this study, contrasted against the above situation where no flowing electrolyte was used, are shown in Figure 6-44 (surfactant adsorption) and Figure 6-45 (metal adsorption).

![Graph showing performance of single direct ethanol fuel cell at 60 °C with 3-dimensional anodes prepared using electrochemically mediated colloidal metal deposition.](image)

**Figure 6-44**: Performance of single direct ethanol fuel cell at 60 °C with a 3-dimensional anodes prepared using electrochemically mediated colloidal metal deposition (surfactant adsorption variant, 9:1 bulk Pt:Sn ratio). Anode: loading 0.44 mg Pt-Sn cm⁻², aqueous 1.0 M ethanol solution with and without 0.5 M H₂SO₄. Flow rate of 5 mL min⁻¹ at atmospheric pressure. Cathode: loading 4.0 mg Pt cm⁻², dry O₂ feed at 550 mL min⁻¹ and 205 kPa. Closed symbols denote cell potential (E), open symbols denote cell power density (P).
Figure 6-45: Performance of single direct ethanol fuel cell at 60 °C with a 3-dimensional anodes prepared using electrochemically mediated colloidal metal deposition (metal adsorption variant, 9:1 bulk Pt:Sn ratio). Anode: loading 0.96 mg Pt-Sn cm$^{-2}$, aqueous 1.0 M ethanol solution with and without 0.5 M H$_2$SO$_4$. Flow rate of 5 mL min$^{-1}$ at atmospheric pressure. Cathode: loading 4.0 mg Pt cm$^{-2}$, dry O$_2$ feed at 100 mL min$^{-1}$ and 148 kN m$^{-2}$ absolute pressure. Closed symbols denote cell potential (E), open symbols denote cell power density (P).

Figure 6-44 and Figure 6-45 show that for both electrochemically mediated variants the inclusion of a flowing electrolyte dramatically improves cell performance, presumably by making use of all the catalyst across the 3-dimensional anode, and not only that in direct contact with the membrane via the Nafion® bond. Some features of the power density curves shown in Figure 6-45 are summarized in Table 6-11.

It is interesting to note that the increase in maximum power density that results from using the flowing electrolyte is nearly identical for both catalysts at 2.93 times.
Table 6-11: Maximum power density from power curves featured in Figures 6-44 and 6-45.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Maximum Power Density</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I (mA cm⁻²)</td>
</tr>
<tr>
<td>Surfactant adsorption variant</td>
<td>8</td>
</tr>
<tr>
<td>Surfactant adsorption variant /H₂SO₄</td>
<td>16</td>
</tr>
<tr>
<td>Metal adsorption variant</td>
<td>8</td>
</tr>
<tr>
<td>Metal adsorption variant/H₂SO₄</td>
<td>30</td>
</tr>
</tbody>
</table>

Literature comparison of the performance of the 3-dimensional anode, to more traditionally prepared DEFC anodes, proves to be difficult as the cell performance is dramatically influenced by catalyst loading, composition and other cell operating parameters (i.e. temperature, cathodic/anodic feed conditions). Recently Zhou et al (2005); however, published fuel cell test results employing a traditional GDE under conditions comparable to those used in the present study. The catalyst in their study was prepared by the Polyol method (Section 4.2.4) and supported on carbon black. Table 6-12 summarizes the operating conditions of the literature study, versus that used for both the surfactant and metal adsorption variant prepared 3-dimensional anodes (in the presence of 0.5 M H₂SO₄). The performances of these catalysts are then compared on a mass activity basis in Figure 6-46.

Table 6-12: Comparison of 3-dimensional anode fuel cell operating conditions and MEA characteristics to that of a conventional MEA study (Zhou et al., 2005).

<table>
<thead>
<tr>
<th>Cell Temperature (°C)</th>
<th>Surfactant Adsorption</th>
<th>Metal Adsorption</th>
<th>Zhou et al (2005)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathodic Conditions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feed Gas</td>
<td>Dry O₂</td>
<td>Dry O₂</td>
<td>Dry O₂</td>
</tr>
<tr>
<td>Absolute feed Pressure (kPa)</td>
<td>205</td>
<td>148</td>
<td>100</td>
</tr>
<tr>
<td>Feed Flow rate (mL min⁻¹)</td>
<td>550</td>
<td>100</td>
<td>unspecified</td>
</tr>
<tr>
<td>Catalyst load (mg Pt cm⁻²)</td>
<td>4.0</td>
<td>4.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Anodic Conditions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethanol Concentration (M)</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Feed Rate (mL min⁻¹)</td>
<td>5.0</td>
<td>5.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Feed Pressure (bar)</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Catalyst load (mg Pt cm⁻²)</td>
<td>0.37</td>
<td>0.83</td>
<td>1.3</td>
</tr>
<tr>
<td>Catalyst Pt-Sn Ratio</td>
<td>3.1</td>
<td>3.9</td>
<td>4.0</td>
</tr>
<tr>
<td>Catalyst particle size (nm)</td>
<td>3-10</td>
<td>3-40</td>
<td>2.3</td>
</tr>
</tbody>
</table>
Figure 6-46: Performance of single direct ethanol fuel cells at 60 °C with 3-dimensional anodes, prepared using surfactant and metal adsorption electrochemically mediated colloidal metal deposition variants, in comparison to literature results from a traditional anode. Operating conditions as detailed in Table 6-12. Closed symbols denote cell potential (E), open symbols denote cell power density (P).

Figure 6-46 shows that, on a mass activity basis, the performance is comparable between the three-dimensional anode and the traditional catalyst, particularly for the surfactant adsorption variant where catalyst particle size is more similar. It has been previously demonstrated for DMFCs that the relationship between catalyst loading and cell current density, at the same cell potential, is linear, particularly at lower catalyst loadings (Nakagawa and Xiu, 2003). This provides some support for the mass activity comparison in Figure 6-46. Another phenomenon; however, is noted in this study, in that the increased catalyst load reduces the effects of fuel crossover. When fuel crossover is reduced, the open circuit potential increases which should give rise to higher fuel cell power output. With this in mind, the mass specific power densities noted in Figure 6-46 should increase for the 3-dimensional anodes if a significant increase in catalyst loading is made.
Additional improvements can also be made in the ionic conductivity of the 3-dimensional matrix, by using electrolytes of higher conductivity than 0.5 M \( \text{H}_2\text{SO}_4 \) (0.2 S cm\(^{-2}\)) or Nafion® (0.1 S cm\(^{-2}\)) (Zawodzinski et al., 1991). It can be determined by the Castell-Amis equation (de Diego et al., 1997) that at 60 °C, the maximum conductivity of \( \text{H}_2\text{SO}_4 \) occurs at a concentration of 4.3 M. Although use of \( \text{H}_2\text{SO}_4 \) at this concentration is not suitable in the test station (due to corrosion concerns), the use of a similarly conductive immobilized electrolyte would reduce ohmic drop (Equation 2-16) across the electrode by 82% (e.g. from 34 to 6 mV at \( i = 30 \) mA cm\(^{-2}\)).

It is on the basis of improved catalyst loading and ionic conductivity that the 3-dimensional anode would likely outperform the traditional catalyst design.
7.0 Conclusions

This work has discussed the use of a novel three-dimensional direct ethanol fuel cell (DEFC) anode created by the deposition of Pt-Sn based nanoparticles on graphite felt. Deposition was conducted using electrochemically assisted organosol methods derived from the colloidal methods of Bonnemann and co-workers (1991), in which metal salt precursors are chemically reduced by tetraoctylammonium triethylhydroborate in tetrahydrofuran (THF). Preliminary results indicate that these electrodes are a promising alternative to conventional gas diffusion electrodes in DEFCs.

Practical Pt-Sn catalyst loadings for fuel cell applications (i.e. \( \geq 0.1 \text{ mg cm}^{-2} \)) cannot be obtained by the method of Bönnemann and coworkers on graphite felt. Modifications of the Bonnemann colloidal method have been developed, in which colloidal formation and deposition are conducted co-currently under the application of an electric field (e.g. 1.25 mA cm\(^{-2}\) and 2 V). In one modification the tetraoctylammonium triethylhydroborate surfactant is introduced to the felt under an electric field and the salt suspension is subsequently added dropwise. This modification results in an increased catalyst loading (0.44 versus \( 4.0 \times 10^{-2} \text{ mg} \)) with particle size (3 – 10 nm) in the same range as expected from the Bonnemann method.

It is proposed that this modified method is primarily electrophoretic, in that the electric field causes the migration and electrosorption of the cationic surfactant onto the cathode graphite felt, concentrating the colloid forming reaction on the substrate surface. However, faradaic effects (i.e. electrodeposition and electrochemical colloid formation) are still apparent as evidenced by a predictable shift in the Pt:Sn atomic ratio of the catalyst deposit versus that in the bulk solution (e.g. 3.1:1 for a 9:1 Pt:Sn bulk solution). The estimated catalyst load developed on the substrate also varies with Pt:Sn ratio (e.g. 0.44 and 8.7E-2 mg cm\(^{-2}\) for respective Pt:Sn bulk solution ratios of 0.5:1 and 9:1). These results are explained by competing mechanisms, both by the homogeneous reduction of the metal ion by hydroborate, and electrodeposition either directly or through the faradaic formation of colloidal metal deposits (Reetz and Helbig, 2004). Faradaic deposition is favoured for Sn as SnCl\(_2\) is fully soluble in THF. Of the Pt:Sn bulk ratios studied, the best performer was the 9:1 ratio which produced a catalyst deposit on graphite felt in a 3.1:1 ratio at a loading of 0.44 mg cm\(^{-2}\).
A metal adsorption variant of the electrochemically mediated method, in which initially metal salts are present in the reaction vessel with the substrate while the tetraoctylammonium triethylhydroborate is added dropwise under the action of the electric field, was also investigated. The metal adsorption variant produced higher catalyst loadings (i.e. 0.96 mg cm\(^{-2}\)) at the expense of larger particles in a greater size range (5 – 43 nm). In this variant a Pt:Sn catalyst ratio of 3.9:1 was produced for a 9:1 bulk ratio.

Using Cu underpotential deposition, a higher total active catalyst surface area was determined for the surfactant adsorption variant (98.0 cm\(^2\) catalyst cm\(^{-2}\) substrate) versus that of the metal adsorption variant (73.2 cm\(^2\) catalyst cm\(^{-2}\) substrate). On the other hand, the Pt:Sn surface area ratio was higher for the metal adsorption variant (7.7:1) than for the surfactant adsorption variant (3.1:1). Therefore, the better performance observed for the metal adsorption variant (measured by chronopotentiometry and chronoamperometry) is likely related to the Pt:Sn surface area ratio and not the improved catalyst loading.

Fuel cell tests using the Pt-Sn deposited three-dimensional electrodes were conducted both in the presence and absence of 0.5 M H\(_2\)SO\(_4\) electrolyte. Both variants performed substantially better with H\(_2\)SO\(_4\) than without, and the metal adsorption variant performed better under both scenarios (i.e. cell voltage of 0.35 V versus 0.20 V for 20 mA cm\(^{-2}\) in 1 M EtOH + 0.5 M H\(_2\)SO\(_4\) at 60 °C). On a mass activity basis; however, the surfactant adsorption variant performed better than the metal adsorption variant, possibly due to the difference in active catalyst surface areas. When contrasted against literature data for conventional Pt – Sn gas diffusion electrode design, the surfactant adsorption variant performed comparably on a mass activity basis. It is believed that with an increase in catalyst loading, and greater ionic conductivity within the three-dimensional anode, the catalyst activity for the three-dimensional anode would be greater than the traditional gas diffusion electrode design. In addition to fuel cell use; however, electrodes produced by this method can be used for other applications, such as electrosynthesis, where three-dimensional electrodes have already proven to be advantageous.
8.0 Recommendations

- Further exploration of the surfactant adsorption variant is recommended. This variant performs better on a mass activity basis and is stable at higher temperatures.

- Increasing the number of deposition sites on the three-dimensional substrate is recommended to improve catalyst loading. Substrate pretreatment methods that roughen the carbon surface, without heavily oxidizing it, are required to avoid surfactant degradation.

- Surface area by Cu UPD should be determined both before and after electrochemical testing so that any changes in the catalyst structure can be noted.

- Pd nucleation should be re-trialed using a reduction in the time allowed for surfactant electrosorption (e.g. 2 min from 10 min). This will reduce the amount of surfactant that catalytically decomposes in the presence of Pd.

- A mixed organic solvent, composed of THF and acetonitrile (e.g. 4:1 volume ratio), should be trialed to determine if increased solubility of metal salts will improve deposit activity and/or loading.

- The electrochemically mediated method should be trialed in the absence of tetraoctylammonium bromide stabilizer. This will determine if its benefit as a metal salt suspension stabilizer prevails over any negative effects resulting from electrochemical colloid formation.

- Bulk Pt:Sn ratios should be explored in a less course variation around the 9:1 atomic ratio (e.g. 7:1, 8:1, 10:1 and 11:1) in order to determine if there is a ratio that is more optimal.

- It is recommended that additional Pt:Sn:Pd ratios be explored, particularly in the area of increasing Pd content (e.g. 9:1:1), as its initial inclusion shows some promise.
Due to promising results in literature, it is recommended that additional bulk Pt:Sn:Ni atomic ratios (e.g. 9:1:0.5 and 9:1:2) be considered to fully evaluate the effect of Ni using this deposition method.

The use of sacrificial Pd and Sn anodes may be trialed as a source of alloying metals instead of using the metal salt precursors.

The use of high surface area deposition anodes should be trialed as counter electrodes to study the effects of changes in current distribution on the deposit.

Thermogravimetry Analysis (TGA) should be used to determine if any residual protective shell remains on the catalyst after chemical and electrochemical cleanings.

Improvements to the fuel cell flow field (depicted in Figure 5-12) should be considered so that fuel is delivered and collected in an upward flow arrangement through the 3-dimensional electrode, as depicted in Figure 8-1. In the existing design, fuel delivered at laminar flow rates (< 400 mL min\(^{-1}\) at 333 K) maybe mostly flowing over the surface of the electrode rather than through it.

![Figure 8-1: Proposed fuel cell anode flow field design to allow flow through the 3-dimensional anode.](image)
• Less corrosive alternatives to high concentration sulphuric acid should be explored to establish protonic conductivity within three-dimensional electrode. This should include the use of immobilized electrolyte (e.g. sulphuric acid immobilized in porous silica gel and Nafion®) or a protonically conductive matrix that coats the substrate fibres (e.g. phosphotungstic acid \( \text{H}_3\text{[P(W}_{3}\text{O}_{10})_4]\text{•xH}_2\text{O} \)).

• SEM should be used to study a cross-section of the three-dimensional electrode/membrane Nafion® bond. This will help evaluate the quality of the bond, and determine if a stronger bond (i.e. more Nafion®, bonding time, or pressure) is required to avoid delamination.

• To determine how much of the three-dimensional electrode thickness is being used, electrodes of varying thickness (i.e. 0.5, 1.0, 1.5, 2.0, 4.0 mm) should be prepared and their effect on fuel cell activity studied.

• Products of anodic oxidation should be measured by gas-liquid chromatography to determine the extent of ethanol oxidation at various test conditions and with different catalysts.

• It is recommended that the fuel cell be fed with air or a lower percentage mix of oxygen and nitrogen. Using these feed gases, it will be possible to obtain higher cathodic backpressures at lower oxygen flow rates. This is not possible in the existing setup (e.g. cathodic backpressure of 2 bar is not attainable at oxidant flow rates below 550 mL min\(^{-1}\)).
References


Kinoshita, K. “Particle size effects for oxygen reduction on highly dispersed platinum in acid electrolytes.” Journal of the Electrochemical Society 137(1990), 845-848.


Salinas, C., Simpson, S. F., Murphy, O. J., Franaszczuk, K., Moaddel, H. and Weng, D. *US patent No. 5958616*, (September 1999).


Zhao, X., Li, W., Jiang, L., Zhou, W., Xin, Q., Yi, B. and Sun, G. “Multi-wall carbon nanotube supported Pt – Sn nanoparticles as an anode catalyst for the direct ethanol fuel cell.” Carbon 42(2004), 3251-3272.


Appendix A: Sample Log
<table>
<thead>
<tr>
<th>Date</th>
<th>Metal Content</th>
<th>Preparation Method</th>
<th>Deposition Scale (mL)</th>
<th>Current (mA)</th>
<th>Deposition Time (h)</th>
<th>Wash/Drying Method</th>
<th>Notes:</th>
</tr>
</thead>
<tbody>
<tr>
<td>042</td>
<td>PtSn</td>
<td>Electrochemically mediated -</td>
<td>196 mL</td>
<td>6.25</td>
<td>7</td>
<td>Wash: 100% EOH, DI Dry: Room conditions</td>
<td>Surface from 01.02.03 (20 mL). Compressed felt used. Metal added 10 min after surfactant with current turned on. Gas evolution on felt. Smaller vessel, 5 cm² felt and 5 cm² Pt-Ti electrodes.</td>
</tr>
<tr>
<td>043</td>
<td>PtSn</td>
<td>Electrochemically mediated -</td>
<td>196 mL</td>
<td>6.25</td>
<td>7</td>
<td>Wash: 100% EOH, DI Dry: Room conditions</td>
<td>Surface from 23.02.05 (20 mL). Surfactant added to metal salt with current turned on. No gas evolution on felt. No conductivity in solution until surfactant is added. Smaller vessel, 5 cm² felt and 5 cm² Pt-Ti electrodes.</td>
</tr>
<tr>
<td>044</td>
<td>PtSn</td>
<td>Electrochemically mediated -</td>
<td>196 mL</td>
<td>6.25</td>
<td>7</td>
<td>Wash: 100% EOH, DI Dry: Room conditions</td>
<td>Surface from 06.03.05 (20 mL). Metal added 10 min after surfactant with current turned on. Gas evolution on felt. Smaller vessel, 5 cm² felt and 5 cm² Pt-Ti electrodes.</td>
</tr>
<tr>
<td>045</td>
<td>PtSn</td>
<td>Electrochemically mediated -</td>
<td>196 mL</td>
<td>6.25</td>
<td>7</td>
<td>Wash: 100% EOH, DI Dry: Room conditions</td>
<td>Surface from 15.03.05 (20 mL). Metal added 10 min after surfactant with current turned on. Gas evolution on felt. Smaller vessel, 5 cm² felt and 5 cm² Pt-Ti electrodes.</td>
</tr>
<tr>
<td>046</td>
<td>PtSn</td>
<td>Electrochemically mediated -</td>
<td>196 mL</td>
<td>6.25</td>
<td>7</td>
<td>Wash: 100% EOH, DI Dry: Room conditions</td>
<td>Surface from 18.03.05 (20 mL). Metal added 10 min after surfactant with current turned on. Gas evolution on felt. Smaller vessel, 5 cm² felt and 5 cm² Pt-Ti electrodes.</td>
</tr>
<tr>
<td>047</td>
<td>PtSn</td>
<td>Electrochemically mediated -</td>
<td>196 mL</td>
<td>6.25</td>
<td>7</td>
<td>Wash: 100% EOH, DI Dry: Room conditions</td>
<td>Surface from 18.03.05 (20 mL). Metal added 10 min after surfactant with current turned on. Gas evolution on felt. Smaller vessel, 5 cm² felt and 5 cm² Pt-Ti electrodes.</td>
</tr>
<tr>
<td>048</td>
<td>PtSn</td>
<td>Electrochemically mediated -</td>
<td>196 mL</td>
<td>6.25</td>
<td>7</td>
<td>Wash: 100% EOH, DI Dry: Room conditions</td>
<td>Surface from 23.02.05 (20 mL). Surfactant added to metal salt with current turned on. Gas evolution on felt. No conductivity in solution until surfactant is added. Smaller vessel, 5 cm² felt and 5 cm² Pt-Ti electrodes.</td>
</tr>
<tr>
<td>049</td>
<td>PtSn</td>
<td>Electrochemically mediated -</td>
<td>196 mL</td>
<td>6.25</td>
<td>7</td>
<td>Wash: 100% EOH, DI Dry: Room conditions</td>
<td>Surface from 23.02.05 (20 mL). Surfactant added to metal salt with current turned on. Gas evolution on felt. No conductivity in solution until surfactant is added. Smaller vessel, 5 cm² felt and 5 cm² Pt-Ti electrodes.</td>
</tr>
<tr>
<td>050</td>
<td>PtSn</td>
<td>Electrochemically mediated -</td>
<td>196 mL</td>
<td>6.25</td>
<td>7</td>
<td>Wash: 100% EOH, DI Dry: Room conditions</td>
<td>Surface from 06.03.05 (20 mL). Metal added 10 min after surfactant with current turned on. Gas evolution on felt. Smaller vessel, 5 cm² felt and 5 cm² Pt-Ti electrodes.</td>
</tr>
<tr>
<td>051</td>
<td>PtSn</td>
<td>Electrochemically mediated -</td>
<td>196 mL</td>
<td>6.25</td>
<td>7</td>
<td>Wash: 100% EOH, DI Dry: Room conditions</td>
<td>Surface from 06.03.05 (20 mL). Metal added 10 min after surfactant with current turned on. Gas evolution on felt. Smaller vessel, 5 cm² felt and 5 cm² Pt-Ti electrodes.</td>
</tr>
<tr>
<td>052</td>
<td>PtSn</td>
<td>Electrochemically mediated -</td>
<td>196 mL</td>
<td>6.25</td>
<td>7</td>
<td>Wash: 100% EOH, DI Dry: Room conditions</td>
<td>Surface from 06.03.05 (20 mL). Metal added 10 min after surfactant with current turned on. Gas evolution on felt. Smaller vessel, 5 cm² felt and 5 cm² Pt-Ti electrodes.</td>
</tr>
<tr>
<td>053</td>
<td>PtSn</td>
<td>Electrochemically mediated -</td>
<td>196 mL</td>
<td>6.25</td>
<td>7</td>
<td>Wash: 100% EOH, DI Dry: Room conditions</td>
<td>Surface from 06.03.05 (20 mL). Metal added 10 min after surfactant with current turned on. Gas evolution on felt. Smaller vessel, 5 cm² felt and 5 cm² Pt-Ti electrodes.</td>
</tr>
<tr>
<td>054</td>
<td>PtSn</td>
<td>Electrochemically mediated -</td>
<td>196 mL</td>
<td>6.25</td>
<td>7</td>
<td>Wash: 100% EOH, DI Dry: Room conditions</td>
<td>Surface from 06.03.05 (20 mL). Metal added 10 min after surfactant with current turned on. Gas evolution on felt. Smaller vessel, 5 cm² felt and 5 cm² Pt-Ti electrodes.</td>
</tr>
<tr>
<td>055</td>
<td>PtSn</td>
<td>Electrochemically mediated -</td>
<td>196 mL</td>
<td>6.25</td>
<td>7</td>
<td>Wash: 100% EOH, DI Dry: Room conditions</td>
<td>Surface from 06.03.05 (20 mL). Metal added 10 min after surfactant with current turned on. Gas evolution on felt. Smaller vessel, 5 cm² felt and 5 cm² Pt-Ti electrodes.</td>
</tr>
<tr>
<td>056</td>
<td>PtSn</td>
<td>Electrochemically mediated -</td>
<td>196 mL</td>
<td>6.25</td>
<td>7</td>
<td>Wash: 100% EOH, DI Dry: Room conditions</td>
<td>Surface from 06.03.05 (20 mL). Metal added 10 min after surfactant with current turned on. Gas evolution on felt. Smaller vessel, 5 cm² felt and 5 cm² Pt-Ti electrodes.</td>
</tr>
<tr>
<td>057</td>
<td>PtSn</td>
<td>Electrochemically mediated -</td>
<td>196 mL</td>
<td>6.25</td>
<td>7</td>
<td>Wash: 100% EOH, DI Dry: Room conditions</td>
<td>Surface from 06.03.05 (20 mL). Metal added 10 min after surfactant with current turned on. Gas evolution on felt. Smaller vessel, 5 cm² felt and 5 cm² Pt-Ti electrodes.</td>
</tr>
<tr>
<td>058</td>
<td>PtSn</td>
<td>Electrochemically mediated -</td>
<td>196 mL</td>
<td>6.25</td>
<td>7</td>
<td>Wash: 100% EOH, DI Dry: Room conditions</td>
<td>Surface from 06.03.05 (20 mL). Metal added 10 min after surfactant with current turned on. Gas evolution on felt. Smaller vessel, 5 cm² felt and 5 cm² Pt-Ti electrodes.</td>
</tr>
<tr>
<td>059</td>
<td>PtSn</td>
<td>Electrochemically mediated -</td>
<td>196 mL</td>
<td>6.25</td>
<td>7</td>
<td>Wash: 100% EOH, DI Dry: Room conditions</td>
<td>Surface from 06.03.05 (20 mL). Metal added 10 min after surfactant with current turned on. Gas evolution on felt. Smaller vessel, 5 cm² felt and 5 cm² Pt-Ti electrodes.</td>
</tr>
<tr>
<td>060</td>
<td>PtSn</td>
<td>Electrochemically mediated -</td>
<td>196 mL</td>
<td>6.25</td>
<td>7</td>
<td>Wash: 100% EOH, DI Dry: Room conditions</td>
<td>Surface from 06.03.05 (20 mL). Metal added 10 min after surfactant with current turned on. Gas evolution on felt. Smaller vessel, 5 cm² felt and 5 cm² Pt-Ti electrodes.</td>
</tr>
<tr>
<td>061</td>
<td>PtSn</td>
<td>Electrochemically mediated -</td>
<td>196 mL</td>
<td>6.25</td>
<td>7</td>
<td>Wash: 100% EOH, DI Dry: Room conditions</td>
<td>Surface from 06.03.05 (20 mL). Metal added 10 min after surfactant with current turned on. Gas evolution on felt. Smaller vessel, 5 cm² felt and 5 cm² Pt-Ti electrodes.</td>
</tr>
<tr>
<td>062</td>
<td>PtSn</td>
<td>Electrochemically mediated -</td>
<td>196 mL</td>
<td>6.25</td>
<td>7</td>
<td>Wash: 100% EOH, DI Dry: Room conditions</td>
<td>Surface from 06.03.05 (20 mL). Metal added 10 min after surfactant with current turned on. Gas evolution on felt. Smaller vessel, 5 cm² felt and 5 cm² Pt-Ti electrodes.</td>
</tr>
</tbody>
</table>

**Notes:**
- EOH: EtOH
- DI: DI water
- CP: Cyclic voltammetry
- SEM: Scanning electron microscopy
<table>
<thead>
<tr>
<th>Date</th>
<th>Metal Content</th>
<th>Preparation Method</th>
<th>Deposition Scale</th>
<th>Current (mA)</th>
<th>Deposition Time (h)</th>
<th>Wash/Drying Method</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>04.07.05</td>
<td>Pt&lt;sub&gt;Sn&lt;/sub&gt;</td>
<td>Electrochemically mediated - metal adsorption. D63 for fuel cell.</td>
<td>50 mL</td>
<td>6.25</td>
<td>7</td>
<td>Wash: 100% EtOH, DI Dry: Room conditions Heat Treat: 300 °C, 1 h under N₂</td>
<td>Surfaceant from 04.07.05 (20 mL). Surfaceant added to metal salt with current turned on. No gas evolution on felt. No conductivity in solution until surfactant is added. Smaller vessel, 5 cm&lt;sup&gt;2&lt;/sup&gt; felt and 5 cm&lt;sup&gt;2&lt;/sup&gt; Pt-Ti electrodes.</td>
</tr>
<tr>
<td>05.07.05</td>
<td>Pt&lt;sub&gt;Sn&lt;/sub&gt;</td>
<td>Electrochemically mediated - metal adsorption. Graphite felt treated for 24 hours in electrolytic felt, boiled in DI 20 minutes and rinsed with 1L of DI by vacuum filtration.</td>
<td>50 mL</td>
<td>6.25</td>
<td>7</td>
<td>Wash: 100% EtOH, DI Dry: Room conditions Heat Treat: 300 °C, 1 h under N₂</td>
<td>Surfaceant from 04.07.05 (20 mL). Surfaceant added to metal salt with current turned on. No gas evolution on felt. No conductivity in solution until surfactant is added. Smaller vessel, 5 cm&lt;sup&gt;2&lt;/sup&gt; felt and 5 cm&lt;sup&gt;2&lt;/sup&gt; Pt-Ti electrodes.</td>
</tr>
<tr>
<td>21.07.05</td>
<td>Pt&lt;sub&gt;Sn&lt;/sub&gt;</td>
<td>Electrochemically mediated - metal adsorption. D63 for fuel cell.</td>
<td>50 mL</td>
<td>6.25</td>
<td>7</td>
<td>Wash: 100% EtOH, DI Dry: Room conditions Heat Treat: 300 °C, 1 h under N₂</td>
<td>Surfaceant from 20.07.05 (20 mL). Surfaceant added to metal salt with current turned on. No gas evolution on felt. No conductivity in solution until surfactant is added. Smaller vessel, 5 cm&lt;sup&gt;2&lt;/sup&gt; felt and 5 cm&lt;sup&gt;2&lt;/sup&gt; Pt-Ti electrodes.</td>
</tr>
<tr>
<td>25.07.05</td>
<td>Pt&lt;sub&gt;Sn&lt;/sub&gt;</td>
<td>Electrochemically mediated - metal adsorption. D63 for fuel cell.</td>
<td>50 mL</td>
<td>6.25</td>
<td>7</td>
<td>Wash: 100% EtOH, DI Dry: Room conditions Heat Treat: 300 °C, 1 h under N₂</td>
<td>Surfaceant from 20.07.05 (20 mL). Surfaceant added to metal salt with current turned on. No gas evolution on felt. No conductivity in solution until surfactant is added. Smaller vessel, 5 cm&lt;sup&gt;2&lt;/sup&gt; felt and 5 cm&lt;sup&gt;2&lt;/sup&gt; Pt-Ti electrodes.</td>
</tr>
<tr>
<td>29.07.05</td>
<td>Pt&lt;sub&gt;Sn&lt;/sub&gt;</td>
<td>Electrochemically mediated - surfactant adsorption. D53 for fuel cell.</td>
<td>50 mL</td>
<td>6.25</td>
<td>7</td>
<td>Wash: 100% EtOH, DI Dry: Room conditions Heat Treat: 300 °C, 1 h under N₂</td>
<td>Surfaceant from 25.07.05 (20 mL). Metal added 10 min after surfactant with current turned on. No gas evolution on felt. No conductivity in solution until surfactant is added. Smaller vessel, 5 cm&lt;sup&gt;2&lt;/sup&gt; felt and 5 cm&lt;sup&gt;2&lt;/sup&gt; Pt-Ti electrodes.</td>
</tr>
<tr>
<td>09.08.05</td>
<td>Pt&lt;sub&gt;Sn&lt;/sub&gt;</td>
<td>Electrochemically mediated - metal adsorption. Carbon cloth as substrate.</td>
<td>50 mL</td>
<td>6.25</td>
<td>7</td>
<td>Wash: 100% EtOH, DI Dry: Room conditions Heat Treat: 300 °C, 1 h under N₂</td>
<td>Surfaceant from 20.07.05 (20 mL). Surfaceant added to metal salt with current turned on. No gas evolution on felt. No conductivity in solution until surfactant is added. Smaller vessel, 5 cm&lt;sup&gt;2&lt;/sup&gt; felt and 5 cm&lt;sup&gt;2&lt;/sup&gt; Pt-Ti electrodes.</td>
</tr>
<tr>
<td>10.08.05</td>
<td>Pt&lt;sub&gt;Sn&lt;/sub&gt;</td>
<td>Electrochemically mediated - surfactant adsorption. Carbon cloth substrate.</td>
<td>50 mL</td>
<td>6.25</td>
<td>7</td>
<td>Wash: 100% EtOH, DI Dry: Room conditions Heat Treat: 300 °C, 1 h under N₂</td>
<td>Surfaceant from 10.08.05 (20 mL). Surfaceant added to metal salt with current turned on. No gas evolution on felt. No conductivity in solution until surfactant is added. Smaller vessel, 5 cm&lt;sup&gt;2&lt;/sup&gt; felt and 5 cm&lt;sup&gt;2&lt;/sup&gt; Pt-Ti electrodes.</td>
</tr>
<tr>
<td>09.08.05</td>
<td>Pt&lt;sub&gt;Sn&lt;/sub&gt;</td>
<td>Electrochemically mediated - metal adsorption. D63 Repeat.</td>
<td>50 mL</td>
<td>6.25</td>
<td>7</td>
<td>Wash: 100% EtOH, DI Dry: Room conditions Heat Treat: Half the sample 200 °C, 1 hour under N₂</td>
<td>Surfaceant from 20.07.05 (20 mL). Surfaceant added to metal salt with current turned on. No gas evolution on felt. No conductivity in solution until surfactant is added. Smaller vessel, 5 cm&lt;sup&gt;2&lt;/sup&gt; felt and 5 cm&lt;sup&gt;2&lt;/sup&gt; Pt-Ti electrodes.</td>
</tr>
</tbody>
</table>
Appendix B: Characterization Data
### Summary of EDX Results

<table>
<thead>
<tr>
<th>D35 - top ave</th>
<th>D35 - mid ave</th>
<th>D35 - ave</th>
<th>D34 - top ave</th>
<th>D34 - mid ave</th>
<th>D34 - ave</th>
<th>D32 - top ave</th>
<th>D32 - mid ave</th>
<th>D32 - ave</th>
<th>D28 - top ave</th>
<th>D28 - mid ave</th>
<th>D28 - ave</th>
<th>D26 - top ave</th>
<th>D26 - mid ave</th>
<th>D26 - ave</th>
<th>D25 - top ave</th>
<th>D25 - mid ave</th>
<th>D25 - ave</th>
<th>D19 - top ave</th>
<th>D19 - mid ave</th>
<th>D19 - ave</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt (at%)</td>
<td>0.41</td>
<td>0.43</td>
<td>0.42</td>
<td>0.42</td>
<td>0.47</td>
<td>0.47</td>
<td>0.47</td>
<td>0.4</td>
<td>0.79</td>
<td>1.27</td>
<td>0.79</td>
<td>1.27</td>
<td>0.79</td>
<td>1.27</td>
<td>0.79</td>
<td>1.27</td>
<td>0.79</td>
<td>1.27</td>
<td>0.79</td>
<td>1.27</td>
</tr>
<tr>
<td>Sn (at%)</td>
<td>0.13</td>
<td>0.16</td>
<td>0.15</td>
<td>0.16</td>
<td>0.27</td>
<td>0.27</td>
<td>0.27</td>
<td>0.27</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>Pt:Sn (atomic)</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Ternary Alloy (at%)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Pre-wt of sample, with filters (mg)</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
<td>7.0</td>
</tr>
<tr>
<td>Catalyst loading by wt difference (mg)</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Pt% by weight difference/EDX ratio (mg)</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Pt-Sn cm* by weight difference (mg)</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
</tr>
</tbody>
</table>

---

MW (Pt) • 192.2 g mol⁻¹
MW (Sn) • 119.2 g mol⁻¹
MW (Pt-Sn cm*) • 215.2 g mol⁻¹
<table>
<thead>
<tr>
<th>Line</th>
<th>Method</th>
<th>Intensity</th>
<th>K-ratio</th>
<th>ZAF</th>
<th>Concentration</th>
<th>2 Sigma</th>
<th>Z</th>
<th>A</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>C KA</td>
<td>PRZ</td>
<td>846.34</td>
<td>0.409</td>
<td>1.887</td>
<td>77.19 wt%</td>
<td>0.48 wt%</td>
<td>0.923</td>
<td>2.045</td>
<td>1.0C</td>
</tr>
<tr>
<td>O KA</td>
<td>PRZ</td>
<td>19.95</td>
<td>0.005</td>
<td>9.160</td>
<td>4.77 wt%</td>
<td>0.23 wt%</td>
<td>0.973</td>
<td>9.410</td>
<td>1.0C</td>
</tr>
<tr>
<td>Ca KA</td>
<td>PRZ</td>
<td>40.09</td>
<td>0.006</td>
<td>1.191</td>
<td>0.76 wt%</td>
<td>0.05 wt%</td>
<td>1.108</td>
<td>1.075</td>
<td>0.95</td>
</tr>
<tr>
<td>Sr LA</td>
<td>PRZ</td>
<td>12.27</td>
<td>0.002</td>
<td>1.256</td>
<td>0.24 wt%</td>
<td>0.04 wt%</td>
<td>1.353</td>
<td>0.928</td>
<td>0.95</td>
</tr>
<tr>
<td>Sn LA</td>
<td>PRZ</td>
<td>70.76</td>
<td>0.018</td>
<td>1.376</td>
<td>2.44 wt%</td>
<td>0.08 wt%</td>
<td>1.444</td>
<td>0.953</td>
<td>0.95</td>
</tr>
<tr>
<td>Pt LA1</td>
<td>PRZ</td>
<td>44.80</td>
<td>0.088</td>
<td>1.664</td>
<td>14.59 wt%</td>
<td>0.45 wt%</td>
<td>1.730</td>
<td>0.962</td>
<td>1.0C</td>
</tr>
</tbody>
</table>

Normalized, Factor : 1
**ANALYSIS REPORT**

Date of Analysis: 11 February 2005  
Date of Report: 14 February 2005  
PROJECT No: 4-03-1015  

APPROVED BY: Anna Becalska

CLIENT: University of British Columbia (UBC)  
Department of Chemical and Biological Engineering  
2216 Main Mall  
Vancouver, BC  
Canada  
V6T 1Z4

CONTACT: Elod Gyenge, Jonghyun Choi, Alex Bauer

**COMMENTS:** Total Pt, Ru and Sn by ICP, following Aqua Regia digestion.

**METHODS:** ICP-AES Analysis of Total & Dissolved Metals in Water and Wastewater, 5240/5245 v.3.1

<table>
<thead>
<tr>
<th>Login ID</th>
<th>Client ID:</th>
<th>Pt (ug/g)</th>
<th>Sn (ug/g)</th>
<th>Sample Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>050203F-11</td>
<td>D38; Pt, Sn</td>
<td>7430</td>
<td>1680</td>
<td>0.0179</td>
</tr>
<tr>
<td>050203F-13</td>
<td>D53; Pt, Sn</td>
<td>14100</td>
<td>1840</td>
<td>0.0263</td>
</tr>
<tr>
<td>050203F-14</td>
<td>D54; Pt, Sn</td>
<td>1470</td>
<td>231</td>
<td>0.0208</td>
</tr>
</tbody>
</table>

Calculations by Derek Lycke:

\[
\text{MW (Pt)} = 195.08 \text{ g mol}^{-1} \\
\text{MW (Sn)} = 118.71 \text{ g mol}^{-1}
\]

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Pt (mg cm(^2))</th>
<th>Sn (mg cm(^2))</th>
<th>Pt:Sn by EDX (average)</th>
<th>Sn adjusted (mg cm(^2))</th>
<th>Pt+Sn adjusted (mg cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>D38</td>
<td>0.13</td>
<td>0.03</td>
<td>2.3</td>
<td>0.04</td>
<td>0.17</td>
</tr>
<tr>
<td>D53</td>
<td>0.37</td>
<td>0.05</td>
<td>3.2</td>
<td>0.07</td>
<td>0.44</td>
</tr>
<tr>
<td>D54</td>
<td>0.63</td>
<td>0.00</td>
<td>2</td>
<td>0.01</td>
<td>0.04</td>
</tr>
</tbody>
</table>
ANALYSIS REPORT

Date of Analysis: 15 April 2005
Date of Report: 18 April 2005
PROJECT No: 4-03-1015

APPROVED BY: Anna Becalska

CLIENT: University of British Columbia (UBC)
Department of Chemical and Biological Engineering
2216 Main Mall
Vancouver, BC
Canada V6T 1Z4

CONTACT: Elod Gyenge, Alex Bauer

COMMENTS: Total Pt, Ru and Sn by ICP following Aqua Regia digestion.

METHODS: ICP-AES Analysis of Total & Dissolved Metals in Water and Wastewater, 5240/5245 v.3.1

<table>
<thead>
<tr>
<th>Login ID:</th>
<th>Client ID:</th>
<th>Pt (ug/g)</th>
<th>Sn (ug/g)</th>
<th>Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>050405R-06</td>
<td>D59 - Pt, Sn</td>
<td>7300</td>
<td>238</td>
<td>0.0168</td>
</tr>
<tr>
<td>050405R-07</td>
<td>D63 - Pt, Sn</td>
<td>50100</td>
<td>7825</td>
<td>0.0165</td>
</tr>
<tr>
<td>050405R-08</td>
<td>D64 - Pt, Sn</td>
<td>16800</td>
<td>523</td>
<td>0.0177</td>
</tr>
</tbody>
</table>

Calculations by Derek Lycke:

MW (Pt) = 195.08 g mol\(^{-1}\)
MW (Sn) = 118.71 g mol\(^{-1}\)

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Pt (mg cm(^{-2}))</th>
<th>Sn (mg cm(^{-2}))</th>
<th>Pt:Sn by EDX (average)</th>
<th>Sn adjusted (mg cm(^{-2}))</th>
<th>Pt+Sn adjusted (mg cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>D59</td>
<td>0.12</td>
<td>4.0E-03</td>
<td>5.6</td>
<td>0.01</td>
<td>0.14</td>
</tr>
<tr>
<td>D63</td>
<td>0.83</td>
<td>0.13</td>
<td>3.9</td>
<td>0.13</td>
<td>0.96</td>
</tr>
<tr>
<td>D64</td>
<td>0.30</td>
<td>0.01</td>
<td>6.2</td>
<td>0.03</td>
<td>0.33</td>
</tr>
</tbody>
</table>
**ANALYSIS REPORT**

**Date of Analysis:** 05 May 2005  
**Date of Report:** 06 May 2005  
**PROJECT No:** 4-03-1015  
**APPROVED BY:** Anna Becalska

**CLIENT:**  
University of British Columbia (UBC)  
Department of Chemical and Biological Engineering  
2216 Main Mall  
Vancouver, BC  
Canada  
V6T 1Z4  
**CONTACT:** Elod Gyeenge, Derek Lycke

**COMMENTS:** Total Pt, Ru, Pd and Sn by ICP following Aqua Regia digestion.

**METHODS:** ICP-AES Analysis of Total & Dissolved Metals in Water and Wastewater, 5240/5245 v.3.1

<table>
<thead>
<tr>
<th>Login ID</th>
<th>Client ID</th>
<th>Pd (ug/g)</th>
<th>Pt (ug/g)</th>
<th>Sn (ug/g)</th>
<th>Sample Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>050429K-01</td>
<td>D-22; Pt, Sn</td>
<td>-</td>
<td>3190</td>
<td>146</td>
<td>0.0174</td>
</tr>
<tr>
<td>050429K-02</td>
<td>D-28; Pt, Sn</td>
<td>-</td>
<td>4730</td>
<td>2300</td>
<td>0.0186</td>
</tr>
<tr>
<td>050429K-03</td>
<td>D-33; Pt</td>
<td>-</td>
<td>10500</td>
<td>-</td>
<td>0.0162</td>
</tr>
<tr>
<td>050429K-04</td>
<td>D-37; Pt, Sn</td>
<td>-</td>
<td>4440</td>
<td>4320</td>
<td>0.0160</td>
</tr>
<tr>
<td>050429K-05</td>
<td>D-42; Pt, Sn, Pd</td>
<td>147</td>
<td>5030</td>
<td>4860</td>
<td>0.0145</td>
</tr>
</tbody>
</table>

Calculations by Derek Lycke:

\[
\text{MW (Pt)} = 195.078 \text{ g mol}^{-1} \\
\text{MW (Sn)} = 118.71 \text{ g mol}^{-1}
\]

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Pt (mg cm(^2))</th>
<th>Sn (mg cm(^2))</th>
<th>Pt:Sn by EDX (mg cm(^2))</th>
<th>Sn adjusted (mg cm(^2))</th>
<th>Pt+Sn adjusted (mg cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>D22</td>
<td>0.06</td>
<td>0.00</td>
<td>2.5</td>
<td>0.01</td>
<td>0.07</td>
</tr>
<tr>
<td>D28</td>
<td>0.09</td>
<td>0.04</td>
<td>1.6</td>
<td>0.03</td>
<td>0.12</td>
</tr>
<tr>
<td>D33</td>
<td>0.17</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.17</td>
</tr>
<tr>
<td>D37</td>
<td>0.07</td>
<td>0.07</td>
<td>1.2</td>
<td>0.04</td>
<td>0.11</td>
</tr>
<tr>
<td>D42</td>
<td>0.07</td>
<td>0.07</td>
<td>0.9</td>
<td>0.05</td>
<td>0.12</td>
</tr>
</tbody>
</table>

*Note due to the fact that the adjusted Sn value is smaller than that measured by ICP, the value by ICP was taken in these cases: D28 = 0.13 mg cm\(^2\), D37 = 0.14 mg cm\(^2\) and D42 = 0.14 mg cm\(^2\)*
Average EDX - ICP Pt Correlation

\[ y = 1.6075x^2 + 5.1337x \]

\[ R^2 = 0.9809 \]
Appendix C: Supplementary Cyclic Voltammetry Data
D24: 5 mV s⁻¹ (Scan I), T = 293 K

- Blank Acid
- 0.5 M EtOH

D24: 5 mV s⁻¹ (Scan II), T = 293 K

- Blank Acid
- 0.5 M EtOH
D28: 5 mV s\(^{-1}\) (Scan I), T = 293 K

- Blank Acid
- 0.5 M EtOH

D28: 5 mV s\(^{-1}\) (Scan II), T = 293 K

- Blank Acid
- 0.5 M EtOH
D32: 5 mV s\(^{-1}\) (Scan I), T = 293 K

D32: 5 mV s\(^{-1}\) (Scan II), T = 293 K
D37: 5 mV s\(^{-1}\) (Scan I), T = 293 K

![Graph showing current (I) vs. potential (E)]

D37: 5 mV s\(^{-1}\) (Scan II), T = 293 K

![Graph showing current (I) vs. potential (E)]
D39: 5 mV s\(^{-1}\) (Scan I), \(T = 293\) K

- Blank Acid
- 0.5 M EtOH

D39: 5 mV s\(^{-1}\) (Scan II), \(T = 293\) K

- Blank Acid
- 0.5 M EtOH

159
D41: 5 mV s\(^{-1}\) (Scan I), \(T = 293\) K

\[ E \text{ (V MSE)} \]

\[ i \text{ (A)} \]

---

D41: 5 mV s\(^{-1}\) (Scan II), \(T = 293\) K

\[ E \text{ (V MSE)} \]

\[ i \text{ (A)} \]
D42: 5 mV s\(^{-1}\) (Scan I), T = 293 K

- Blank Acid
- 0.5 M EtOH

D42: 5 mV s\(^{-1}\) (Scan II), T = 293 K

- Blank Acid
- 0.5 M EtOH
D43: 5 mV s\(^{-1}\) (Scan I), \(T = 293 \text{ K}\)

- Blank Acid
- 0.5 M EtOH

D43: 5 mV s\(^{-1}\) (Scan II), \(T = 293 \text{ K}\)

- Blank Acid
- 0.5 M EtOH
D45: 5 mV s\(^{-1}\) (Scan I), \(T = 293\) K

- Blank Acid
- 0.5 M EtOH

D45: 5 mV s\(^{-1}\) (Scan II), \(T = 293\) K

- Blank Acid
- 0.5 M EtOH
D46: 5 mV s$^{-1}$ (Scan I), $T = 293$ K

- Blank Acid
- 0.5 M EtOH

---

D46: 5 mV s$^{-1}$ (Scan II), $T = 293$ K

- Blank Acid
- 0.5 M EtOH

---
D47: 5 mV s\(^{-1}\) (Scan I), T = 293 K

D47: 5 mV s\(^{-1}\) (Scan II), T = 293 K
D53: 5 mV s\(^{-1}\) (Scan I), T = 293 K

- Blank Acid
- 0.5 M EtOH

D53: 5 mV s\(^{-1}\) (Scan II), T = 293 K

- Blank Acid
- 0.5 M EtOH
D56: 5 mV s\(^{-1}\) (Scan I), T = 293 K

D56: 5 mV s\(^{-1}\) (Scan II), T = 293 K
D59: $5 \text{ mV s}^{-1}$ (Scan I), $T = 293 \text{ K}$

- Blank Acid
- $0.5 \text{ M EtOH}$

D59: $5 \text{ mV s}^{-1}$ (Scan II), $T = 293 \text{ K}$

- Blank Acid
- $0.5 \text{ M EtOH}$
D62: 5 mV s\(^{-1}\) (Scan I), \(T = 293\) K

- Blank Acid
- 0.5 M EtOH

---

D62: 5 mV s\(^{-1}\) (Scan II), \(T = 293\) K

- Blank Acid
- 0.5 M EtOH
D63: 5 mV s\(^{-1}\) (Scan I), T = 293 K

- Blank Acid
- 0.5 M EtOH

D63: 5 mV s\(^{-1}\) (Scan II), T = 293 K

- Blank Acid
- 0.5 M EtOH

E (V MSE)
D64: 5 mV s⁻¹ (Scan I), T = 293 K

![Graph 1](image1)

D64: 5 mV s⁻¹ (Scan II), T = 293 K

![Graph 2](image2)
D81: 5 mV s⁻¹ (Scan I), T = 293 K

Blank Acid
- 0.5 M EtOH

D81: 5 mV s⁻¹ (Scan II), T = 293 K

Blank Acid
- 0.5 M EtOH
D83: $5 \text{ mV s}^{-1}$ (Scan I), $T = 293 \text{ K}$

- Blank Acid
- $0.5 \text{ M EtOH}$

D83: $5 \text{ mV s}^{-1}$ (Scan II), $T = 293 \text{ K}$

- Blank Acid
- $0.5 \text{ M EtOH}$
D91H: 5 mV s^{-1} (Scan I), T = 293 K

D91H: 5 mV s^{-1} (Scan II), T = 293 K
Appendix D: Electrodeposition Calculations
Electrodeposition of Pt

Pt$^{2+} + 2e^- \rightarrow Pt^0 \quad 1.188 \text{ V}$

Limiting Current Density:

$$i_L = nFkC_{Pt^2+}$$

$$k = 1E-05 \text{ m s}^{-1} \quad \text{(assumed)}$$
$$F = 96480 \text{ C mol}^{-1}$$
$$C_{Pt^2+} = 7.1 \text{ mol m}^{-3}$$
$$i_{L,Pt^{2+}} = 1.38 \text{ mA cm}^{-2}$$
$$= 5.50 \text{ mA [4 cm}^2\text{]}^{-1}$$

Theoretical Amount of Deposition:

$$R_{Pt\text{ formation}} = \frac{i_{L,Pt^{2+}}}{nF}$$

$$n = 2$$

$$R_{Pt\text{ formation}} = 2.85E-05 \text{ mmol s}^{-1} \quad \text{on all 4 cm}^2$$

Pt Deposited = $$R_{Pt\text{ formation}} \times M_{Pt} \times t$$

$$M_{Pt} = 195.1 \text{ g mol}^{-1}$$
$$t = 7 \text{ h}$$

Pt Deposited = 140 mg on all 4 cm$^2$

Electrodeposition of Sn

Sn$^{2+} + 2e^- \rightarrow Sn^0 \quad -0.1375 \text{ V}$

Using the equations outlined above at various Sn concentrations:

$$M_{Sn} = 118.7 \text{ g mol}^{-1}$$

<table>
<thead>
<tr>
<th>Pt:Sn</th>
<th>$C_{Sn^{2+}}$ (mol m$^{-3}$)</th>
<th>$i_{L,Sn^{2+}}$ (mA cm$^{-2}$)</th>
<th>$i_{L,Sn^{2+}}$ (mA [4 cm$^2$]$^{-1}$)</th>
<th>Sn Deposited (mg in 7 h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>14.3</td>
<td>2.75</td>
<td>11.01</td>
<td>171</td>
</tr>
<tr>
<td>1</td>
<td>7.1</td>
<td>1.38</td>
<td>5.50</td>
<td>82</td>
</tr>
<tr>
<td>2</td>
<td>3.6</td>
<td>0.69</td>
<td>2.75</td>
<td>41</td>
</tr>
<tr>
<td>9</td>
<td>0.8</td>
<td>0.15</td>
<td>0.61</td>
<td>9</td>
</tr>
<tr>
<td>25</td>
<td>0.3</td>
<td>0.06</td>
<td>0.22</td>
<td>3</td>
</tr>
</tbody>
</table>
Appendix E: Chronoamperometry and Tafel Parameters
Figure E-1 clearly shows that the Cottrell Equation (Equation 2-20) does not apply above -0.28 V MSE and thus diffusion control is not apparent at these potentials. Therefore it is probable that diffusion control is also not present -0.28 V MSE and -0.35 V MSE, where kinetic control should have a stronger influence. It is likely that the apparent linear relationship at these potentials is due to adsorption and/or poisoning of the catalyst.

Figure E-1: Cottrell plot of ethanol electro-oxidation on Pt-Sn catalyst supported on graphite felt using electrochemically mediated colloidal metal deposition (surfactant adsorption, 9:1 bulk Pt:Sn ratio).
Operation temperature: 20°C. Electrolyte: 0.1 M H₂SO₄ + 0.5 M EtOH.
Figure E-2: Cottrell plot of ethanol electro-oxidation on Pt-Sn catalyst supported on graphite felt using electrochemically mediated colloidal metal deposition (surfactant adsorption, 9:1 bulk Pt:Sn ratio).
Operation temperature: 80°C. Electrolyte: 0.1 M H₂SO₄ + 0.5 M EtOH

Figure E-2 clearly shows that the Cottrel Equation (Equation 2-20) does not apply and thus diffusion control is not apparent at these potentials.
Tafel Parameter Calculation: Ethanol electro-oxidation on Pt-Sn catalyst supported on graphite felt using electrochemically mediated colloidal metal deposition (surfactant adsorption, 9:1 bulk Pt:Sn ratio). Operation temperature: 20°C. Electrolyte: 0.1 M H₂SO₄ + 0.5 M EtOH

t = 180 s

| E (V MSE) | E (mV MSE) | i (A cm⁻²) | i (mA cm⁻²) | |LOG(|i|)| | E°(298K) = | \( \Delta S° = \) |
|----------|------------|-----------|-------------|---|---|---|---|
| -0.35    | -350       | -8.0E-05  | -0.06       | -1.22 | -722 mV MSE |
| -0.28    | -280       | 4.4E-04   | 0.44        | -0.36 | 56.9 J mol⁻¹ K⁻¹ |
| -0.23    | -230       | 8.9E-04   | 0.89        | -0.05 | -722 mV MSE |
| -0.18    | -180       | 1.4E-03   | 1.44        | 0.16  | [H⁺] = 0.2 M |
| -0.13    | -130       | 2.1E-03   | 2.15        | 0.33  | [EtOH] = 0.5 M |
| 0        | 0          | 4.6E-03   | 4.58        | 0.66  | E°ₑ(293K) = -683 mV MSE |

**Linear Fitting:**

-0.35, -0.28, -0.23 V MSE

<table>
<thead>
<tr>
<th>Slope = 98 mV/dec</th>
<th>Y-Intercept = -233 mV</th>
<th>R² = 0.97</th>
</tr>
</thead>
<tbody>
<tr>
<td>b = 98 mV/dec</td>
<td>i₀ = 2.5E-05 mA cm⁻²</td>
<td></td>
</tr>
</tbody>
</table>

-0.18, -0.13, 0 V MSE

<table>
<thead>
<tr>
<th>Slope = 363 mV/dec</th>
<th>Y-Intercept = -243 mV</th>
<th>R² = 0.99</th>
</tr>
</thead>
<tbody>
<tr>
<td>b = 363 mV/dec</td>
<td>Intersection</td>
<td></td>
</tr>
</tbody>
</table>

| | LOG(|i|)| | E (mV) | |
|---|---|---|---|
| 0.034218 | -230 |
Tafel Parameter Calculation: Ethanol electro-oxidation on Pt-Sn catalyst supported on graphite felt using electrochemically mediated colloidal metal deposition (surfactant adsorption, 9:1 bulk Pt:Sn ratio).

Operation temperature: 80°C. Electrolyte: 0.1 M H₂SO₄ + 0.5 M EtOH

| E (V MSE) | E (mV MSE) | i (A cm⁻²) | i (mA cm⁻²) | LOG(|i|) | E°(298K) = | ΔS° = | E°(353K) = | [H⁺] = | [EtOH] = | E°₂(353K) = |
|-----------|------------|------------|------------|---------|-------------|--------|-------------|--------|---------|---------------|
| -0.35     | -350       | 1.7E-03    | 1.66       | 0.22    | -722 mV MSE |        |             | 0.2 M  | 0.5 M   | -672 mV MSE   |
| -0.28     | -280       | 3.4E-03    | 3.41       | 0.53    |             |        |             |        |         |                |
| -0.23     | -230       | 4.7E-03    | 4.73       | 0.68    |             |        |             |        |         |                |
| -0.18     | -180       | 6.1E-03    | 6.10       | 0.79    |             |        |             |        |         |                |
| -0.13     | -130       | 7.6E-03    | 7.55       | 0.88    |             |        |             |        |         |                |
| 0.00      | 0          | 1.2E-02    | 11.68      | 1.07    |             |        |             |        |         |                |

Linear Fitting:

-0.35, -0.28, -0.23 V MSE

\[ \text{Slope} = 257 \text{ mV/dec} \]
\[ \text{Y-Intercept} = -409 \text{ mV} \]
\[ \text{R}^2 = 0.99 \]

-0.18, -0.13, 0 V MSE

\[ \text{Slope} = 645 \text{ mV/dec} \]
\[ \text{Y-Intercept} = -690 \text{ mV} \]
\[ \text{R}^2 = 1.00 \]

Intersection

\[ |\text{LOG}(|i|)| = 0.7255 \]
\[ \text{E (mV)} = -223 \]
Figure E-3: Cottrell plot of ethanol electro-oxidation on Pt-Sn catalyst supported on graphite felt using electrochemically mediated colloidal metal deposition (metal adsorption, 9:1 bulk Pt:Sn ratio).

Operation temperature: 20°C. Electrolyte: 0.1 M H₂SO₄ + 0.5 M EtOH

Figure E-3 shows that the Cottrel Equation (Equation 2-20) does not apply above -0.35 V MSE and thus diffusion control is not apparent at these potentials. By argument parallel to that in for Figure E-1, it is probable that diffusion control is also not present at -0.35 V MSE. It is again likely that the apparent linear relationship at this potential is due to adsorption and/or poisoning of the catalyst.
Tafel Parameter Calculation: Ethanol electro-oxidation on Pt-Sn catalyst supported on graphite felt using electrochemically mediated colloidal metal deposition (metal adsorption, 9:1 bulk Pt:Sn ratio).
Operation temperature: 20°C. Electrolyte: 0.1 M H₂SO₄ + 0.5 M EtOH

\[ t = 180 \text{ s} \]

| E (V MSE) | E (mV MSE) | i (A cm⁻²) | i (mA cm⁻²) | | LOG(|i|) | E°(298K) | ΔS° | E°(293K) | [H⁺] | [EtOH] | E°ₓ(293K) |
|-----------|------------|------------|-------------| |         |         |     |         |     |        |          |
| -0.35     | -350       | 6.4E-04    | 0.64        | -0.19       |         | -722 mV MSE |
| -0.28     | -280       | 1.5E-03    | 1.51        | 0.18        |         | 56.9 J mol⁻¹ K⁻¹ |
| -0.23     | -230       | 2.2E-03    | 2.24        | 0.35        |         | -722 mV MSE |
| -0.18     | -180       | 3.0E-03    | 3.05        | 0.48        |         | [H⁺] = 0.2 M |
| -0.13     | -130       | 3.9E-03    | 3.87        | 0.59        |         | [EtOH] = 0.5 M |
| 0.00      | 0          | 6.5E-03    | 6.55        | 0.82        |         | -683 mV MSE |

Linear Fitting:

-0.35, -0.28, -0.23 V MSE

Slope = 216 mV/dec  \( Y \)-Intercept = -311 mV  \( R^2 \) = 0.99

b = 216 mV/dec  \( i_o \) = 1.9E-02 mA cm⁻²

-0.18, -0.13, 0 V MSE

Slope = 546 mV/dec  \( Y \)-Intercept = -447 mV  \( R^2 \) = 1.00

b = 546 mV/dec  \( E \) (mV) = -222

Intersection

| LOG(|i|) | E (mV) |
|---------|--------|
| 0.411952 | -222   |
Appendix F: Fuel Cell Test Station Schematic
PS: Pressure switch
SV: Solenoid valve
PR: Pressure regulator
MFC: Mass flow controller
CV: Check valve
WKT: Water knock-out tank
P: Pump
......: Gas flow

VSP: Pump (variable speed)
FC: Fuel cooler (variable fan speed)
FH: Fuel heater
CH: Cell heater (electric)
CV: Check valve
———: Liquid reactant flow