Development of differential electrochemical mass spectrometry (DEMS) technique for electrocatalysis studies

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Development of differential electrochemical mass spectrometry (DEMS) technique for electrocatalysis studies

by

Subramanian Venkatachalam

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

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2015

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The initial target was to develop an electrocatalyst for electrochemical reduction of CO₂ to selectively produce ethylene. An in-situ mass spectrometric technique namely Differential Electrochemical Mass Spectrometry (DEMS) was used for the study. Majority time was spent on CO₂ reduction. Various strategies have been explored including alloy catalysts, modified Cu electrodes, increasing CO₂ solubility using monoethanolamine solutions, ionic liquids to bypass the high activation energy requiring pathway and using guanidinium salts to stabilize intermediates. During the CO₂ reduction project, certain limitations were felt using the DEMS technique which includes no control of/ low CO₂ supply to electrocatalyst and inability to detect non-volatile products like formic acid. So in the thesis project “Development of DEMS technique for electrocatalysis studies”, the identified limitations of DEMS technique were eliminated to fulfill the CO₂ reduction experiment requirements. An enhanced version of DEMS was developed by integrating capabilities of enhancement and control of reactant supply to the electrocatalyst by using an impinging jet and detection of non-volatile products produced using an additional electrochemical ring detector.
CHAPTER 1. INTRODUCTION

1.1. General introduction

Usage of fossil fuels like coal, oil and natural gas for the past 300 years have led to the accumulation of carbon dioxide in the atmosphere. The nature’s carbon cycle had been broken since the industrial revolution. The current global emission rate of carbon dioxide is approximately 38 gigatonnes\(^1\) annually and the concentration of carbon dioxide in the atmosphere has increased over the years and is approximately 400 ppm at present. This has led to climate change and other serious consequences. Thus it is necessary to reduce carbon dioxide emissions.

There are various carbon dioxide mitigation technologies\(^2\) namely (i) **Usage of alternative fuels**: replacing carbonaceous fuels with non-carbonaceous fuels have been investigated. (ii) **Sequestration**: is storing the large volumes of carbon dioxide produced in large geological structures. It is energy intensive. (iii) **Direct utilization**: carbon dioxide could be directly utilized as supercritical carbon dioxide, for oil recovery, food industry, biomass creation etc. and (iv) **Conversion**: carbon dioxide could be used as a raw material to produce formic acid, methanol, urea, salicylic acid, polycarbonates, fine chemicals and pharmaceuticals etc. Carbon dioxide is a stable molecule. External energy is required to activate the compound to do conversions. The external energy could be from light radiation (photochemical), heat (thermochemical), electricity (electrochemical) or by reacting with another compound that has high energy. Significant impact on carbon dioxide mitigation would be possible only when used to produce something that has a very high demand like fuels. Conversion of carbon
dioxide to hydrocarbons is possible by the thermocatalytic route with Fe based alloys and the electrochemical route with copper electrode in aqueous electrolyte solutions. The thermocatalytic route requires high temperatures in the range of 200 to 400 °C, pressure of 1-5 MPa and hydrogen gas. The electrochemical route produces hydrocarbons at ambient conditions and uses water as its hydrogen source. Electrochemical reduction of carbon dioxide produces a range of products like carbon monoxide, formic acid and hydrocarbons like methane, ethylene in aqueous electrolyte solutions. The reactions involved are

\[
2H^+ + 2e^- \rightleftharpoons H_2 \quad (1.1)
\]

\[
2CO_2 + 12H^+ + 12e^- \rightleftharpoons C_2H_4 + 4H_2O \quad (1.2)
\]

\[
CO_2 + 8H^+ + 8e^- \rightleftharpoons CH_4 + 2H_2O \quad (1.3)
\]

\[
CO_2 + 2H^+ + 2e^- \rightleftharpoons CO + H_2O \quad (1.4)
\]

\[
CO_2 + H^+ + 2e^- \rightleftharpoons HCOO^- \quad (1.5)
\]

The uniqueness of electrochemical reduction of carbon dioxide is that hydrocarbons are produced only on copper electrodes. At the high voltages required for CO\(_2\) reduction also water is reduced to produce hydrogen. The potential of this conversion possibility could make a tremendous impact only if a suitable electrocatalyst could be found with a high selectivity to produce ethylene with high current efficiency. Ethylene is the most produced organic chemical in the world. Its consumption is twice that of the next two contenders propylene and benzene. Ethylene is considered a basic
feedstock to the petrochemical industry as production of most of the major petrochemical intermediates and petrochemicals are derived from ethylene\textsuperscript{6}.

The global energy demand is rising continuously. But there is a growing need to move away from the fossil fuels and shift to renewable energy sources. The first challenge will be to continue to supply energy to the infra-structure that requires liquid fuels. The second challenge is to level the fluctuating nature of renewable energy and make it more reliable. It is predicted that reactions like electrochemical reduction of carbon dioxide to hydrocarbons will play a major role in the transition to renewable energy as it can be used to produce liquid fuels and store excess electrical energy as chemical energy.\textsuperscript{7}

1.2. Objectives

The possibility of hydrocarbon production through electrochemical reduction of CO\textsubscript{2} on copper electrode\textsuperscript{8} suffers various problems namely (i) Hydrocarbon production efficiency is low. The product distribution is broad and there are competitive reactions like solvent reduction (hydrogen production) due to the over-potential required for the reaction.\textsuperscript{5} (ii) deactivation of copper electrode over time.\textsuperscript{9} The project proposal involved fabricating copper alloy electrode that could produce ethylene selectively during electrochemical reduction of CO\textsubscript{2} with the following characteristics\textsuperscript{10} (i) Economical (Low over-potential) (ii) High productivity (High Current Density) (iii) High selectivity (High Hydrocarbon current efficiency) (iv) High stability (Stable Current Density and hydrocarbon current efficiency).
CO2 reduction is a complex problem with complex analytical needs. We chose to use the DEMS technique to detect the product distribution of the various systems during CO2 reduction. The basic DEMS setup was not fulfilling our experimental needs. So we were required to develop the basic DEMS setup to effectively study CO2 reduction on various catalysts.

1.3. Thesis organization

This dissertation includes 7 chapters. In chapter 2, background information on CO2 reduction and CO2 reduction to hydrocarbons on copper, basic DEMS setup and data that is consistent with the literature obtained using the basic DEMS setup is presented.

The solubility of CO2 in water at ambient conditions is low (~ 33 mM). CO2 is a stable molecule and so high voltage is required to reduce CO2. So water also reduces producing hydrogen bubbles along with CO2 reduction. Therefore in chapter 3 “Combining an electrode-coated membrane with hydrodynamic flow in a wall-tube configuration”, an impinging jet was integrated to the electrode coated membrane inlet so that electrocatalytic reactions can be studied in enhanced and well-defined mass transfer conditions.

The possible products of CO2 reduction in aqueous electrolyte solutions are CO, formic acid, methane, ethylene and hydrogen. Besides non-volatile formic acid, all the other volatile products can be detected by DEMS. So in chapter 4 “Integration of electrochemical detection into differential electrochemical mass spectrometry using a thin layered wall jet ring disc electrode”, a second detecting electrode
coated on a carbon fiber ring was integrated to the electrode coated membrane inlet. The second electrochemical detector enables detection of products that were not detected by DEMS.

Various systems were explored to reduce CO$_2$ electrocatalytically to ethylene selectively. Initially Cu alloys namely Cu:W, Cu:Ta and Cu:Ag of various compositions were fabricated using co-sputtering method and tested. Then CO$_2$ solubility was increased using monoethanolamine (MEA) solutions$^{11}$ and reduced, ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM BF$_4$)$^{12}$ and guanidinium species$^{13}$ were used to bypass the high energy requiring CO$_2$ pathway and Cu electrode was modified by dipping in various metal solutions and tested. The obtained results are compiled and presented in chapter 5 “Electrochemical reduction of CO$_2$ using Cu alloys, monoethanolamine solution, ionic liquids, guanidinium species and Cu electrodes modified by galvanic displacement”.

Pt:Pb$^{14}$ is a stable formic acid detector which could be used for detecting non-volatile formic acid produced during CO$_2$ reduction. So in chapter 6 “Formic acid detection integrated Differential Electrochemical Mass Spectrometry using Pt:Pb electrode : Application in formaldehyde, methanol oxidation and CO$_2$ reduction”, Pt:Pb was used as the detector electrode in the previously developed electrochemical detection integrated DEMS. The setup was used to detect formic acid produced during simple reactions like methanol and formaldehyde oxidation and ultimately extend it’s application to complex reactions like CO$_2$ reduction.
1.4. References


CHAPTER 2. BACKGROUND

2.1. Electrochemical reduction of CO$_2$

In 1870, Royers performed experiments with zinc electrode in sodium bicarbonate solution and produced formic acid.$^1$ Subsequently, it was believed that formic acid was the only possible product of this reaction until 1985, when Dr. Hori performed experiments on a copper electrode and observed production of hydrocarbons like methane and ethylene.$^2$ Hori’s work led to an explosion of exploratory research in this field. Almost all electrodes ranging from metals,$^3$ semiconductors,$^4$ conducting polymers,$^5$ metallic oxides,$^6$ homogeneous catalysts (enzymes,$^7$ transition metal complexes$^8$) were tried and product distribution reported. Then combination electrodes like alloys$^9$ and film electrodes$^{10}$ were tried.

Azuma et al.,$^3$ identified that there was a systematic change in the major CO$_2$ reduction products based on the position of the electrode metal in the periodic table. Light transition metals and light metals in Groups IIIB and IVB produced mainly hydrogen, some of VIII and IB metals produced CO and heavy metals in groups IIIB to IVB produced majorly formic acid during the electrochemical reduction of carbon dioxide reaction. Copper which produced hydrocarbons were located between the metals producing CO and formic acid.

All reactions in the electrochemical reduction of CO$_2$ are multi-electron transfer processes with successive electronation and protonation. Various reaction mechanisms namely electron transfer mechanism and an adsorbed hydrogen mechanism have been proposed.$^{11}$ According to the electron transfer mechanism, CO$_2$ reduction is initiated by
electronation to form $\text{CO}_2^-$ anion radical while for the adsorbed hydrogen mechanism, reduction is started by reaction with adsorbed hydrogen. CO and HCOO are 2 electron processes while methane and ethylene are 8 and 12 electron processes. It was proposed that either CO or HCOO might be intermediates for the formation of hydrocarbons. But electrolysis of formic acid produced no hydrocarbons. While CO electrolysis gave a similar product distribution as CO$_2$ reduction. Thus, it was proposed that CO further reacts to produce hydrocarbons on copper electrodes. This hypothesis was further supported by IR spectroscopy data. Stabilized CO$_2^-$ anion radicals lead to CO pathway while unstabilized CO$_2^-$ radicals lead to formate pathway. Reaction rate depends on the surface coverage of adsorbed CO$_2$ and hydrogen. The adsorbed hydrogen coverage increases with current density while adsorbed CO$_2$ coverage remains constant.

pH alters the form in which CO$_2$ is available as determined by the CO$_2$ – bicarbonate – carbonate equilibrium. CO$_2$ is the reducible species. During CO$_2$ reduction high pH is formed in the electrode vicinity as hydroxides ions are produced during hydrogen evolution and CO$_2$ reduction. So local concentration at the electrode surface is different from bulk concentration. CO$_2$ reduction was less favored at pH less than or greater than neutral pH. At less pH values hydrogen evolution was favored while at high pH values non-reducible carbonate was formed. CO produced during CO$_2$ reduction didn’t adsorb on the electrode at pH less than 2.5. CO$_2$ reduction depends on the amount of CO$_2$ that reaches the electrode surface.

Product distribution also changes with the solvent. Although water has low CO$_2$ solubility, it favors hydrocarbon production being a good hydrogen source.
Experiments have also been carried out at high pressure\textsuperscript{21} and low temperature\textsuperscript{22} to increase the solubility of carbon dioxide in water and at different pH\textsuperscript{19} with regard to the CO\textsubscript{2}-bicarbonate-carbonate equilibria.\textsuperscript{23} Various solvents like organic solvents (methanol,\textsuperscript{24} Dimethyl formamide (DMF)), solid zirconia electrolytes and molten salt media have also been used for the electrochemical reduction of CO\textsubscript{2}.\textsuperscript{25} Organic solvents have high solubility of CO\textsubscript{2} (see Table 2.1). Carboxylation of alkyl halides are done in DMF. Solid oxide electrolytes are used in life support systems to produce O\textsubscript{2} from CO\textsubscript{2}. Molten salt media is used to produce CO from CO\textsubscript{2}. Due to high temperature, there is fast kinetics. Certain solvents like acetonitrile, dimethylformamide and propylene carbonate were tested and found unsuitable due to decomposition at high potential.\textsuperscript{26}

At ambient conditions solubility of CO\textsubscript{2} in aqueous solutions is 33 mM. So CO\textsubscript{2} reduction is mass transfer limited. To perform CO\textsubscript{2} reduction at large current densities the solubility of CO\textsubscript{2} can be increased by performing experiments at high CO\textsubscript{2} pressure or shifting to three-phase electrode configuration with gas diffusion electrodes where CO\textsubscript{2} supply is no longer limited by solubility. Metals were classified into four categories based on their behavior in high pressure CO\textsubscript{2} experiments.\textsuperscript{21} (i) Metals that produced hydrocarbons at ambient conditions and CO and HCOOH at high pressure (Cu). It was observed that the product selectivity of Cu changed from H\textsubscript{2} to hydrocarbons to CO and HCOOH as CO\textsubscript{2} pressure was increased. Product selectivity changed from CO and HCOOH to hydrocarbons to H\textsubscript{2} as voltage was increased. To produce hydrocarbons there need to be a balance between current density and CO\textsubscript{2} flux.\textsuperscript{27} Surface coverage of adsorbed H and CO played a key role in the product selectivity. (ii) Metals that produced H\textsubscript{2} at ambient conditions and continued to produce H\textsubscript{2} at high pressure (Ti, Nb, Ta, Mo,
Mn and Al). These metals form stable oxide layers and CO$_2$ adsorption is suppressed due to the oxide layers. (iii) Metals that produced H$_2$ at ambient conditions and CO and HCOOH at high pressure (Zr, Cr, W, Fe, Co, Rh, Ir, Ni, Pd, Pt, C and Si). In these metals CO$_2$ reduction and H$_2$ evolution happened simultaneously. As the pressure was increased the product selectivity is changed with increase in the faradaic efficiency of CO$_2$ reduction and decrease in H$_2$ evolution. There was no increase in current density with increase in CO$_2$ pressure. Rather there was a negative shift to the overvoltage attributed to the adsorption of CO intermediate. At ambient conditions CO$_2$ reduction stops with CO as CO is strongly adsorbed on these metals. At high pressures it is believed that CO is desorbed due to the equilibrium with CO$_2$ at high pressure. (iv) Metals that produced CO and HCOOH at ambient conditions and continued to produce CO and HCOOH at high pressure (Ag, Au, Zn, In, Sn, Pb and Bi). In these metals CO$_2$ reduction and H$_2$ evolution happens independently. So as the CO$_2$ pressure increases there is decrease in overvoltage and increase in current density. The product selectivity is not changed.

Pt nanoparticles on carbon-based gas diffusion electrodes produced long chain hydrocarbons at ambient conditions. It was observed that the mechanism was not similar to the Fischer-tropsch but rather involved desorption-readsorption and further conversion to long chain hydrocarbons. At high pressures Pt electrode produced H$_2$ in the normal gas diffusion electrode arrangement but produced methane in the reverse arrangement. At 30 atm of CO$_2$, methane was produced at a faradaic efficiency of 35% when operated at a current density of 900 mA/cm$^2$. In the reverse arrangement hydrogen formation was suppressed due to reduced contact between water and the Pt.
catalyst. Fe and Pt nanoparticles confined in CNT showed CO₂ reduction producing long carbon chain oxygenates particularly isopropanol. Confinement in CNT leads to reduction conditions similar to high pressure like effect at ambient pressure due to space-restriction effect.

Various electrochemical cells have been proposed and tested for this reaction namely trickle bed electrochemical reactor, microfluidic reactor, membrane flow reactor, filter press cell, zero gap electrochemical cell, undivided and divided fixed bed reactor and gas diffusion based electrolytic cell. Gas diffusion electrodes can be used to solve the CO₂ solubility problem.

Various techniques have been used for CO₂ reduction study. Gas Chromatography (GC) and Differential Electrochemical Mass Spectrometry (DEMS) have been used to detect gaseous products like hydrocarbons, hydrogen and CO. High Performance Liquid Chromatography (HPLC) and Nuclear Magnetic Resonance (NMR) have been used to detect liquid products like formic acid. Infrared spectroscopy and Surface Enhanced Raman Scattering (SERS) have been used to detect intermediates like adsorbed CO. SERS, Auger Electron Spectroscopy (AES) and X-ray Photoelectron Spectroscopy (XPS) have been used to detect poisonous species like graphitic carbon and copper oxide patina.

2.2. CO₂ reduction to ethylene on Cu

The product distribution varies with potential, the prime driving force. At potentials anodic of -1.12 V vs SHE only CO, formate and hydrogen are produced on copper. But potentials cathodic of -1.12 V vs SHE hydrocarbons start to form with
ethylene first and then methane. Hydrogen production is suppressed by CO production which adsorbs and blocks the electrode surface at -0.95 V vs SHE. Hydrocarbon production dominates over CO and formate production starting from -1.35 V vs SHE. Copper electrodes undergoes deactivation by adsorption of a byproduct, graphitic carbon. As a result the hydrocarbon production efficiency decreases drastically over time. XPS data showed that most of the graphite carbon was formed from the formate pathway. There is also a school of thought that attributes deactivation to impurities present in the electrolyte system. It was found that pulsed electro-reduction stabilized the hydrocarbon production efficiency. The anodic cycle helps to suppress the production of graphite carbon and maintain an oxide layer. It was observed that copper oxide prevents the poisoning by carbon and also has similar electrocatalytic behavior as copper.

XPS data of an electrode surface that had undergone CO₂ electroreduction for 3 hours also showed an increase in the oxygen peak. It was proposed that the source of adsorbed oxygen might be adsorption of water or from OH⁻ ions or from CO₂. Adsorbed oxygen lowers the work function of the surface and increases the electron availability thereby helps in hydrocarbon formation. Surface chemical composition has an effect on the product distribution. Formation of CO is favored on metallic Cu. Formation of CH₄ is favored in intermediate Cu/Cu₂O compositions. Formation of C₂H₄ requires both Cu and Cu₂O.

Electrocatalysis is a surface phenomenon and hydrocarbon production from CO₂ is a hydrogen intensive process. Watanabe et al. engaged on electrocatalyst design.
for CO₂ reduction. Their alloy catalyst design strategies were based on catalytic mechanism and electrochemical mechanism. Catalytic mechanism strategies involved enhancing the synergetic effects between different surface atoms by introducing hydrogen adsorption sites and oxygen adsorption sites. The electrochemical mechanism involved combining metals with different electronegativity, steric effect and electron structure etc. Consequently Cu:Ag, Cu:Sn, Cu:Zn, Cu:Ni, Cu:Cd, Cu:Pb were tried. Most of their alloys were formed by electrodeposition from an electrolytic bath of specific compositions and argon-ion sputter etching technique. They observed an improvement in ethylene production in a Cu:Ag alloy mixture. Ohkawa et al., worked with Cu:Pd based on the strategy of using hydrogen storing metals like Pd.

Pulsed mode reduction consists of applying a cathodic and anodic bias for specific intervals on the electrode successively. Anodic bias doesn’t actually mean anodic. It can be less cathodic. It interrupts the reactions happening at the cathodic bias and gives us a control over the surface intermediates like CO₂⁺ radical and adsorbed hydrogen. Higher the anodic bias highly stabilized is the CO₂⁺ anion radical. Higher the anodic bias lesser the adsorbed hydrogen coverage on the surface. CO₂ coverage could be increased by elimination of adsorbed hydrogen during an anodic bias. Pulsing doesn’t change only the potential but also alters the chemical conditions like pH at the electrode. The local concentrations of CO₂ and hydrogen ions change during pulsing. During normal operation copper electrodes got deactivated during CO₂ reduction due to deposition of graphitic carbon formed from the formate pathway. When CO₂ reduction was done on pulsed mode stable and enhanced hydrocarbon production was observed with less deactivation. A maximum faradaic efficiency of 65 % was achieved for
hydrocarbons.\textsuperscript{59} This was attributed to the oxide formed during the anodic bias which inhibits the deposition of graphitic carbon and catalyzes the CO\textsubscript{2} reduction.\textsuperscript{60} Anodic bias for ethylene selectivity was high compared to methane as the adsorbed hydrogen coverage decreased with high anodic bias. Higher ethylene selectivity was observed with electrodeposited copper with ethylene faradaic efficiency of 33.3 \% and methane faradaic efficiency of 3.6 \%.\textsuperscript{61} The selectivity was attributed to the increased presence of (1 0 0) crystal face which favors ethylene production.\textsuperscript{62} Roughened Cu surface prepared by anodization in KCl solution showed stable hydrocarbon production compared to a smooth Cu surface.\textsuperscript{63} Anodization in KCl solution created new crystal planes with catalytic sites of proper adsorption strengths.

Larger cations with low hydration number favored ethylene production i.e. Cs\textsuperscript{+} ~ K\textsuperscript{+} > Na\textsuperscript{+} > Li\textsuperscript{+} while methane production was favored in the reverse order.\textsuperscript{64} Higher the hydration number higher is the radius and so lower is the potential around it. Small Li\textsuperscript{+} ions suppressed CO\textsubscript{2} reduction by forming highly stabilized ion pairs (Li\textsuperscript{+} - CO\textsubscript{2}\textsuperscript{-}) incapable of further reduction.\textsuperscript{26} Tetra-butyl ammonium cation creates a hydrophobic atmosphere in the electrode vicinity and so enhances CO production on Cu electrodes in a CO\textsubscript{2} purged aqueous methanol electrolyte solution.\textsuperscript{26} Tetra-butyl ammonium ion catalyzes electronation of CO\textsubscript{2} to CO\textsubscript{2}\textsuperscript{-} anion radical by a mediation process and stabilizes intermediate by forming an ion pair that is capable of further reduction. Halide anions enhance ethylene selectivity on copper electrodes. Ethylene faradaic efficiencies of about 80 \% was obtained using Cu electrodes in CO\textsubscript{2} purged 3 M KBr and KI aqueous electrolyte solutions.\textsuperscript{65} It adsorbs on the electrode surface and inhibits hydrogen evolution. Stronger the halide ions were adsorbed to the electrode, stronger
the CO₂ molecules could be restrained and so higher was the CO₂ reduction current density. Current density was observed in the order Cl⁻ < Br⁻ < I⁻. Electron transfers occurs by nucleophilic attack on the C atom of CO₂ through a bond which chemically activates CO₂. A decrease in overpotential for CO₂ reduction was observed. Onset of CO₂ reduction took place at -0.28 V Vs NHE which is close to the standard potential for forming ethylene (E° = 0.079 V Vs NHE). In other cases CO₂ molecules required additional energy to reach the electrode amidst the solvent molecules. Adsorbed sulfide anions change the product selectivity. On Cu electrode the faradaic efficiency of methane decreased from 36 % to 2 % while C2 components (ethylene and ethanol) increased from 13% to 25%. Adsorbed sulfide anions decrease the adsorbed CO coverage during CO₂ reduction and so suppression effect of hydrogen evolution is decreased.

Enhanced production of hydrocarbons was observed with copper gas diffusion electrodes. Methane and ethylene were produced at faradaic efficiencies of 9 and 69 %. Copper was believed to be the only unique metal that possessed the ability to convert CO₂ to CO and further convert CO to hydrocarbons. So gas diffusion electrodes were fabricated by alloying Cu with Ag that possessed the ability to only convert CO₂ to CO and with Pb that possessed the ability to only convert CO to hydrocarbons. Ag and Pb were alloyed with Cu in low compositions between 1 to 0.05 %. It was observed that other compositions showed low catalytic activity. Lower overpotentials for hydrocarbon production was observed in both the cases. Overpotentials for promoting electrochemical CO₂ reduction to hydrocarbons at dispersed Cu:Pb (0.2 %) and Cu:Ag (0.2 %) electrocatalysts were 900 mV and 1.2 V less than for dispersed Cu. Cu-Ag
showed enhanced decrease in overpotential for hydrocarbon production as Ag populates the catalyst surface with CO readily.

Lower the temperature higher the solubility of CO$_2$. Temperature also affects the kinetics of the reaction. It was observed that ethylene was produced more at high temperatures with a faradaic efficiency of 20% at 40 °C and methane production was favored at lower temperatures with a faradaic efficiency of 65% at 0 °C.$^{69}$ Hydrocarbon formation is favored at high temperatures as hydrocarbon formation from electrochemically produced adsorbed CO and hydrogen is a thermal surface reaction.$^{28}$

2.3. Differential Electrochemical Mass Spectrometry (DEMS)

DEMS technique$^{70}$ was used to detect the product distribution of the fabricated electrocatalytic CO$_2$ reduction systems. The pros of DEMS are it's in-situ, instantaneous, highly sensitive and can detect a particular product or different products at the same time. The cons are it can detect only volatile products and limited by the samples that could be studied. We fabricate our electrodes by sputter deposition. So in our case materials that could be sputtered.

In DEMS, a nanoporous hydrophobic membrane (extended PTFE) is used to detect volatile products produced during an electrocatalytic reaction and prevent the electrolyte from entering into the mass spectrometer. DEMS could be implemented by placing the membrane inlet near the electrode or the electrode could be coated over the membrane as seen in Fig.2.2.
Membrane electrodes are made by the following procedure as seen in Fig.2.3. (i) One end of the tube is covered with membrane (extended PTFE gore-tex). (ii) Silver epoxy is applied and electrical lead is attached. (iii) Epoxy is cooked in oven for 2 hours. (iv) About 100nm of metal (working electrode) is deposited over the membrane either by vapor deposition or sputtering. (v) The silver epoxy part is covered using a heat shrink tubing. The conductive silver epoxy could be replaced by conductive tape.

The electrochemical cell is a four neck round bottomed 100ml flask as seen in Fig.2.4. The membrane electrode containing the working electrode deposited on it's tip, counter electrode (palladium coil), reference electrode (Hg/HgSO₄) and sparger are inserted into the four necks and sealed using rubber corks. The other end of the membrane electrode is connected to the mass spectrometer. 0.5 M KHCO₃ aqueous electrolyte solution is used. The solution pH is 8.4 and after CO₂ saturation pH decreases to 7.5. The stirring rate is maintained at 300rpm. This basic DEMS setup was used to obtain data that were consistent with the literature.

Potential could be scanned (Fig.2.5) or applied as steps (Fig.2.6) using the potentiostat. The corresponding mass spectrometer response for various masses is recorded simultaneously. The recorded ion current is calibrated using calibration values found for solubility values of the respective gases according to Henry’s law. When the inlet silica capillary size of the DEMS inlet is changed it leads to change in ion current magnitudes. But the log of the ion current change produced was found to be consistent for all inlet capillary sizes and was used for calibration when required. The normalized faradaic efficiency is found using the following formula
\[
\text{FE (\%)} = \frac{n_1 M_1}{(n_1 M_1 + n_2 M_2 + \ldots)} \times 100
\]

where \( n \) refers to the number of electrons required to produce the product (2 for \( \text{H}_2 \), \( \text{CO} \) and \( \text{HCOOH} \), 8 for \( \text{CH}_4 \), 12 for \( \text{C}_2\text{H}_4 \)) \(^{17}\) and \( M \) refers to the number of moles of the product produced. The normalized faradaic efficiency is based on the assumption that only hydrogen, methane and ethylene are produced during CO\(_2\) reduction.

Various metals were tried initially and their product distribution detected. Metals like copper, gold, silver and aluminum were vapor deposited. While platinum and palladium were electrodeposited over gold. It confirmed that copper was the electro-catalyst that produced hydrocarbons during electrochemical reduction of carbon dioxide.\(^3\) (see Fig.2.7). Hydrocarbon production was not stable as copper deactivated over time with deposition of carbonaceous material.\(^47\) Potential of -2.2 V was applied to copper electrode for a period of 90 minutes and signals for 26 amu (ethylene), 15 amu (methane) and 2 amu (hydrogen) were detected. It was found that initially the product distribution was stable for about 30 minutes and then the hydrocarbon efficiency dropped drastically and hydrogen efficiency increased. (see Fig.2.8). Electrodeposited copper produced ethylene selectively.\(^61\) As copper was electrodeposited the deactivated copper resumed hydrocarbon production as before with the renewed copper surface. But as copper electrodeposition continued ethylene was selectively produced. (see Fig.2.9). Copper selectively produced ethylene with a faradaic efficiency of \( \sim 80 \% \) in concentrated potassium halide aqueous electrolytes.\(^65\) The halide ions adsorbed strongly on the copper electrode inhibiting reactions particularly hydrogen evolution to give high ethylene faradaic efficiencies. (see Fig.2.10 and Fig.2.11).
2.4. Figures

Figure 2.1. Mechanism proposed for electrochemical reduction of carbon dioxide to hydrocarbons.

Figure 2.2. Basic DEMS setup A) membrane inlet placed near electrode B) electrode coated over membrane.
Figure 2.3. Image depicting the different stages in the fabrication of membrane electrodes.
Figure 2.4. Image of experimental setup showing three electrode electrochemical cell in a four-neck 100ml round bottom flask with sparger and connected to mass spectrometer inlet. A) front view B) top view.
Figure 2.5. Potential scan for electrochemical reduction of CO$_2$ on copper electrode in argon purged (---) and CO$_2$ purged (—) 0.1 M KHCO$_3$ aqueous electrolyte solution. Potentiostat response A) current vs potential. Mass spectrometer response B) 2 amu – hydrogen C) 15 amu -methane D) 26 amu-ethylene.
Figure 2.6. Potential step for electrochemical reduction of CO₂ using copper electrode at -1.4 V, -1.6 V, -1.8 V, -2 V and -2.2 V in CO₂ purged 0.1 M KHCO₃ aqueous electrolyte solution. Potentiostat response A) current vs time. Corresponding mass spectrometer response B) 2 amu - hydrogen C) 15 amu - methane D) 26 amu – ethylene.
Figure 2.7. Potential scan for electrochemical reduction of \( \text{CO}_2 \) on various metal electrodes Cu (---), Ag (---), Al (---), Au (---), Pt (---) in \( \text{CO}_2 \) purged 0.1 M KHCO\(_3\) aqueous electrolyte solution. Potentiostat response A) current vs potential. Mass spectrometer response B) 2 amu – hydrogen C) 15 amu -methane D) 26 amu-ethylene.
Figure 2.8. Electrochemical reduction of CO$_2$ using copper electrode held at -2.2 V. Potentiostat response A) current vs time. Corresponding mass spectrometer response B) 2 amu - hydrogen C) 15 amu - methane D) 26 amu – ethylene.
Figure 2.9. Electrochemical reduction of CO₂ using deactivated copper electrode held at -2.2 V in CO₂ purged 0.1 M K₂SO₄ aqueous electrolyte solution with 8 mg of CuSO₄ introduced for in-situ Cu electrodeposition. Potentiostat response A) current vs time. Corresponding mass spectrometer response B) 2 amu - hydrogen C) 15 amu - methane D) 26 amu – ethylene.
Figure 2.10. Potential scan for electrochemical reduction of CO₂ on copper electrode in CO₂ purged 1 M KI aqueous electrolyte solution. Potentiostat response A) current vs potential. Mass spectrometer response B) 2 amu – hydrogen C) 15 amu -methane D) 26 amu-ethylene.
Figure 2.11. Faradaic efficiency for hydrogen (——), methane (——) and ethylene (——) produced during electrochemical reduction of CO$_2$ on copper electrode in CO$_2$ purged 1 M KI aqueous electrolyte solution.

2.5. Tables

Table 2.1. Solubility of CO$_2$ in various solvents at 25 °C

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Concentration(M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.033</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.06</td>
</tr>
<tr>
<td>Tetrahydrofuran (THF)</td>
<td>0.205±0.008</td>
</tr>
<tr>
<td>Acetonitrile(AN)</td>
<td>0.279 ± 0.008</td>
</tr>
<tr>
<td>Dimethylformamide (DMF)</td>
<td>0.199 ± 0.006</td>
</tr>
<tr>
<td>Dimethylsulphoxide (DMSO)</td>
<td>0.138 ± 0.003</td>
</tr>
</tbody>
</table>
Table 2.2. Mass spectrometer calibration values for various gaseous products

<table>
<thead>
<tr>
<th></th>
<th>solubility in water (mM)</th>
<th>calibration peak</th>
<th>Change in Mass Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>0.78</td>
<td>2 amu</td>
<td>$1.89 \times 10^{-9}$</td>
</tr>
<tr>
<td>Methane</td>
<td>1.5</td>
<td>15 amu</td>
<td>$7.25 \times 10^{-10}$</td>
</tr>
<tr>
<td>Ethylene</td>
<td>4.9</td>
<td>26 amu</td>
<td>$1.56 \times 10^{-9}$</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>34</td>
<td>44 amu</td>
<td>$1.23 \times 10^{-8}$</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>0.8</td>
<td>12 amu</td>
<td>$2.85 \times 10^{-11}$</td>
</tr>
</tbody>
</table>

2.6. References


23. Emerson, H., Chemical Oceanography and marine carbon cycle.


CHAPTER 3. COMBINING AN ELECTRODE-COATED MEMBRANE WITH HYDRODYNAMIC FLOW IN A WALL-TUBE CONFIGURATION


Subramanian Venkatachalam\(^2\),\(^3\), Robert J. Angelici\(^1\), L. Keith Woo\(^1\), and Andrew C. Hillier\(^2\),\(^4\)

3.1. Abstract

We present an experimental system that combines differential electrochemical mass spectrometry with hydrodynamic flow consisting of an impinging jet in a wall-tube configuration. This assembly allows simultaneous detection of electrochemical signals along with monitoring of dissolved gas species using differential electrochemical mass spectrometry under well-defined hydrodynamic conditions and over a wide range of mass transfer rates. The working electrode is deposited directly onto a thin, hydrophobic membrane, which also serves as the inlet to the mass spectrometer. This inlet provides extremely rapid mass detection as well as a high flux of products from the electrode surface into the mass spectrometer. The impinging jet is designed in a wall-tube configuration, in which the jet diameter exceeds that of the electrode, thus providing

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uniform and rapid mass transfer conditions over the entirety of the electrode surface. This combination of rapid detection and controllable flow conditions allows a wide range of hydrodynamic conditions to be accessed with simultaneous electrochemical and mass spectrometric detection of dissolved gas species, which is important in the analysis of a range of electrochemical reactions. The capabilities of this configuration are illustrated using a platinum-coated electrode and several electrochemical reactions, including ferrocyanide oxidation, proton reduction and oxalic acid oxidation.

3.2. Introduction

The characterization of electrochemical processes has benefited tremendously from the ability to combine traditional electrochemical measurements with complementary analytical techniques. One of the more notable coupled methods that allows direct measurement of both the quantity and identity of solution species involved in electrochemical reactions is one that combines an electrochemical interface with a mass spectrometer. This was originally accomplished by using a Teflon-coated frit to separate the aqueous phase of an electrochemical cell from the vacuum present within a mass spectrometer, thus allowing volatile gases to diffuse from the solution phase into the spectrometer for detection. Subsequent improvements included the introduction of Differential Electrochemical Mass Spectrometry (DEMS), which substantially reduced detection time by connecting the electrochemical cell directly to the ionization chamber of the mass spectrometric system, and thereby significantly increasing the gas flux into the detector. Coupled electrochemical mass spectrometric techniques have further been extended to detect non-volatile products, for use during the indirect detection of solid and single crystal electrodes, for scanning detection near electrode surfaces,
combined with quartz crystal microbalance, combined with infrared reflection measurements, and in several configurations coupled to hydrodynamic electrolyte flow, as will be discussed below. Several reviews on these techniques have been published.

One of the difficulties encountered when studying electrochemical reactions and with DEMS measurements involves mass transfer limitations near the electrode surface. When reactant solubility is low and reactions occur at mass transfer limited conditions, it is difficult to quantitatively study electrochemical reaction kinetics. Hydrodynamic electrochemical techniques such as the rotating disc electrode (RDE) and impinging jets were designed to overcome such limitations. These techniques facilitate the examination of reaction kinetics by providing well-defined and enhanced mass transfer rates to an electrode surface. The RDE technique exploits electrode rotation to induce a centrifugal flow at the electrode surface. For stationary electrodes, the impinging jet electrode can be used to direct rapid flow to an electrode surface, which creates a thin boundary layer and associated high mass transfer rates to the surface. The hydrodynamics associated with an impinging jet form a stagnation region at the center of the electrode surface that is surrounded by a decaying radial flow away from the electrode’s center in the wall-jet region. Impinging jet electrodes are generally classified according to two limiting types, wall-tube and wall-jet electrodes, whose classification is based on the electrode and the nozzle dimensions. Wall-tube electrodes involve a smaller electrode with a jet formed from a larger nozzle in such a way that the electrode falls completely within the stagnation region, giving a uniformly accessible electrode surface. In contrast, wall-jet electrodes are configured with the jet from a smaller nozzle impinging on a larger electrode in such a way that the electrode
extends into the wall-jet region. Impinging jet electrodes can be implemented using either a thin layer flow cell or a large volume cell.

Hydrodynamics have been integrated into electrochemical mass spectrometric techniques in several ways. Examples include the use of a rotating vacuum feed to integrate RDE with mass spectrometry and the use of a dual, thin layer cell designed to integrate a wall-jet electrode with a DEMS detector system. A design based upon the latter has also been used in the context of a hydrodynamic DEMS system coupled to a quartz crystal microbalance electrode. A recent example of an advanced hydrodynamic system used a generator/detector electrode arrangement combined with channel flow and a DEMS detection system while another demonstrated the combination of flow with a hanging meniscus electrode.

In a 2012 report, a unique hydrodynamic DEMS system was described that coupled a wall-jet electrode configuration to online mass spectrometry using a solid disk electrode embedded in a porous Teflon ring, with the latter serving as the inlet to a mass spectrometer. This electrode/jet design provided hydrodynamic online mass spectrometry that functioned in traditional, large volume electrochemical cells and could be used to interrogate large solid electrodes and even single crystal surfaces. However, it did exhibit a limitation related to a relatively low permeability rate of dissolved gases through the porous Teflon ring. This low permeability resulted in reduced collection efficiencies (of the mass spectral signals) at high fluid flow rates.

Here, we describe a variation on this method that borrows from the original DEMS design where the working electrode is deposited directly onto a thin, hydrophobic
membrane, which also serves as the inlet to the mass spectrometer. This configuration, although restricted to electrode materials that can be formed as thin, coated layers, is relatively simple, yet allows for a very rapid and high flux of volatile solution species into the DEMS detector, with no apparent permeability limitations over the range of flow-rates examined. By attaching the membrane electrode to a small length of tubing, we also allow for electrochemical measurements in large volume cells. This is then combined with a wall-tube impinging jet through which the hydrodynamic conditions at the electrode surface can be controlled and widely varied over a large range of flow rates. Example reactions used to probe the capabilities of this method include ferrocyanide oxidation, proton reduction, and oxalic acid oxidation.

### 3.3. Experimental section

A schematic of the impinging jet/DEMS system used in this work is illustrated in Figure 3.1, including the electrochemical cell, fluid pumping system, and mass spectrometer. The electrochemical cell consisted of a 150 mL glass beaker with electrochemical and auxiliary components mounted through a gas-tight Teflon lid. The working electrode consisted of a thin layer of Pt sputtered onto a porous, hydrophobic membrane. The membrane (extended PTFE, Gore-Tex, 20 nm pore diameter, 75 \(\mu\)m thickness and 50% porosity) was mounted on one end of the 1/16” PTFE tube and held in position using heat shrink, Teflon tubing. The PTFE tube was directly attached to the mass spectrometer inlet. Several prepared PTFE tubes with membranes were prepared as working electrodes by sputter coating a thin Pt film. The PTFE tubes were mounted in an aluminum disc in an array of 1/16” holes, which was then fixed to the substrate holder of a sputtering system. A sputter-up-type sputtering system (ATC 1800-F, AJA
International) was used for DC sputtering of \(~100\) nm of Pt onto the membranes. The sputtering system was equipped with a quartz crystal thickness monitor (TM-350/400, Maxtek) to measure the film thicknesses. Pt sputtering was achieved using a DC power of \(112.5\) W, an argon flow of \(25\) sccm, a chamber pressure of \(7.4\) mTorr, and a substrate rotation rate of \(20\) RPM. Following deposition, silver epoxy was used to make electrical contact to the Pt film. Heat shrink tubing was then used to cover and insulate areas other than the exposed Pt film over the membrane.

The impinging jet consisted of a custom 1/16” (nominal) diameter PTFE nozzle, which was fixed to the end of a contoured glass tube and positioned directly beneath the membrane/working electrode. The glass tube and nozzle were secured to a manual positioning stage for control of the nozzle position and to maintain the nozzle-electrode gap. The nozzle and tubing were connected to a high flow-rate peristaltic pump (Peri-Star 291, World Precision Instruments) with a maximum rotation rate of \(100\) RPM. The pump was equipped with a four channel pump head possessing eight rollers (to reduce pulsation) and the four channels were combined using a manifold fitting to give a maximum pumping rate of \(127\) mL/min (or \(2.11\) cm\(^3\)/sec).

The mass spectrometer consisted of an HPR-20 gas analysis system with a HAL RC quadropole mass spectrometer and a QIC Fast sampling capillary inlet (Hiden Analytical Inc.). The vacuum pumping system had a 60 L/s turbo pump (Edwards, Model EXT75DX) backed by a 2.2 m\(^3\)/h two-stage, rotary vane pump (Edwards, Model E2M1.5) on the mass spectrometer’s main ionization chamber, and a high capacity (6.7 m\(^3\)/h) dry scroll pump (Edwards, Model XDS 5) attached through a variable exhaust valve for differential pumping of the backside of the membrane electrode.
Electrochemical experiments were performed using a CH Instruments model 760B electrochemical workstation (CH Instruments Inc., Austin, TX). A Pd coil (100% Pd wire, 0.2mm, SPI Supplies, West Chester, PA) was used as the counter electrode. A 12 mm diameter glass tube (Ace Glass Inc) with a porous frit was used as the counter electrode compartment, with the porous frit serving to separate the counter electrode reaction from the working electrode compartment. A mercury/mercurous sulfate reference electrode (CHI 151, CH Instruments Inc, Austin, TX) was used as the reference electrode.

All experiments are performed with Nanopure water with resistivity 18M\(\Omega\). (Barnstead Inc). Electrolyte solutions were prepared from reagent grade chemicals: potassium sulfate (Fischer), potassium ferrocyanide trihydrate (A.C.S. reagent grade, Aldrich), potassium ferricyanide (Aldrich), sodium perchlorate monohydrate (Fischer), perchloric acid (70% reagent A.C.S, Fischer), sulfuric acid (certified A.C.S plus, Fischer), oxalic acid dihydrate (certified A.C.S crystalline, Fischer).

3.4. Results and discussion

The quality of the sputtered Pt membrane electrode was verified by performing cyclic voltammetry in an acidic solution. Fig.3.2 illustrates a typical cyclic voltammogram of a sputtered Pt membrane electrode in a 0.1 M H\(_2\)SO\(_4\) solution. The response includes a well-defined set of underpotential hydrogen adsorption/desorption peaks between -0.4 and -0.6 V (vs Hg/Hg\(_2\)SO\(_4\)). A featureless double layer region during the positive-going scan between -0.4 and 0.2 V reflects a clean surface. The characteristic Pt oxidation peak begins at 0.2 V, and the corresponding oxide reduction peak appears at 0.0 V on
the return scan. All of these features are typical of a clean, polycrystalline Pt surface in a sulfuric acid solution. A roughness factor of 10 +/- 2 was determined for this sputtered electrode based upon the charge associated with hydrogen adsorption.

The flow characteristics of the impinging jet and membrane electrode were determined via oxidation of ferrocyanide as a function of fluid flow rate through the jet. Fig.3.3A depicts a series of potential scans in a 5 mM solution of Fe(CN)$_6^{3+}$ in 0.2 M K$_2$SO$_4$ over a range of jet flow rates ranging from a stagnant solution up to a maximum flow rate of 2.11 cm$^3$/sec. In all cases, the current increases at potentials above -0.2 V as the oxidation of ferrocyanide commences. The current then reaches a plateau value indicating mass transfer limited oxidation rates at more positive potentials. As the flow rate through the jet increases, there is a corresponding increase in the plateau current. Oscillations are observed in the current at the two lowest flow rates of 0.1 and 0.2 cm$^3$/sec, which can be ascribed to fluid pulsation from the peristaltic pump. These oscillations diminish at higher flow rates.

According to theoretical predictions, the limiting current for an impinging jet follows one of two limiting trends with increasing flow rate, depending upon the relative diameter of the nozzle to that of the electrode. For a wall-tube configuration, which occurs under conditions where the jet nozzle radius ($r_T$) is greater than half the electrode radius ($R$), the electrode can be considered to be uniformly accessible (with uniform mass transfer across the electrode surface) and the limiting current is described by

$$i_{lim} = 0.61 \pi R^2 n F D^{2/3} v^{-1/6} V_f^{1/2} r_T^{-3/2} c_\infty$$

(3.1)
where $R$ is the electrode diameter, $D$ is the diffusion coefficient, $\nu$ is the kinematic viscosity, $V_f$ is the fluid flow rate, $r_T$ is the radius of the jet nozzle, and $c_\infty$ is the bulk concentration of the reacting species. According to Eqn. 3.1, the limiting current will increase in proportion to the square root of the flow rate. For a wall-jet configuration, where the nozzle diameter is less than one-eighth the electrode diameter, the limiting current is described by:

$$i_{lim} = (1.60k)R^{3/4}nFD^{2/3}\nu^{-5/12}V_f^{3/4}d_T^{-1/2}c_\infty \quad (3.2)$$

where $d_T$ is the jet nozzle diameter and $k$ is a constant. The relationship shown in Eqn. 3.2 predicts an increase in limiting current that is proportional to the $\frac{3}{4}$ power of the flow rate. For the ferrocyanide data measured here, Fig.3B depicts the limiting electrochemical current ($i_{lim}$) measured at 0.4 V versus the square root of the flow rate ($V_f^{1/2}$). The experimentally measured limiting current values fall uniformly along a straight line on this plot, indicating that the flow characteristics of the impinging jet are indeed following that of the wall-tube configuration. This behavior is also consistent with the nozzle and electrode sizes, which are of approximately the same diameter for this system. A best fit of the data provides a flow-rate dependence to the power of 0.48, which is an excellent match to the theoretical prediction for a wall-tube flow for an impinging jet. At the highest flow rate achievable with this system of $V_f = 2.11 \text{ cm}^3/\text{sec}$ and a nozzle diameter of 0.158 cm, this jet provides hydrodynamic conditions equivalent to a RDE at a rotation rate of ~14,000 RPM. \textsuperscript{10, 20}

The working electrode configuration used in this work, where the electrode material is deposited directly onto a thin, hydrophobic membrane, allows for rapid sampling of
dissolved gases near the electrode interface when the electrode is attached to the inlet of a mass spectrometer. Fig. 3.4 depicts the results of a mass spectral cyclic voltammogram (MSCV) of the Pt-coated membrane electrode in a solution containing 0.1 M NaClO₄ and 1 mM HClO₄. In this measurement, the electrode potential is scanned (at 5 mV/s) while electrochemical current (i) is recorded (Fig. 3.4A) as well as mass spectral signals corresponding to hydrogen (iH₂, m/z = 2 amu) (Fig. 3.4B) and oxygen (iO₂, m/z = 32 amu) (Fig. 3.4C). Scanning the electrode potential between the solvent limits in this solution results in several reactions that can be observed both in the electrochemistry and in the mass spectral signals. Four regions and their corresponding reactions contributing to the recorded responses are identified in the figure.

Region (i)  \[ \text{H}_2\text{O} \rightarrow \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \] (3.3)

Region (ii)  \[ \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O} \] (3.4)

Region (iii)  \[ \text{H}^+ + \text{e}^- \rightarrow \frac{1}{2} \text{H}_2 \] (3.5)

Region (iv)  \[ \text{H}_2\text{O} + \text{e}^- \rightarrow \frac{1}{2} \text{H}_2 + \text{OH}^- \] (3.6)

In region (i), oxidation of water (Eqn.3.3) occurs on the Pt surface as the potential is scanned positive, commencing at values of ~1 V. This is indicated by a substantial increase in electrochemical current (Fig. 3.4A) at these potential values. The oxygen that is generated by this reaction is readily detected by the ion current associated with a mass of 32 amu (iO₂) (Fig. 3.4C). The magnitude of the oxygen ion current reflects the rate of oxygen production at the electrode, and tracks with the increase in electrochemical current, as well as the decrease when the potential is reversed at the
highest limit. During the reverse scan, the electrochemical and oxygen ion currents decrease back to zero and remain there until oxygen reduction begins (Eqn.3.4) during the reverse scan at ~ -0.25 V at region (ii), where a drop in the \( i_{\text{O}_2} \) signal is observed. A further decrease in potential initiates hydrogen evolution (Eqn.3.5) in region (iii). Under these conditions, the solution pH has a value of ~3, and hydrogen evolution occurs at a mass transfer limited rate. Scanning the potential beyond -1 V results in further hydrogen production via the reduction of water (region iv, Eqn.3.6).

The impact of flow on the electrochemical and mass spectral responses can be seen by tracking the hydrogen evolution reaction in region (iii) versus flow rate through the impinging jet. Fig.3.5 depicts a series of linear potential sweep measurements tracking the electrochemical current (Fig.3.5A) and hydrogen ion current (Fig.3.5B) as a function of fluid flow rate. The flow through the jet is varied from 0 up to a maximum of 2.11 cm\(^3\)/sec. In each current trace, the electrochemical current and the hydrogen ion current increase as hydrogen evolution begins, and then plateau to reflect mass transfer limited conditions. Although the hydrogen evolution reaction becomes mass transfer limited under these conditions, there is slight increase in the magnitude of current at decreasing potentials in this region. This is likely due overlap with the onset of water reduction at these potentials, as seen in Fig.3.4A.

A plot of the limiting current values versus the square root of the flow rate (Fig.3.6A) again provides a straight line, indicating wall-tube flow behavior consistent with Eqn.1. This behavior is seen in both the electrochemical current (\( i_{\text{ir}} \)) and the hydrogen ion current (\( i_{\text{H}_2} \)). In addition, a plot of the electrochemical current versus the hydrogen ion current (Fig.3.6B) provides a straight line. This indicates that the collection efficiency of
the mass spectrometer is unchanged with increasing flow, and that the permeability of hydrogen through the membrane into the detector is sufficiently fast so as not to pose a detection limitation. Indeed, given that the highest flow rate achieved in this system is equivalent to a RDE rotating at 14,000 rpm, sampling by the mass spectrometer must be occurring at a very high rate.

As a test of another reaction involving the production of gas-phase species, we examined the oxidation of oxalic acid. A MSCV for this reaction at several different solution flow rates is depicted in Fig.3.7 at a Pt-sputtered membrane electrode in an argon-purged electrolyte containing 0.5 M H₂SO₄ and 5 mM oxalic acid. The electrochemical current ($i_f$) in Fig.3.7A shows an increase in current starting at ~0.4 V corresponding to the oxidation of oxalic acid (H₂C₂O₄).

$$\text{H}_2\text{C}_2\text{O}_4 \rightarrow 2\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \quad (3.7)$$

This reaction proceeds with the consumption of oxalic acid and the production of CO₂. Indeed, tracking of the ion signal for carbon dioxide ($i_{\text{CO}_2}$, m/z = 44 amu) shows an increase in CO₂ ion current simultaneously with the increase in electrochemical current. At no flow conditions, the diffusion limited oxalic acid oxidation current is dominated by the oxide layer formation at the Pt electrode film. Therefore, the diffusion limited current is not well developed (Fig.S.1, Supporting Information). Nevertheless, the reaction current does plateau in the region between 0.6 and 0.8 V. A measurement of the oxygen ion current ($i_{\text{O}_2}$) shows a featureless response until the onset of water oxidation, where an increase in the oxygen signal appears. As was observed in the case of the ferrocyanide oxidation and hydrogen evolution reactions, the impact of increasing flow
from the impinging jet is to increase the rate of mass transfer to the surface, and consequently the measured electrochemical and mass spectral currents also increase. As the flow is increased from 0 up to 2.11 cm³/sec, the electrochemical current (Fig.3.7A) and carbon dioxide ion current (Fig.3.7C) both increase according to the wall-tube profile (Fig.S.2, Supporting Information). A plot of the electrochemical current versus the carbon dioxide ion current (Fig.3.8) displays a linear dependence. Thus, just as was observed with the hydrogen evolution reaction, the collection efficiency at the mass spectrometer remains constant over the entire range of sampled flow rates. This indicates a very rapid flux of carbon dioxide into the detector that is not limited due to insufficient permeation rates through the membrane. The high flux of species into the mass spectrometer in the configuration described here is due to the fact that the electrode material is deposited directly on the membrane surface, and the thickness of the membrane (ca. ~ 75 µm) is sufficiently small as to not to pose a limitation to transport of gases into the mass spectrometer. Indeed, if one estimates the mass transfer rates to the electrode surface at the highest jet flow rate, it remains approximately 1 to 2 orders of magnitude lower than that through the mass spectrometer’s membrane inlet.

3.5. Conclusions

In this work, we describe a configuration of differential electrochemical mass spectrometry that employs a wall-tube impinging jet to provide controlled hydrodynamic conditions and rapid mass transfer of solution species to the electrode surface. By combining this with an electrode design that exploits a very thin, coated membrane as the inlet to the mass spectrometer, we are able to achieve high flux rates of volatile
solution species into the spectrometer, and achieve uniform collection efficiency that is maintained over a large range of hydrodynamic conditions. Although this configuration is limited to electrodes in the form of thin, coated layers, it does provide an improvement in terms of the range of hydrodynamic conditions that can be accessed and quantitatively measured using the mass spectrometer.

The performance of this system in terms of flow characteristics and electrochemical/chemical detection has been demonstrated using several common electrochemical reactions, including ferrocyanide oxidation, hydrogen evolution, and oxalic acid oxidation. The hydrodynamics clearly followed a wall-tube flow characteristic, which has the benefit of providing a uniformly accessible electrode, where mass transfer is equal over the entire electrode surface. Our flow system was able to achieve hydrodynamic conditions similar to that achieved in a RDE at rotation rates near 14,000 rpm, although this performance could be increased with simple modifications to enhance the pumping system. And most notably, even at the highest flow rates, we were able to demonstrate rapid species detection in the spectrometer, reflecting a uniform collection efficiency. We anticipate that this instrument design can be used to study a variety of interesting and important electrochemical and electrocatalytic reactions.
3.6. Figures

Figure 3.1. Schematic diagram of electrochemical cell and system components for combined DEMS with wall-tube impinging jet. The electrochemical cell includes gas purge lines, Hg/Hg$_2$SO$_4$ reference electrode, counter electrode compartment, and metal-coated membrane as working electrode that is directly attached to DEMS inlet. The wall-tube impinging jet includes a high flow peristaltic pump with tubing and nozzle directed at working electrode. (Inset) Details of working electrode/membrane/impinging jet configuration with dimensions noted (nozzle diameter = 1.06 mm, electrode diameter = 1.22 mm, DEMS inlet diameter = 0.508 mm).
Figure 3.2. Cyclic voltammogram of 100 nm thick, Pt-coated membrane electrode in argon-purged aqueous solution containing 0.1 M H₂SO₄. (electrode diameter: 2.4 mm, Pt layer thickness: 100 nm, scan rate: 100 mV/sec).
Figure 3.3. (A) Diffusion-limited ferrocyanide oxidation (scan rate = 5 mV/sec) at Pt-coated membrane electrode with different jet flow rates ranging from 0 up to 2.11 cm$^3$/sec in argon-purged aqueous electrolyte containing 0.2M K$_2$SO$_4$, 5mM K$_4$[Fe(CN)$_6$], and 5mM K$_3$[Fe(CN)$_6$]. (B) Plot of limiting current ($i_{\text{lim}}$) of ferrocyanide oxidation versus square root of jet flow rate ($V_f^{1/2}$).
Figure 3.4. Electrochemical and mass spectral response of Pt-coated membrane electrode in argon-purged solution containing 0.1 M NaClO₄ and 1.0 mM HClO₄ at a scan rate of 5 mV/sec. (A) Electrochemical (Faradaic) current ($i_f$), (B) H₂ ion current ($i_{H2}$, m/z = 2 amu), and (C) O₂ ion current ($i_{O2}$, m/z = 32 amu). Regions i, ii, iii, and iv represent different reactions on the Pt surface, as described in the text.
Figure 3.5. Electrochemical and mass spectral responses of Pt electrode during proton reduction at flow rates ranging of 0, 0.105, 0.422, 1.26, and 2.11 cm³/sec in a aqueous solution containing 0.1 M NaClO₄ and 1.0 mM HClO₄ at a scan rate of 5 mV/sec. (A) Electrochemical current ($i_f$) and (B) H₂ ion current ($i_{H₂}$, m/z = 2 amu).
Figure 3.6. (A) Plot of limiting electrochemical current ($i_{f,\text{lim}}$) and limiting mass spectral signal for H$_2$ ion current ($i_{H_2,\text{lim}}$, m/z = 2 amu) measured at a potential of -1.1 V (vs Hg/Hg$_2$SO$_4$) versus square root of flow rate ($V_f^{1/2}$) through impinging jet. (B) Plot of limiting electrochemical current ($i_{f,\text{lim}}$) versus limiting mass spectral signal for H$_2$ ion current ($i_{H_2,\text{lim}}$, m/z = 2 amu).
Figure 3.7. Electrochemical and mass spectral response of Pt electrode during oxalic acid oxidation at flow rates of 0, 0.105, 0.21, 0.844, and 2.11 cm$^3$/sec in an aqueous solution containing 0.5 M H$_2$SO$_4$ and 5.0 mM oxalic acid at a scan rate of 5 mV/sec (A) Electrochemical current, (B) O$_2$ ion current (I$_{O2}$, m/z = 32 amu), and (C) CO$_2$ ion current (I$_{CO2}$, m/z = 44 amu).
Figure 3.8. Plot of limiting electrochemical current ($i_{\text{f,lim}}$) measured at $\sim 0.6$ V (vs Hg/Hg$_2$SO$_4$) versus limiting mass spectral signal for CO$_2$ ion current ($i_{\text{CO}_2,\text{lim}}$, m/z = 44 amu) for oxalic acid oxidation at Pt electrode at different flow rates in an aqueous solution containing 0.5 M H$_2$SO$_4$ and 5.0 mM oxalic acid.

3.7. References


CHAPTER 4. INTEGRATION OF ELECTROCHEMICAL DETECTION INTO DIFFERENTIAL ELECTROCHEMICAL MASS SPECTROMETRY USING A THIN LAYERED WALL JET RING DISC ELECTRODE

A paper to be submitted to analytical chemistry

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4.1. Abstract

We integrated a hydrodynamic electrochemical detection system into online mass spectrometry. The integration was made possible by fabricating a ring disk electrode assembly in combination with a jetted Differential Electrochemical Mass Spectrometry analogue of a rotating ring/disk electrode. This integration enabled detection of non-volatile products by electrochemical detection at the ring in addition to detection of volatile products by online mass spectrometry. The fabricated ring disk assembly was tested in thin layer wall jet configuration. The hydrodynamics and performance of the fabricated ring disk arrangement was tested with several reactions including ferrocyanide oxidation and hydroxylamine oxidation.

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4.2. Introduction

Electrochemical detectors are electrodes that are biased at a particular voltage to enable detection of molecules of interest in a liquid stream by an electrochemical reaction. Dual electrode detectors have two working electrodes and the generator-collector type has the detector electrodes integrated with the generator electrode that generates the molecule of interest.\(^1\) The detection is made possible by flow of supporting electrolyte that carries reactants to upstream generator electrode and the generated products to the downstream collector electrode. Various designs of dual detector electrodes include ring-disk, disk-disk and band-band electrodes.\(^2\) The most widely used is the ring-disk electrode (RDE) where the generator disk electrode is surrounded by a concentric detector ring electrode.\(^3\) The RDE can be operated as Rotating Ring Disk electrode (RRDE) and Wall jet Ring-Disk electrode (WJRDE) in large volume configuration and Thin Layered Wall Jet Ring-Disk Electrode (TLWJRDE). The ring electrode in an RDE can be replaced by split rings to enable multiple detection or carbon fiber microelectrode array\(^4\) to integrate the microelectrode advantage to the assembly. Disk-disk and band-band electrodes have been used in thin layer configuration. Dual Thin-Layer Flow Cell with a Double Disk Electrode (DTLFC-DDE)\(^5\) design contained a jet impinging on a generator disk electrode in the first compartment linked to the second compartment with the collector disk electrode through four capillaries. Piaxao et al.,\(^6\) fabricated thin layered dual band electrochemical cell containing dual band electrodes prepared from a gold recordable CD by removing a thin strip of gold in between and housed in a thin layer flow cell formed by two plexiglass blocks separated by a cellulose acetate membrane spacer.
Collection efficiency is an important parameter that determines the efficiency of operation of the detector electrode in the dual electrode assembly. It signifies the amount of product that is measured at the detector electrodes. The electrode geometry plays an important role in determining the collection efficiency of RRDE in which rotation of the RDE creates a flow that has three velocity components namely axial, radial and tangential. Albery et al., deduced a formula for calculation of collection efficiency for RRDE which can be improved by reduction of inter-electrode gap and increase of size of the detector electrode. A jet from a small nozzle is impinged normally on a stationary RDE in WJRDE. The resulting flow has axial and radial velocity and consists of two regions over the surface namely the uniformly accessible stagnation region and wall jet region consisting of a decaying and broadening radial velocity profile. The collection efficiency of WJRDE is low compared to RRDE due to loss of products to the bulk of the solution and can be improved by either using a bigger nozzle to enclose the entire RDE in the stagnation region or by using a nozzle with a back wall to form a thin layer flow cavity between the electrode and the nozzle wall as in the TLWJRDE to enhance mass transfer. Chin et al., used bigger nozzles and was able to obtain collection efficiencies similar to RRDE. In TLWJRDE the confined wall jet starts with axial flow which transforms to a completely radial flow after impinging on the electrode surface. Toda et al., obtained high collection efficiencies at low flow rates (nearly 100%) and smaller flow cavities of micrometer order in their TLWJRDE. Fabrication was done using glass substrate by photolithography and etching to form the RDE and the flow cavity.

The application of online mass spectrometry is limited to volatile products and so online mass spectrometry has been integrated with other complementary techniques
such as Electrochemical quartz crystal microbalance (EQCM)\textsuperscript{14}, Attenuated total reflection – Fourier transform infrared reflection (ATR-FTIRS)\textsuperscript{15} and electrochemical detection\textsuperscript{16} in an attempt to obtain more complete information of the processes occurring during an electrochemical reaction. Online mass spectrometry was integrated with EQCM\textsuperscript{14} and ATR-FTIRS\textsuperscript{15} using a dual thin layer flow cell containing two chambers connected by capillaries. The electrode was sputtered on a quartz crystal to implement EQCN and obtain additional information regarding adsorbates and solid products by tracking the mass change. The electrode was prepared on the flat reflecting face of hemi-cylindrical Si prism by electroless deposition to implement ATR-FTIRS and obtain additional information regarding reaction intermediates and reaction mechanism.

Wang et al.,\textsuperscript{16} fabricated a double band electrode channel flow cell to integrate online mass spectrometry with electrochemical detection where the working and detecting band electrodes were separated by porous teflon membrane inlet. The detector electrode was held at a suitable voltage to enable detection of non-volatile products that have escaped detection by electrochemical reaction. The conceptual purpose of the system rightly deserved the name DEMS analogue of a rotating ring/disk electrode.

Our experimental setup consisted of an electrode coated membrane mounted over a capillary with a electrolyte jet impinging on it in wall-tube configuration.\textsuperscript{17} We have attempted to integrate electrochemical detection by fabricating a ring detector electrode and press fitting to create a ring-disk arrangement with controlled dimensions. The ring electrode consisted of a carbon fiber tube over which detector electrode is coated. This electrode arrangement was tested by performing ferrocyanide oxidation and hydroxylamine oxidation\textsuperscript{8} at the disk electrode.
and detecting the products produced at the ring electrode in thin layer configuration formed by confining a wall jet between the electrode assembly and teflon wall holding the nozzle. The hydroxylamine oxidation demonstrated the integration of online mass spectrometry and electrochemical detection.

### 4.3. Experimental section

**Materials and Reagents.** All experiments are performed with nanopure water with resistivity 18MΩ. (Barnstead Inc). Electrolyte solutions were prepared from reagent grade chemicals: potassium sulfate (Fischer), potassium ferrocyanide trihydrate (A.C.S. reagent grade, Aldrich), sodium phosphate monobasic (A.C.S. reagent grade, Fischer), sodium phosphate dibasic (Sigma Aldrich) and hydroxylamine (Aldrich). Membrane (Gore-tex); PTFE tubing – 1/16” OD, 0.015” ID (VICI Valco Instruments); heat shrink tubing (3M); 4 mm carbon fiber tube (Hobbylin.com); conductive tape (Ted pella, inc.); 0.68 mm ID glass capillary (World Precision Instruments, Inc); 60 ml syringe with luer-lock (Becton, Dickinson and company); viton tubing (Cole-Parmer); barb fittings and stopcocks (World Precision Instruments, Inc) were purchased.

A schematic of the experimental setup used in this work is illustrated in Fig.4.1. The improvements and additions made to the setup described previously have been highlighted in this report. The additions included the ring detector and the custom shaped teflon nozzle.

**Fabrication of ring-disc electrode assembly.** 4 mm carbon fiber tube was cut to desired size and ID was altered to press fit with the sputtered Au membrane electrodes. Prior to sputtering, the carbon fiber substrates were cleaned by polishing
successively in 400, 600 and 1200 grit sandpaper, 3-micron diamond slurry and 1-micron alumina powder, rinsing well with acetone and methanol and RF substrate cleaning using plasma by applying RF power of 18W on the substrate holder. Then similar to the membrane electrodes, ~100 nm of Au was sputtered onto the carbon fiber substrates. The Au sputtered carbon fiber substrates were press fitted to the Au sputtered membrane electrodes. Electrical contact was made using conductive tape. Heat shrink tubing was used to cover the other exposed areas.

**Fabrication of custom shaped teflon nozzle.** The nozzle was a 0.68 mm ID glass capillary tube. This glass tube was fitted to a custom made teflon piece that served as a back wall. The teflon piece was polished at the surface that served as a wall and attached to the bent glass tube using a tygon tube. The ring disc electrode assembly was positioned above the teflon wall such that the jet from the nozzle impinged on the disc electrode.

**Syringe pump.** YA-12 genie pump (Kent scientific) was used for all experiments. The pump can be used for both infusion and withdrawal. It can be programmed to pump with constant rate, ramp, step and pulse. 60 ml syringe with ID of 26.59 mm was used. With the 60 ml syringe the pump can obtain minimum rate of 0.389 µL/min and maximum rate of 28.32 ml/min. Barb fittings and stopcocks were used to link the syringe with the viton tubing. Viton tubing reduced oxygen diffusion to argon purged electrolyte.
4.4. Results and discussion

The intactness of the sputtered electrode film on the carbon fiber tube pieces were verified by performing cyclic voltammetry in an acidic solution. Fig.4.3 illustrates the results obtained while 40 continuous cyclic voltammograms were performed on the ring electrode in an argon purged 0.5M H₂SO₄ solution. CV performed on sputtered Pt ring electrodes showed the characteristic Pt oxidation and oxide reduction peaks, underpotential hydrogen adsorption/desorption peaks and the featureless double layer region. CV performed on sputtered Au ring electrodes also showed the characteristic Au oxidation and oxide reduction peaks.

The performance of the fabricated ring disk electrode assembly was determined via oxidation of ferrocyanide on the disk electrode as a function of fluid flow rate through the jet and detection of produced ferricyanide at the ring electrode. Fig.4.4A depicts a series of potential scans in a 2 mM solution of Fe(CN)₆²⁻ in 0.1 M K₂SO₄ over a range of jet flow rates ranging from a stagnant solution up to a maximum flow rate of 20 ml/min. Fig.4.4B depicts the corresponding produced ferricyanide detection responses at the ring electrode biased at -0.7 V. The produced ferricyanide was reduced back to ferrocyanide at the ring electrode. In all cases, as the potential was scanned at the disk electrode the current increased at potentials above -0.3 V as the oxidation of ferrocyanide commenced. The current then reached a plateau value indicating mass transfer limited oxidation rates at more positive potentials. As the flow rate through the jet increased, there was a corresponding increase in the plateau current. The ring electrode held at -0.7 V to detect the produced ferricyanide also showed increase in current as the disk electrode potential scanned above -0.3 V and plateaued at high
positive potentials. As the disk electrode current increased with high flow rates the ring electrode current also increased till a flow rate of 8 ml/min and then decreased as more ferricyanide was produced at the disk and reached the Ring.

The reactant supply to the generator electrode measured by the limiting current ($i_{lim}$) depends on the geometric parameters of the cell design and the hydrodynamic parameters of the flow established while operation.\textsuperscript{19} $i_{lim}$ can be estimated using a relation which depends on the flow rate $V_f$.

$$i_{lim} = \text{constant} \times V_f^\alpha$$  \hspace{1cm} (4.1)

where $\alpha$ is the apparent flow exponent using which the flow can be described. Perpendicular, parallel and oblique flow relative to the electrode leads to a flow exponent $\alpha$ of $\frac{1}{2}$, $\frac{1}{3}$, $\frac{3}{4}$ respectively.\textsuperscript{19} Rotating ring disc electrode and wall tube electrode has a perpendicular flow. Thin layer electrode has a parallel flow. Wall jet electrode has an oblique flow. In Thin-layer wall jet electrode, perpendicular, parallel and oblique flows are present simultaneously.\textsuperscript{19} Perpendicular flow is present in the central stagnation zone. Oblique flow is present in the mid wall-jet zone. Parallel flow is present in the thin layer zone. Based on the size of the mid wall-jet zone the behavior of the thin-layer wall jet electrode can be categorized into four types.\textsuperscript{19} In the Type 1, the wall jet zone size is negligible leading to a stagnation-thin layer behavior. In Type 2 the wall jet zone size varies from negligible to below maximum leading to a behavior that varies from stagnation-thin layer to triple flow. In Type 3 the wall jet zone size varies from above negligible to maximum leading to a behavior that varies from triple flow to
stagnation wall-jet. In Type 4, the wall jet zone size is maximum leading to a stagnation wall-jet behavior.

Diffusion limited current $i_{\text{lim}}$ obtained at different flow rates is a measure of the ferrocyanide supply to the Au disk electrode. It increased from 39 µA to 116 µA as the flow rate was increased from 2 to 20 ml/min. The flow can be characterized by estimating the apparent flow exponent, $\alpha$ in $i_{\text{lim}}$ equation. $\alpha$ can be calculated from the logarithm of the $i_{\text{lim}}$ equation as the slope of log ($i_{\text{lim}}$) Vs log ($V_f$).

$$\log (i_{\text{lim}}) = \log \text{const} + \alpha \log V_f \quad (4.2.)$$

In our experimental setup the apparent flow exponent $\alpha$ was estimated to be 0.46 from Fig.4.5 suggesting a type 1 behavior. Due to the very narrow thin-layer design the wall jet zone is negligible as at all flow rates the oblique flow hits the back wall at negligible distance leading to fast transition to thin layer flow.

Collection efficiency is the important parameter that estimates the performance of the ring detector electrode. Collection efficiency is calculated using formula

$$\text{CE} \, (\%) = \frac{-I(\text{ring})}{I(\text{disk})} \quad (4.3)$$

$I(\text{disk})$ is the mass transfer limited current at the disk electrode at a particular flow rate and $I(\text{ring})$ is the corresponding current recorded at the ring electrode. From Fig.4.4 $I(\text{disk})$ and corresponding $I(\text{ring})$ was taken at 0.2 V. The estimated collection efficiencies at different flow rates was plotted in Fig.4.6. It was observed that collection efficiency decreased from 15 % at a flow rate of 2 ml/min to 4 % at flow rate of 20
ml/min which could be attributed to the sweeping away of products formed at the disk electrode away from the ring electrode at high flow rates thereby escaping detection.

The integration of online mass spectrometry and electrochemical detection is demonstrated by performing hydroxylamine oxidation on Au\textsuperscript{20}. In aqueous phosphate buffer solutions (pH 7) gold electrodes produced a mixture of products namely NO and N\textsubscript{2}O. Jebaraj et al.,\textsuperscript{20} detected the produced NO electrochemically and N\textsubscript{2}O using insitu infrared techniques.

Hydroxylamine oxidizes on a gold electrode to produce NO by the following reaction

\[
\text{NH}_2\text{OH} \rightarrow \text{NO} + 3e^- + 3\text{H}^+ \quad (4.4)
\]

The produced NO further reacts through an electrochemical-chemical (EC) mechanism to produce N\textsubscript{2}O. Production of N\textsubscript{2}O through an entirely electrochemical process is impossible on Au electrodes as the weakly adsorbed NO desorbs before interacting with other adsorbed species to form N\textsubscript{2}O on the surface. Jebaraj et al., proposed an EEECE mechanism to explain the responses they obtained while performing hydroxylamine oxidation on Au electrode in a phosphate buffer solution (pH 7).

\[
\text{NO} + \text{H}_2\text{O} \rightarrow \text{NO}_2^- + e^- + 2\text{H}^+ \quad (4.5)
\]

\[
\text{NO}_2^- + \text{H}_2\text{O} \rightarrow \text{NO}_3^- + 2e^- + 2\text{H}^+ \quad (4.6)
\]

\[
\text{NO}_2^- + \text{NH}_2\text{OH} \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} + \text{OH}^- \quad (4.7)
\]

\[
2\text{NH}_2\text{OH} \rightarrow \text{N}_2\text{O} + 4e^+ 4\text{H}^+ + \text{H}_2\text{O}^+ \quad (4.8)
\]
Fig. 4.7A depicts a series of potential scans in a 0.5 mM solution of hydroxylamine in 0.1 M phosphate buffer at jet flow rates of 2, 6 and 8 ml/min at a scan rate of 5 mV/sec. Fig. 4.7B depicts the corresponding produced NO detection responses of the mass spectrometer using 30 amu signal. Contribution from NO$^+$ fragment derived from N$_2$O was subtracted. The cracking pattern of N$_2$O is NO$^+$ : N$_2$O$^+$ = 0.344 : 1$^{21}$. Increase in NO production was observed with increase in flowrate as more hydroxylamine reacted. The mass spectrometer showed a NO peak at the initial oxidation voltages. Fig. 4.7C depicts the ion current of N$_2$O (44 amu) recorded using the mass spectrometer. It can be observed that the N$_2$O production commences later at -0.185 V compared to NO production at -0.27 V. N$_2$O production increases steadily and reaches a stable value as voltage is increased. The decrease in NO coincides with increase in N$_2$O due to consumption of NO for N$_2$O production.

Product distribution can be estimated from the mass spectrometer signal using the fragmentation factor. This is an alternative method proposed for product distribution calculation compared to the conventional method where a constant is estimated which relates the ion current to the number of moles$^{22}$. In this case, the calibration constant was not able to be obtained for NO and N$_2$O since there is no electrochemical reaction which selectively produces NO or N$_2$O. Fragmentation factor represents the fraction of total ions of particular mass produced from a molecule. Generally each molecule on ionization produces an ion fragment and uncharged free radical. Different ion fragments produced during the ionization process leads to obtaining the corresponding mass spectrums. For quantification purpose, ionization is reasonably simplified to production of one ion from one molecule. Ionization probability and relative sensitivity of NO and
N₂O were assumed to be equal. So fragmentation factor was estimated from the relative intensity mass spectrum data. For 30 amu the fragmentation factor for NO and N₂O was estimated to be 0.91 and 0.19. 30 amu signal for 100% fragmentation factor was estimated for NO and N₂O and used to estimate the product distribution since it represented the amount of NO and N₂O produced. In Fig.4.8A it can be seen that NO production decreased and stabilized at 58% with increase in voltage. Whereas N₂O production increased and stabilized at 42%. It was observed that irrespective of the flow the product distribution followed the same trend. Faradaic efficiency can be estimated using the product distribution % calculated.

\[ i_{\text{NH}_3\text{OH}} = i_{\text{NO}} + i_{\text{N}_2\text{O}} \]  \hspace{1cm} (4.9)

\[ n_{\text{NO}} = \frac{i_{\text{NO}}}{3} \] \hspace{1cm} (3 electron reaction) \hspace{1cm} (4.10)

\[ n_{\text{N}_2\text{O}} = \frac{i_{\text{N}_2\text{O}}}{4} \] \hspace{1cm} (4 electron reaction) \hspace{1cm} (4.11)

\[ x_{\text{NO}} = \frac{n_{\text{NO}}}{n_{\text{NO}} + n_{\text{N}_2\text{O}}} \] \hspace{1cm} (4.12)

\[ F.E_{\text{NO}} = \frac{i_{\text{NO}}}{i_{\text{NO}} + i_{\text{N}_2\text{O}}} \] \hspace{1cm} (4.13)

where \( i_{\text{NH}_3\text{OH}}, i_{\text{NO}}, i_{\text{N}_2\text{O}} \) are hydroxylamine oxidation current, NO current and N₂O current. \( n_{\text{NO}} \) and \( n_{\text{N}_2\text{O}} \) are the number of moles of NO and N₂O produced. \( x_{\text{NO}} \) is the mole fraction of NO produced during hydroxylamine oxidation. \( F.E_{\text{NO}} \) is the faradaic efficiency of NO produced. \( i_{\text{NO}} \) was estimated by optimization until \( x_{\text{NO}} \) equaled the previously calculated \( x_{\text{NO}} \) using the mass spectrometer signals. In Fig.4.9B it can be seen that NO faradaic efficiency decreased and stabilized at 50% with increase in voltage. Whereas N₂O faradaic efficiency increased and stabilized at 50%.
Fig. 4.9A depicts a series of potential scans in a 0.5 mM solution of hydroxylamine in 0.1 M phosphate buffer at jet flow rates of 2, 4 and 8 ml/min at a scan rate of 50 mV/sec. Oxidation currents due to NO production and further reaction of NO increased with increasing flow rates. The produced NO was reduced and detected at the ring electrode held at a potential of -0.6 V as shown in Fig. 4.9B. NO production increased with increase in voltage and then decreased due to further reaction to produce N₂O as observed in the mass spectrometer response. At the Au ring electrode held at -0.6 V, NO was reduced to N₂O²⁻ by the following reactions

\[
\text{NO}_{\text{sol}} + * \rightarrow \text{NO}_{\text{ads}} \quad (4.14)
\]

\[
\text{NO}_{\text{ads}} + \text{NO}_{\text{sol}} + \text{H}^+ + \text{e}^- \rightarrow \text{HN}_2\text{O}_2,\text{ads} \quad (4.15)
\]

\[
\text{HN}_2\text{O}_2,\text{ads} + \ldots \rightarrow \text{N}_2\text{O} + \ldots \quad (4.16)
\]

Faradaic efficiency of NO produced was estimated using the following formula and plotted versus voltage in Fig. 4.10.

\[
\text{FE}_{\text{NO}} \, (\%) = \frac{i(\text{NO})}{I(\text{disk})} \times 100 \quad (4.17)
\]

where \( i_{\text{disk}} = i_{\text{NO}} + i_{\text{N}_2\text{O}} \)

\[
i_{\text{NO}} = \frac{n(\text{disk})}{n(\text{ring}) + I(\text{ring})} \times 100 \quad (4.18)
\]

Where \( n_{\text{disk}} (=3) \) is the number of electrons involved in NO production reaction at the disk electrode and \( n_{\text{ring}} (=2) \) is the number of electrons involved in NO reduction reaction at the ring electrode. \( n_{\text{ring}} \) was estimated from the fact that NO faradaic efficiency is \(~100\ %\) initially as N₂O production starts only at higher oxidation voltages from NO. CE
values calculated from ferrocyanide oxidation reaction was used for the estimation. \( \text{INO} \) was calculated for 100 % collection efficiency and 3 electron NO reaction. The faradaic efficiency of NO decreased from 100 % at -0.3 V and stabilized at 42 % compared to 50 % calculated using the mass spectrometer signal. This clearly shows that both the mass spectrometer and electrochemical detection techniques can be used to effectively study and quantify the products formed during any reaction.

4.5. Conclusions

In this work, we describe ring electrode that can be press-fitted to a capillary mounted with an electrode coated membrane and served as the online mass spectrometry inlet. Products produced could be detected by online mass spectrometry and the ring electrode simultaneously. The detection was made possible by a thin layered confined wall jet flow that carried the products formed at the disk working electrode to the ring electrode.

The performance of this system was demonstrated by performing ferrocyanide oxidation and hydroxylamine oxidation at the disc working electrode and detecting the products using ring electrode biased at a particular voltage and using online mass spectrometry. Both the techniques were effectively used to quantify the detected product distribution. We plan to extend the application of this setup to study other complex reactions that produce volatile and non-volatile products.
4.6. Figures

Figure 4.1. Schematic diagram of electrochemical cell and system components for DEMS combined thin layered wall jet ring disc Electrode. The electrochemical cell includes gas purge lines, Hg/Hg$_2$SO$_4$ reference electrode, counter electrode compartment, metal-coated membrane as disc electrode that is directly attached to DEMS inlet and metal-coated carbon fiber tube as Ring electrode. The confined wall-jet includes a high flow peristaltic pump with tubing and thin layer formed between the electrode assembly and teflon wall holding the nozzle directed at disc electrode at the middle. (Inset) Details of Ring-Disc electrode/thin layered wall-jet configuration with dimensions noted (nozzle diameter = 0.68 mm, Disc electrode diameter = 1.58 mm, Ring inner diameter = 2.2 mm, Ring outer diameter = 4 mm, DEMS inlet diameter = 0.381 mm).
Figure 4.2. Schematic of top view of ring-disc electrode assembly labeled with dimensions of the important components of the thin-layer DEMS system.
Figure 4.3. Testing of carbon fiber tube as an inert ring electrode substrate by performing 40 continuous cyclic voltammograms (scan rate = 100 mV/sec) in 0.5 M H₂SO₄ argon purged aqueous electrolyte solution to test the sputtered electrode film’s intactness. (A) 100 nm Pt (B) 100 nm Au. Comparison has been done with carbon fiber tube background scan (---).
Figure 4.4. (A) Diffusion-limited ferrocyanide oxidation (scan rate = 5 mV/sec) at Au-coated membrane disc electrode with different jet flow rates of 0, 2, 4, 8 ml/min in aqueous electrolyte containing 0.1 M K$_2$SO$_4$ and 2 mM K$_4$[Fe(CN)$_6$]. (B) Disc electrode generated ferricyanide reduction at Au-coated carbon fiber tube ring electrode at the different jet flow rates. Detecting electrode potential: -0.7 V.
**Figure 4.5.** Logarithmic dependence of the diffusion-limited ferrocyanide oxidation current ($i_{lim}$) at the Au-coated membrane disc electrode on the volumetric flow rate ($V_f$). Data from Figure 2.2.3. $i_{lim}$ measured at 0.2 V vs Hg/Hg$_2$SO$_4$. Slope ($\alpha$, apparent flow exponent) = 0.46

**Figure 4.6.** Plot of collection efficiency measured from the diffusion-limited ferrocyanide oxidation current at the disc electrode and the detected ferricyanide reduction current at ring electrode versus flow rate ($V_f$) through impinging jet confined within the thin layer formed between electrode assembly and teflon wall.
Figure 4.7. Electrochemical and mass spectral response of Au/Au Ring Disc electrode assembly during hydroxylamine oxidation at flow rates of 2, 6 and 8 ml/min in an aqueous solution containing 0.1 M Phosphate buffer and 0.5 mM Hydroxylamine at a scan rate of 5 mV/sec (A) Hydroxylamine oxidation current at Au disk electrode, (B) NO ion current (I_{NO}, m/z = 30 amu, after subtracting contribution from NO^{+} fragment derived from N_{2}O) (C) N_{2}O ion current (I_{N_{2}O}, m/z = 44 amu).
Figure 4.8. Plot of A) product distribution and B) faradaic efficiency of NO and N₂O produced at Au disk electrode versus voltage during hydroxylamine oxidation on an Au/Au ring disc electrode assembly in an aqueous solution containing 0.1 M phosphate buffer and 0.5 mM hydroxylamine.
Figure 4.9. Hydroxylamine oxidation on an Au/Au ring disc electrode assembly at flow rates of 2, 4 and 6 ml/min in an aqueous solution containing 0.1 M phosphate buffer and 0.5 mM hydroxylamine at a scan rate of 50 mV/sec (A) Hydroxylamine oxidation current at Au disk electrode, (B) Produced NO reduction current at Au ring electrode. Detecting electrode potential: -0.6 V
Figure 4.10. Plot of faradaic efficiency of NO produced at Au disk electrode calculated using 30 amu mass signal (NO\textsubscript{MS}) and the NO reduction current at Au ring electrode (NO\textsubscript{ring}) versus voltage during hydroxylamine oxidation on an Au/Au ring disc electrode assembly in an aqueous solution containing 0.1 M phosphate buffer and 0.5 mM hydroxylamine.

4.7. References


CHAPTER 5. ELECTROCHEMICAL REDUCTION OF CO₂
USING Cu ALLOYS, MONOETHANOLAMINE SOLUTION,
IONIC LIQUIDS, GUANIDINIUM SPECIES AND MODIFIED Cu
ELECTRODE BY GALVANIC DISPLACEMENT.

5.1. Abstract

In this report we have fabricated Cu:W, Cu:Ta and Cu:Ag alloy films by co-sputtering and tested them for CO₂ reduction to explore the possibility of selective ethylene production. It was observed that hydrocarbon production decreased and hydrogen production increased as the Cu content in the alloy film decreased. Reasons for the failure of Cu alloys to produce hydrocarbons were explored. CO₂ reduction was also performed by Cu electrodes modified by galvanic displacement and in electrolyte solutions containing monoethanolamine to increase CO₂ solubility, ionic liquid and guanidinium species to bypass a high energy pathway involving CO₂⁻ radical. It was observed that neither of them led to hydrocarbon production but led to increased hydrogen evolution.

5.2. Introduction

CO₂ is a stable molecule that can be reduced to various products electrochemically using high energy. Producing hydrocarbons like ethylene from CO₂ would be viable as it's requirements are large as a fuel and as a petrochemical intermediate and so would lead to decreased CO₂ accumulation. Copper is the only
unique metal that produces hydrocarbons like methane and ethylene by
electrochemically reducing CO\textsubscript{2} at ambient conditions. There are various interpretations
associated with copper’s ability to produce hydrocarbons. Copper’s medium hydrogen
overvoltage allows CO\textsubscript{2} reduction to occur simultaneously along with hydrogen
evolution at ambient conditions. Metals with low hydrogen overvoltage produced
hydrogen as the major product and metals with high hydrogen overvoltage produced
formic acid as the major product.\textsuperscript{1} Copper’s electronic structure provides a moderate
adsorption energy for the intermediates leading to hydrocarbon formation.\textsuperscript{2} While CO\textsubscript{2}
reduction stops with stable intermediates like CO in the metals with high adsorption
energy and doesn’t form CO in the metals with low adsorption energy. Adsorbed
hydrogen formed on Copper reacts with CO\textsubscript{2} to form products.\textsuperscript{3} Copper is the only metal
that possesses both the abilities to convert CO\textsubscript{2} to CO and further convert CO to
hydrocarbons.\textsuperscript{4} Other metals lack one of these abilities. This work describes the design
of new electrocatalysts that could produce ethylene by electrochemically reducing CO\textsubscript{2}
selectively and efficiently.

The new electrocatalyst had to be designed to accommodate and promote the
reaction mechanism that leads to ethylene formation from CO\textsubscript{2}. It is necessary to design
a catalyst that eliminates limitations in any step in the ethylene reaction pathway to
achieve selectivity and efficiency. The rate limiting step in CO\textsubscript{2} reduction is CO\textsubscript{2}⁻ radical
formation by electronation.\textsuperscript{5} Metals that stabilized CO\textsubscript{2}⁻ radical produced CO,\textsuperscript{6} an
intermediate that leads to hydrocarbon formation. The key step in hydrocarbon
formation is hydrogenation of CO to form CHO.\textsuperscript{7} Ethylene production starts at a low
voltage compared to methane. The mechanisms for ethylene and methane formation
are different. There are various mechanisms proposed in the literature for the C-C bond formation required for ethylene production. They include methylene dimerization, methylene – CO insertion, CO dimerization, enediol-oxametallacycle formation and other non-electrochemical reactions between adsorbed species on the surface. The methylene-CO insertion was inspired from the Fischer-Tropsch reaction. The enediol-oxametallacycle type intermediate formation mechanism was proposed to address the ethylene selectivity. Starting from CO, different mechanisms suggest different rate limiting steps for ethylene formation. Some of them includes the first electron transfer uncoupled from proton transfer and formation of a CO dimer accompanied by the first electron transfer. Single-crystal work on Cu suggests that crystal orientation also plays an important role in ethylene formation. It was observed that ethylene formation was favored more on the 100 crystal plane. It was further enhanced when defects like steps were introduced to the 100 crystal plane. The ethylene selectivity and production stability of electrodeposited copper surface, roughened copper surface are associated to the crystal faces present. The 100 crystal face provides an orientation ideal for CO dissociation. The pulsed electroreduction literature proposed the role of oxidized copper sites on enhanced hydrocarbon production. Surfaces with Cu and Cu$_2$O sites showed enhanced production of hydrocarbons. The adsorbed hydrogen produced readily at the Cu$_2$O sites interacted with the CO$_2$ adsorbed in Cu sites to produce hydrocarbons.

Fabrication of electrocatalysts with different metal sites can be done by alloying, ad-atom method and in situ electrodeposition. Selection of metals for alloying was done using two strategies based on either a catalytic mechanism or an electrochemical
mechanism. Catalytic mechanism strategies involved enhancing the synergetic effects between different surface atoms by introducing hydrogen adsorption sites and oxygen adsorption sites. The electrochemical mechanism involved combining metals with different electronegativity, steric effect and electron structure etc. Various Cu alloys have been studied namely Cu:Ni, Cu:Ag, Cu:Pd, Cu:Sn, Cu:Zn, Cu:Pb and Cu:Cd. Cu:Ag (2:3) was reported to show enhanced ethylene selectivity compared to methane when compared to Cu. Ag sites enhanced availability of CO leading to ethylene selectivity. Cu:Ni produced methanol with faradaic efficiency of 10% that neither Cu or Ni produced. It also reduced the overpotentials of HCOOH and methanol formation. Ni served as the hydrogen adsorption sites and Cu the CO2 reduction sites. At compositions of upto Cu:Ni (3:1) the Ni atoms were isolated inhibiting H atom recombination and thereby reducing hydrogen formation. Pd sites served as hydrogen absorption sites providing reactive hydrogen for CO2 reduction. Enhanced CO2 reduction producing HCOOH was observed on Pd+H electrode modified with Cu. Cu:Cd produced formic acid at a reversible voltage at high efficiency. Cd as a high hydrogen overvoltage metal decreased hydrogen evolution. Cu:Sn (5.6:1) and Cu:Zn (5:8) showed enhanced production of CO compared to the elemental metals used to form the alloy. This was ascribed to the microcrystalline structure of the catalyst irrespective of the alloy composition. Cu:Pb (46:54) produced HCOOH almost at the reversible potential with a high faradaic efficiency of 50% compared to the individual metals. Cu:Cd (38:62) produced CO with a high current efficiency of 43%. Cu has also been modified by in-situ electrodeposition. Cu modified with in-situ deposited Cd produced more CO with suppressed hydrocarbon formation.
deposited Fe and Ni had increased methane selectivity compared to ethylene due to increased adsorbed hydrogen availability.\textsuperscript{21} Palladium electrodes modified with Cu had high formic acid, methane and methanol selectivity.\textsuperscript{17} This effect was attributed to palladium’s ability to absorb hydrogen.

In high pressure CO\textsubscript{2} experiments, high pressure led to high CO\textsubscript{2} solubilities and thus more CO\textsubscript{2} reduction and less H\textsubscript{2} evolution.\textsuperscript{22} Monoethanolamine (MEA) is a weak base and is used in scrubbers to chemically absorb CO\textsubscript{2} from flue gases by forming carbamates, carbonates and bicarbonates. CO\textsubscript{2} solubilities of \(~\text{500 mM}\) can be achieved in 1M aqueous MEA solutions compared to \(~\text{30 mM}\) at ambient conditions.\textsuperscript{23} In pyridinium catalyzed CO\textsubscript{2} reduction\textsuperscript{24} and ionic liquid mediated CO\textsubscript{2} reduction,\textsuperscript{25} CO\textsubscript{2} reduction was carried out at low overpotentials by bypassing the high-energy CO\textsubscript{2}^- pathway. In pyridinium catalyzed CO\textsubscript{2} reduction, multiple electron transfer catalysis was proposed to happen by the increased electron donating ability of the pyridyl nitrogen. Pyridinium (1-6 mM) catalyzed production of methanol from CO\textsubscript{2} at low potentials. In ionic liquid mediated CO\textsubscript{2} reduction, ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM BF\textsubscript{4}) was used and it was proposed that an EMIM (CO\textsubscript{2})---BF\textsubscript{4}^- intermediate was formed with low activation energy. CO was produced selectively using Pt electrode by ionic liquid mediated CO\textsubscript{2} reduction. Similar to ionic liquids, guanidinium species are known to bind the carboxylate\textsuperscript{26} and so accessing alternate low energy pathways using this stabilization was attempted.

In this report, we have continued the search for selective ethylene producing catalysts by working with Cu:Ta, Cu:W and Cu:Ag alloy films prepared by co-sputtering and Cu electrodes modified by dipping in various metal solutions. The choice of metals
to be alloyed with Cu was based on the hypothesis that by introducing high overvoltage metal sites hydrogen evolution would be inhibited and introducing a stable oxide producing metal site would enhance hydrocarbon production. CO₂ reduction was also done on aqueous electrolyte solutions containing MEA, EMIM-BF₄ and guanidinium salts to explore possibility of hydrocarbon formation by increase in CO₂ solubility and ionic liquid / guanidinium mediation.

5.3. Experimental

Pt:Pb (60:40) alloy films were prepared by simultaneous sputtering of Pt and Pb on to a carbon fiber substrate. The power to be used for sputtering Pt and Pb to produce a 60:40 composition was estimated as seen in Table 5.1. The Quartz Crystal Microbalance (QCM) thickness monitor was used for the experiment. The carbon fiber samples were polished successively in 400, 600 and 1200 grit sandpaper, 3 micron diamond slurry and 1 micron alumina powder and rinsed well with DI water. The polished carbon fiber samples were cleaned using methanol and acetone and then placed in the sample holder and 100 nm of Pt:Pb (60:40) was deposited by sputtering. The sputtering was done with an argon flow setpoint of 25 sccm, chamber pressure 7.4 mTorr and a substrate rotation rate of 20 RPM. Similarly Cu:Ta, Cu:W and Cu:Ag films of various compositions were prepared over membrane electrodes. Membrane electrodes were made by the covering one end of the tube with extended PTFE gore-tex and applying silver epoxy to attach the electrical lead. The epoxy was heated in an oven at 60 °C for 2 hours and about 100 nm of metal (working electrode) was deposited on the membrane by sputtering. The silver epoxy was covered using heat shrink tubing.
Guanidinium experiments were performed with Pt, Au and glassy carbon microelectrodes (CH instruments, Inc).

All experiments are performed with nanopure water with a resistivity of 18 MΩ (Barnstead Inc). Guanidinium experiments were performed in dimethyl sulfoxide solvent. Electrolyte solutions were prepared from reagent grade chemicals: potassium sulfate (Fischer), potassium bicarbonate (Fischer), monoethanolamine (Sigma-aldrich), 1-ethyl-3-methylimidazolium tetrafluoroborate (Iolitec Inc), guanidinium chloride (Sigma-aldrich), guanidinium sulfate (Sigma-aldrich), tetramethyl ammonium hexafluorophosphate (Sigma-aldrich), tetrabutyl ammonium chloride (Sigma-aldrich), tin chloride dihydrate, chloroplatinic acid hydrate, silver nitrate, ruthenium chloride hydrate, palladium chloride, ammonium iron sulfate hexahydrate, zinc sulfate heptahydrate. Argon (Airgas) and CO₂ (Airgas) was used.

5.4. Results and discussion

Carbon fiber substrates coated with about 100 nm of Pt and Pt:Pb (60:40) films were used to perform the electrochemical oxidation of formic acid and test the fabrication of Pt:Pb alloy films. An aqueous electrolyte containing 0.1 M H₂SO₄ and 0.1 M HCOOH was prepared in a 150 mL beaker. The electrochemical cell containing the Pt coated working electrode, Pd coil counter electrode and Hg/Hg₂SO₄ reference electrode was setup in the 150 mL beaker using a plexiglass support with holes in it. A potential scan (Fig.5.1) was performed from -0.6 to 0.4 V vs Hg/Hg₂SO₄ at a scan rate of 20 mV/sec. The Pt electrode was poisoned by CO formed during formic acid oxidation and thus had less oxidation current. When the potential was made more
anodic, CO oxidation resulted in a current peak. In the case of the Pt:Pb electrode, the formic acid oxidation currents were enhanced considerably as there was less CO poisoning due to the presence of Pb and also the oxidation starting voltage was reduced.

Cu (100 nm thick) coated membrane electrodes were fabricated and electrochemical reduction of CO$_2$ was performed in a four neck round-bottomed 100 mL flask. The membrane electrode containing the Cu working electrode deposited on it’s tip, counter electrode (palladium coil), reference electrode (Hg/HgSO$_4$) and sparger were inserted into each of the four necks and sealed using rubber corks. The other end of the membrane electrode was connected to the mass spectrometer. KHCO$_3$ (0.5 M) aqueous electrolyte solution was used. The solution pH was 8.4 and after CO$_2$ saturation, the pH decreased to 7.5. The stirring rate is maintained at 900 rpm. Various potential steps were performed by increasing the potential to -1.4 V, -1.6 V, -1.8 V, -2 V and -2.2 V (vs Hg/Hg$_2$SO$_4$). Then the corresponding electrochemical current and mass spectrometer response for 2 amu, 15 amu and 26 amu was recorded simultaneously. The recorded ion current was calibrated using calibration values found for solubility values of the respective gases according to Henry’s law (Table 5.2). The normalized faradaic efficiency was found using the following formula

$$ FE = \frac{n_1 M_1}{(n_1 M_1 + n_2 M_2 + \cdots)} \quad (5.1) $$

where $n$ refers to the number of electrons required to produce the product (2 for H$_2$, 8 for CH$_4$, 12 for C$_2$H$_4$) and $M$ refers to the number of moles of the product produced. The
normalized faradaic efficiency is based on the assumption that only hydrogen, methane and ethylene are formed during CO$_2$ reduction.

Copper was alloyed with tungsten Cu:W, silver Cu:Ag and tantalum Cu:Ta using the sputtering system. A range of alloy compositions (0:100, 20:80, 50:50, 80:20, 100:0) were prepared by varying the power of the sputtering sources and tested for their product distribution which were recorded and plotted as faradaic efficiency graphs. (Fig.5.3, Fig.5.4 and Fig.5.5) It was found that none of the alloys tried were producing hydrocarbons higher than copper. The alloys produced more hydrogen as the Cu content was decreased.

CO is the important intermediate that leads to hydrocarbon production. When Cu is alloyed with other metals, the CO adsorption strength of the Cu sites decrease$^{27}$ thus leading to CO desorption rather than further reaction to form hydrocarbons. C-C bond formation is necessary for ethylene production. This bond can be formed by various mechanisms as previously mentioned. It involves participation of many sites on the catalyst surface. So if the metal that Cu is alloyed with is inert and not capable of handling the necessary intermediates C-C bond formation will be inhibited. It was observed that 99.99% Cu produced only one third of the ethylene compared to that produced with 99.999% Cu, while methane production was same.$^{28}$ The Fischer-Tropsch metals like Fe and Ni are metals that could handle the CO intermediate well while high hydrogen over-voltage metals like Cd can’t. So when in-situ electrodeposition of Cd was done on Cu the hydrocarbon production was prevented and CO production increased.$^{20}$ When in-situ electrodeposition of Fe and Ni was done on Cu, Hydrogen
evolution increased and methane was produced more than ethylene as more adsorbed hydrogen was available on the catalyst surface.\textsuperscript{21}

In monoethanolamine experiments as shown in Fig.5.6 it was observed that more hydrogen and no hydrocarbons was produced on a Pt electrode in CO\textsubscript{2} purged MEA solution. This might be due to a reaction between protonated MEA. The pH of the MEA solutions employed for the experiments are listed in Table 5.3. The following are the equilibriums that exist in MEA solution loaded with CO\textsubscript{2}.

\begin{align*}
2 \text{H}_2\text{O} &\rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^- \quad (5.2) \\
\text{CO}_2 + 2 \text{H}_2\text{O} &\rightleftharpoons \text{HCO}_3^- + \text{H}_3\text{O}^+ \quad (5.3) \\
\text{MEA} + \text{HCO}_3^- &\rightleftharpoons \text{MEACOO}^- + \text{H}_2\text{O} \quad (5.4) \\
\text{MEA} + \text{H}_3\text{O}^+ &\rightleftharpoons \text{MEA}^+ + \text{H}_2\text{O} \quad (5.5) \\
\text{HCO}_3^- + \text{H}_2\text{O} &\rightleftharpoons \text{CO}_3^{2-} + \text{H}_3\text{O}^+ \quad (5.6)
\end{align*}

In ionic liquid (EMIM-BF\textsubscript{4}) experiments as shown in Fig.5.7 it was also observed that hydrocarbon production decreased on Cu electrodes with addition of EMIM-BF\textsubscript{4}. Addition of ionic liquid led to more hydrogen production. The pH of the EMIM-BF\textsubscript{4} solutions employed for the experiments are listed in Table 5.4.

Guanidinium chloride and guanidinium sulfate were used for guanidinium experiments in dimethylsulfoxide (DMSO) solvent. Since guanidinium sulfate had solubility issues, guanidinium chloride was used. Pt, Au, Cu and glassy carbon microelectrodes were used for the study. Significant CO\textsubscript{2} reduction currents were observed with an Au microelectrode. On further investigation it was observed that the increase in reduction current and lower potential was a chloride effect as seen on
Fig. 5.8. Au is known to produce CO, oxalate or carbonate in DMSO solvent. First on electronation CO$_2^-$ is formed. In CO$_2^-$ the extra electron resides at the C atom and would protonate at this site. In tetramethyl ammonium hexafluorophosphate (TMAHFP) electrolyte, the CO$_2^-$ adsorbs on the Au electrode promoting CO formation. In tetrabutyl ammonium chloride (TBAC) electrolyte, chloride adsors on the Au electrode, preventing CO$_2^-$ adsorption on the surface. In this case, two CO$_2^-$ will couple to form oxalic acid. The reaction current increased exponentially and became reaction limited. DEMS studies were conducted with different amounts of water as a proton source to access the hydrocarbon pathway. No methane and ethylene were detected. Hydrogen was detected when a large amount of water such as 1400 mM was involved.

The KHCO$_3$ electrolyte was pre-electrolyzed for 30 minutes at a negative potential of -2 V (vs Hg/Hg$_2$SO$_4$) using Ag wire electrode to remove impurities that could deactivate or modify the Cu electrode. The Cu electrode was modified by dipping in solutions containing 10 mM of Pb$^{2+}$, Ag$^{1+}$, Pt$^{2+}$, Hg$^{2+}$, Sn$^{2+}$, Zn$^{2+}$, Pd$^{2+}$, Fe$^{2+}$ and Ru$^{3+}$. There was a visual change in the electrode by galvanic displacement when Cu was dipped in Ag$^{1+}$, Pt$^{2+}$ and Hg$^{2+}$ solutions. As shown in Fig. 5.9 Cu modified by Pt, Hg, Ru and Sn deactivated and didn’t produce hydrocarbons. It can be seen that Hg increased the hydrogen overpotential while Pt decreased the hydrogen overpotential. Further Pd increased methane selectivity by decreasing ethylene production as Pd increased adsorbed hydrogen availability on the catalyst surface.
5.5. Conclusion

Various compositions of Cu:Ta, Cu:W and Cu:Ag were prepared and tested for CO₂ reduction. The Cu alloys didn’t produce hydrocarbons as efficiently as Cu. Introduction of other metal sites to the Cu catalytic surface inhibited hydrocarbon production and led to increased hydrogen production. CO₂ reduction leads to both volatile and non-volatile products like HCOOH. So it is necessary to design alternative means to monitor products that the mass spectrometer is not capable of detecting. We are limited to quantification using normalized faradaic efficiency. There is a need to develop efficient calibration and quantification techniques.

Monoethanolamine, ionic liquid (EMIM-BF₄) and guanidinium species didn’t lead to hydrocarbon production. The CO₂ is present in different form in monoethanolamine solutions and thus affected the reaction mechanisms. Hydrocarbon production is a catalyst surface sensitive reaction and thus changing the reaction pathway by forming different intermediate using ionic liquid or guanidinium species didn’t work. Further modifying the Cu surface by dipping in different metal salt solutions decreased hydrocarbon production.
5.6. Figures

**Figure 5.1.** Electrochemical oxidation of formic acid in 0.1 M formic acid containing 0.1 M H$_2$SO$_4$ aqueous electrolyte solution using Pt electrode (---) and Pt:Pb (60:40) (----) electrode prepared by co-sputtering on a carbon fiber substrate. Scan rate = 20 mV/sec.

**Figure 5.2.** Normalized faradaic efficiency of hydrogen (O), methane (□) and ethylene (Δ) produced by Cu during electrochemical reduction of CO$_2$ in CO$_2$ purged 0.5 M KHCO$_3$ aqueous electrolyte solution.
**Figure 5.3.** Normalized ethylene efficiency of various compositions of Cu:Ta (O), Cu:W (□) and Cu:Ag (Δ) during electrochemical reduction of CO$_2$ at -2.2 V in CO$_2$ purged 0.5 M KHCO$_3$ aqueous electrolyte solution.

**Figure 5.4.** Normalized methane efficiency of various compositions of Cu:Ta (O), Cu:W (□) and Cu:Ag (Δ) during electrochemical reduction of CO$_2$ at -2.2 V in CO$_2$ purged 0.5 M KHCO$_3$ aqueous electrolyte solution.
Figure 5.5. Normalized hydrogen efficiency of various compositions of Cu:Ta (O), Cu:W (□) and Cu:Ag (△) during electrochemical reduction of CO₂ at -2.2 V in CO₂ purged 0.5 M KHCO₃ aqueous electrolyte solution.
Figure 5.6. Voltage scan for electrochemical reduction of CO\textsubscript{2} on Pt electrode in argon purged (---), CO\textsubscript{2} purged (—) 0.1 M K\textsubscript{2}SO\textsubscript{4} electrolyte and argon purged (—), CO\textsubscript{2} purged (—) 0.1 M K\textsubscript{2}SO\textsubscript{4} electrolyte containing 1 M MEA. Potentiostat response A) current Vs potential. Mass spectrometer response B) 2 amu -hydrogen C) 15 amu -methane d) 26 amu-ethylene
Figure 5.7. Voltage scan for electrochemical reduction of CO₂ on Cu electrode in CO₂ purged (—) 0.1 M KHCO₃ electrolyte and argon purged (—), CO₂ purged (—) 0.1 M KHCO₃ electrolyte containing 0.1 M EMIM BF₄. Potentiostat response A) current Vs potential. Mass spectrometer response B) 2 amu –hydrogen C) 15 amu -methane d) 26 amu-ethylene
Figure 5.8. Voltage scan for electrochemical reduction of CO$_2$ on Au microelectrode in CO$_2$ purged (——) and argon purged (- - -) in A) 0.1 M tetra-methyl ammonium hexafluoro phosphate and B) 0.1 M tetra-butyl ammonium chloride dimethyl sulfoxide electrolyte.
Figure 5.9. Voltage scan for electrochemical reduction of CO$_2$ on Cu electrode (---) and Cu electrode modified by dipping in Ag (--), Pt (---), Hg (---) and Pd (---) in CO$_2$ purged 0.1 M KHCO$_3$ electrolyte. Potentiostat response A) current Vs potential. Mass spectrometer response B) 2 amu-hydrogen C) 15 amu-methane d) 26 amu-ethylene
5.7. Tables

Table 5.1. Sputtering source powers used for fabrication of Pt:Pb (60:40) alloy films by co-sputtering of Pt and Pb.

<table>
<thead>
<tr>
<th></th>
<th>Pt</th>
<th>Pb</th>
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</thead>
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<tr>
<td><strong>RF power</strong></td>
<td>90W</td>
<td>30W</td>
</tr>
<tr>
<td><strong>sputtering rate</strong></td>
<td>0.9 Å/sec</td>
<td>0.6 Å/sec</td>
</tr>
<tr>
<td><strong>composition expected</strong></td>
<td>60%</td>
<td>40%</td>
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</table>

Table 5.2. Calibration values for various gaseous products

<table>
<thead>
<tr>
<th></th>
<th>solubility in water (mM)</th>
<th>calibration peak</th>
<th>Change in Mass Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>0.78</td>
<td>2 amu</td>
<td>1.89*10^{-9}</td>
</tr>
<tr>
<td>Methane</td>
<td>1.5</td>
<td>15 amu</td>
<td>7.25*10^{-10}</td>
</tr>
<tr>
<td>Ethylene</td>
<td>4.9</td>
<td>26 amu</td>
<td>1.56*10^{-9}</td>
</tr>
</tbody>
</table>

Table 5.3. pH values of electrolytes used during monoethanolamine experiments.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1M K₂SO₄ + argon purged</td>
<td>6.54</td>
</tr>
<tr>
<td>0.1M K₂SO₄ + CO₂ purged</td>
<td>3.9</td>
</tr>
<tr>
<td>0.1M K₂SO₄ + 1M MEA + argon purged</td>
<td>11.96</td>
</tr>
<tr>
<td>0.1M K₂SO₄ + 1M MEA + CO₂ purged</td>
<td>9.38</td>
</tr>
</tbody>
</table>
Table 5.4. pH values of electrolytes used during EMIM-BF₄ experiments.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1M KHCO₃ + argon purged</td>
<td>9.17</td>
</tr>
<tr>
<td>0.1M KHCO₃ + CO₂ purged</td>
<td>7.03</td>
</tr>
<tr>
<td>0.1M KHCO₃ + 0.1M EMIM-BF₄ + argon purged</td>
<td>8.94</td>
</tr>
<tr>
<td>0.1M KHCO₃ + 0.1M EMIM-BF₄ + CO₂ purged</td>
<td>6.95</td>
</tr>
</tbody>
</table>

5.8. References


CHAPTER 6. FORMIC ACID DETECTION INTEGRATED DIFFERENTIAL ELECTROCHEMICAL MASS SPECTROMETRY USING Pt:Pb ELECTRODE: APPLICATION IN FORMALDEHYDE, METHANOL OXIDATION AND CO₂ REDUCTION

6.1. Abstract

Electrochemical reduction of CO₂ in aqueous electrolyte solutions led to production of volatile and non-volatile products. When Differential Electrochemical Mass Spectrometry (DEMS) was used for the CO₂ reduction study it detected the volatile products namely hydrogen, methane and ethylene. But non-volatile products like formic acid went undetected. A Pt:Pb electrode fabricated by electrodepositing Pb over Pt was integrated as a formic acid detector. It detected formic acid by oxidizing formic acid without poisoning. It’s performance was characterized as a function of formic acid concentration. The characterized formic acid detector was used in methanol oxidation, formaldehyde oxidation and CO₂ reduction experiments.

6.2. Introduction

Usage of fossil fuels like coal, oil and natural gas produce CO₂. The usage has increased over the year and the global annual CO₂ emission is 38 gigatonnes.¹ The nature’s carbon cycle is not able to handle such high quantities of CO₂ and so leads to accumulation in the atmosphere, resulting in global warming. The concentration of CO₂
in the atmosphere is 400 ppm now. To an environmentalist, this is an accumulation problem. But to an engineer, this is a process design problem. There is a need of a process to utilize CO₂, a cheap raw material produced everywhere and everyday. To create a sustainable process there is a need to produce something of high demand. Fuels are burned to produce CO₂. So a potential option is to produce fuels from CO₂. Hydrocarbon fuels can be produced at ambient conditions using an electrochemical route.² Electrochemical reductions of CO₂ on copper electrodes in aqueous electrolytes produce hydrocarbons like methane and ethylene.³ Furthermore, ethylene is the world’s most produced organic chemical and serves as a basic feedstock to the petrochemical industry.⁴ But the electrochemical product mixture also contains hydrogen, formic acid and CO making the process unattractive. There is a need to design an electrocatalytic system that could produce hydrocarbons selectively. For this task we need a detection technique or a system of detection techniques that could detect all the products produced in the reaction.

Differential Electrochemical Mass Spectrometry (DEMS)⁵ is an in-situ mass spectrometric technique which uses a membrane as a barrier to prevent the electrolyte but allowing the volatile products to diffuse to the mass spectrometer for detection. The electrode can be separate or coated over the membrane. Over the years the technique has been developed to address it’s various limitations such as reactant supply, electrode material and detection limitations. To eliminate the reactant supply limitation, various hydrodynamic techniques such as Rotating Disc Electrode (RDE) and impinging jet have been integrated with DEMS. As a result RDE-DEMS⁶, wall-jet DEMS⁷, thin-layer wall jet DEMS⁸ and wall-tube DEMS⁹ have been developed. To eliminate the
electrode material limitation, scanning DEMS\textsuperscript{10} was developed to enable scanning the DEMS inlet across a series of electrodes. To eliminate detection limitation, various other detection techniques like Electrochemical Quartz Crystal Microbalance (EQCM), Infra Red (IR) and electrochemical detection have been integrated with DEMS to enable detection of non-volatile products. As a result EQCM-DEMS\textsuperscript{6}, IR-DEMS\textsuperscript{11} and electrochemical DEMS\textsuperscript{12} have been developed.

Various groups used Gas Chromatography (GC) and High Performance Liquid Chromatography (HPLC) to analyze the gaseous and liquid products produced during electrochemical reduction of CO\textsubscript{2}\textsuperscript{13} Infrared spectroscopy\textsuperscript{14} and Surface Enhanced Raman Scattering (SERS)\textsuperscript{15,16} have been used to identify adsorbed CO. SERS, Auger Electron Spectroscopy (AES) and X-ray Photoelectron Spectroscopy (XPS) have been used to study the poisoning species. Dewulf et al.,\textsuperscript{17} used XPS and AES and identified graphitic carbon which poisoned the copper surface during electrochemical reduction of CO\textsubscript{2}. While Smith et al.,\textsuperscript{16} used SERS and identified the poisoning species as a copper oxide patina. Volatile products such as hydrogen, methane, ethylene, carbon monoxide, formaldehyde and methanol can be detected using DEMS with 2 amu, 15 amu, 26 amu, 28 amu, 30 amu and 31 amu signals.\textsuperscript{18} Furthermore Nuclear Magnetic Resonance (NMR) has been used to identify and quantify liquid phase CO\textsubscript{2} reduction products. Recently Kuhl et al.,\textsuperscript{19} used GC and NMR to study CO\textsubscript{2} reduction on copper and reported a total of 16 different products including previously reported methane, ethylene, CO, formate, ethanol, n-propanol, allyl alcohol, acetaldehyde, propionaldehyde, acetate, methanol and newly identified ethylene glycol, glycolaldehyde, hydroxyacetone, acetone and glyoxal.
Zhang et al.\textsuperscript{20} used a rotating ring-disc electrode with a Pt ring detector to detect CO produced from CO\textsubscript{2} reduction by a cobalt tetramethylpyridoporphyrine complex, and Aoki et al.\textsuperscript{21} detected formic acid produced during CO\textsubscript{2} reduction on a SnO\textsubscript{2} electrode. But Pt is not a suitable detector for formic acid as formic acid oxidation poisons the Pt surface. So Wang et al.\textsuperscript{12} used a double-band electrode in a thin-layer configuration with a Pt:Pb detector electrode to detect the formic acid produced during methanol and formaldehyde oxidation. In this report we have attempted to detect non-volatile formic acid produced during CO\textsubscript{2} reduction using a Pt:Pb ring electrode and monitor volatile products using DEMS in a ring-disc electrode setup in thin-layer wall-jet configuration\textsuperscript{22}.

6.3. Experimental section

The experimental setup and materials used have been described in detail in our previous work\textsuperscript{22}. All experiments are performed with nanopure water with resistivity 18 M\(\Omega\) (Barnstead Inc). Electrolyte solutions were prepared from reagent grade chemicals: potassium nitrate (A.C.S. reagent grade, Fischer), sodium sulfate (A.C.S. reagent grade, Fischer), lead nitrate (Fischer), formic acid (A.C.S. reagent grade 88 \%, Fischer), 10 \% formaldehyde solution (methanol free ultrapure EM reagent grade, Polysciences, Inc), methanol (A.C.S. reagent grade, Fischer), sulfuric acid (A.C.S. reagent grade, Fischer). Nitrogen (Airgas) and CO\textsubscript{2} (Airgas) were also used.

6.4. Results and Discussion

Formic acid detecting Pt:Pb electrodes were fabricated by electrodepositing Pb on Pt electrodes. Fig.6.1 illustrates the cyclic voltammogram of a Pt microelectrode in a
0.1 M KNO$_3$ electrolyte containing 10 mM of PbNO$_3$. The cyclic voltammogram clearly shows that deposition of Pb is favored from -0.9 V to -1.3 V (vs Hg/Hg$_2$SO$_4$) in the negative scan by an increase in reduction current. Lead is stripped from -0.9 V to -0.5 V (vs Hg/Hg$_2$SO$_4$) by an increase in oxidation current in the positive scan. Pb loading was increased by increasing the number of Pb doses which comprised of a 2 segment scan between the deposition voltages -0.9 V and -1.3 V at a scan rate of 100 mV/sec.

Pb loading needs to be optimized to obtain increased and consistent formic acid oxidation currents for detection purposes. It was observed that the formic acid oxidation currents increased with increased Pb loading. But after a maximum it decreased and started to behave like a Pb electrode as the Pt surface got covered with Pb. Fig.6.2 depicts the formic acid oxidation response of a Pt electrode loaded with 5 doses of Pb in 0.1 M H$_2$SO$_4$. With a Pt electrode formic acid oxidation lead to deactivation by adsorbed CO which was oxidized at 0.2 V. With a Pt:Pb electrode formic oxidation was favored starting at a low potential -0.6 V and leading to large oxidation currents at higher voltages. Five doses of Pb on a Pt coated carbon fiber ring substrate resulted in a deposition of 51 monolayers of Pb.

The performance of the fabricated Pt:Pb detector was characterized as a function of formic acid concentration. Fig.6.3 illustrates the detector response when exposed to different formic acid concentrations in no-flow and flow conditions. The data was obtained by performing experiments in the flow setup with the electrolyte at particular formic acid concentrations. In no-flow conditions the detector response increased with increase in formic acid concentration. The non-linearity of the increase is due to a limitation from formic acid diffusion. In flow condition the behavior was not as expected.
The expectation was a linear and larger response compared to the no-flow conditions.
But the obtained response clearly showed influence of another reduction reaction. This
was probably oxygen reduction supported by the residual oxygen in the electrolyte
whose supply is enhanced with flow. The detector behavior was different in low
concentration of formic acid compared to high concentrations of formic acid. In low
concentration of formic acid, the response was dominated by oxygen reduction and so
was negative compared to no-flow conditions. In high concentration, the formic acid
oxidation dominated the oxygen reduction and so the response was larger than the no-
flow conditions.

To demonstrate the application of the fabricated formic acid detection system in a
thin-layered wall jet configuration, methanol oxidation and formaldehyde oxidation was
performed on a Pt electrode. Fig.6.4 depicts the results obtained from the methanol
oxidation experiment. As the voltage was scanned methanol oxidation was favored
leading to oxidation currents as seen in Fig.6.4A and the products produced were
simultaneously detected using mass spectrometer and the Pt:Pb ring electrode held at -
0.2 V. During methanol oxidation CO₂ and formic acid were produced. CO₂ was
detected using the 44 amu signal as seen in Fig.6.4B. Formic acid was detected using
the methyl formate 60 amu signal as seen in Fig.6.4C and the Pt:Pb ring detector held
at -0.2 V as seen in Fig.6.4D. The ring detector had a negative background current due
to oxygen reduction. Thus formic acid detection sensitivity was reduced and not
detected.

Fig.6.5 depicts the results obtained from formaldehyde oxidation experiment. As
the voltage was scanned formaldehyde oxidation was favored leading to oxidation
currents as seen in Fig.6.5A and the products produced were simultaneously detected using mass spectrometer and Pt:Pb ring electrode held at -0.2 V. During formaldehyde oxidation CO₂ and formic acid were produced. CO₂ was detected using 44 amu signal as seen in Fig.6.5B. Formic acid was detected using Pt:Pb ring detector held at -0.2 V as seen in Fig.6.5C. The ring detector had a positive background current due to formaldehyde oxidation. Thus formic acid detection sensitivity was reduced and not detected. Other reasons leading to unsuccessful formic acid detection are reaction limitation, sensitivity limitation and design limitations. We are limited by the reaction to produce formic acid. The major product of both methanol and formaldehyde oxidation is CO₂. Furthermore in methanol oxidation part of formic acid produced is lost as methyl formate. Since low amounts of formic acid are produced, the detector requires high sensitivity to perform the detection. Background current contributing reactions like oxygen reduction lower the detector sensitivity considerably. The size of the disc electrode limits the amount of reaction. The formic acid reaching the detector is determined by the collection efficiency at the particular flow rate of ring disc electrode in thin-layer configuration.

Fig.6.6 and Fig.6.7 depicts the results obtained during a scan and step experiment with CO₂ reduction on a Pb electrode fabricated by depositing 100 doses of Pb on a Pt electrode. The CO₂ purged case was compared with a N₂ purged case in both the experiments. The solution pH of the CO₂ purged case was 3.92. So the pH of N₂ purged case was modified from 6.33 to 3.92 by addition of sulfuric acid for comparison. As the voltage was scanned and stepped negatively, reduction currents were observed as seen in Fig.6.6A and Fig.6.7B and the products produced were
simultaneously detected using mass spectrometer and a Pt:Pb ring electrode held at -0.1 V. During reduction only H$_2$ was produced in the N$_2$ purged case while H$_2$ and formic acid were produced in the CO$_2$ purged case. H$_2$ was detected using the 2 amu signal as seen in Fig.6.6B and Fig.6.7C. Formic acid and H$_2$ were detected using a Pt:Pb ring detector held at -0.1 V as seen in Fig.6.6C and Fig.6.7D. The ring detector had a background current due to H$_2$ detection by oxidation. In the scan and step experiment, higher reduction currents were observed in the N$_2$ purged case. Correspondingly, a higher hydrogen ion MS current and ring current were observed. In the scan experiment it can be observed that there is a mismatch in the disk and ring currents for the CO$_2$ and N$_2$ purged cases indicating signs of formic acid detection along with H$_2$ in the CO$_2$ purged case.

6.5. Conclusions

A Pt:Pb electrode was fabricated by loading an optimized amount of Pb onto Pt electrode by electrodeposition. It was observed that residual oxygen present in the electrolyte interfered with the detecting capability of the Pt:Pb electrode in flow conditions. Oxygen reduction dominated the detector response in low formic acid concentrations. Formic acid detection was unsuccessful during methanol and formaldehyde oxidation. The detector faced sensitivity issues as some of the formic acid produced during methanol oxidation was further converted to methyl formate, and formaldehyde oxidation at the detection voltage led to huge background currents. While extending the application of the formic acid detector to CO$_2$ reduction, background currents due to H$_2$ detection posed a problem.
6.6. Figures

**Figure 6.1.** Voltage scan for electrodeposition of Pb on Pt microelectrode in 0 mM PbNO₃ (---) and 10 mM PbNO₃ (——) in 0.1 M KNO₃ aqueous electrolyte solution. Scan rate = 100 mV/sec.

**Figure 6.2.** Electrochemical oxidation of formic acid in 0.1 M formic acid containing 0.1 M H₂SO₄ aqueous electrolyte solution using Pt electrode (——) and Pt:Pb (60:40) (----) electrode prepared by electrodepositing Pb on a Pt film coated carbon fiber substrate. Scan rate =20 mV/sec.
Figure 6.3. Pt:Pb formic acid detector response at detection potential of -0.2 V vs Hg/Hg$_2$SO$_4$ as a function of formic acid concentration in 0.1 M H$_2$SO$_4$ aqueous electrolyte solution in no flow condition (○) and 1 ml/sec in thin-layered wall tube configuration (■).
Figure 6.4. Voltage scan for electrochemical oxidation of methanol on Pt disc electrode in nitrogen purged 0.1 M H$_2$SO$_4$ electrolyte containing 1 M CH$_3$OH. Potentiostat response A) current vs potential. Mass spectrometer response B) 44 amu –carbon dioxide C) 60 amu –methyl formate and Pt:Pb ring electrode response D) detection potential = -0.2 V vs Hg/Hg$_2$SO$_4$. Electrolyte flow of 1 ml/sec was maintained in thin-layered wall-tube configuration.
Figure 6.5. Voltage scan for electrochemical oxidation of formaldehyde on Pt disc electrode in nitrogen purged 0.1 M H₂SO₄ electrolyte containing 10 % HCHO. Potentiostat response A) current vs potential. Mass spectrometer response B) 44 amu – carbon dioxide. Pt:Pb ring electrode response C) detection potential = -0.2 V vs Hg/Hg₂SO₄. Electrolyte flow of 2 ml/sec was maintained in thin-layered wall-tube configuration.
Figure 6.6. Voltage scan for electrochemical reduction of CO$_2$ on Pb disc electrode in N$_2$ purged (----) and CO$_2$ purged (——) 0.1 M Na$_2$SO$_4$ electrolyte of pH 3.92. Potentiostat response A) current vs potential. Mass spectrometer response B) 2 amu – hydrogen. Pt:Pb ring electrode response C) detection potential = -0.1 V vs Hg/Hg$_2$SO$_4$. Electrolyte flow of 2 ml/sec was maintained in thin-layered wall-tube configuration.
Figure 6.7. Voltage step for electrochemical reduction of CO$_2$ on Pb disc electrode in N$_2$ purged (----) and CO$_2$ purged (——) 0.1 M Na$_2$SO$_4$ electrolyte of pH 3.92. Potential program A) voltage vs time. Potentiostat response B) current vs time. Mass spectrometer response C) 2 amu – hydrogen. Pt:Pb ring electrode response D) detection potential = -0.1 V vs Hg/Hg$_2$SO$_4$. Electrolyte flow of 2 ml/sec was maintained in thin-layered wall-tube configuration.
6.7. References


Formation during Methanol Electrooxidation. *Analytical Chemistry* 2010, 82 (11), 4319-4324.


22. Venkatachalam, S.; Angelici, R. J.; Woo, L. K.; Hillier, A. C., Integration of electrochemical detection into differential electrochemical mass spectrometry using a thin layered wall jet ring disc electrode. (to be published soon).

24. Vielstich, W., Adsorbate formation during the electrochemical reduction of carbon

25. Azuma, M.; Hashimoto, K.; Hiramoto, M.; Watanabe, M.; Sakata, T.,
Electrochemical Reduction of Carbon Dioxide on Various Metal Electrodes in Low-
(6), 1772-1778.
CHAPTER 7. CONCLUSIONS AND FUTURE DIRECTIONS

In this thesis, DEMS technique has been developed for electrocatalytic studies.

In hydrodynamic DEMS (chapter 3),\(^1\) capability of control and enhancement of reactant supply has been integrated to DEMS technique and demonstrated. This was achieved by placing a nozzle besides the electrode and creating an impinging jet in wall-tube configuration. Proton reduction and oxalic acid oxidation on Pt electrode was performed to demonstrate the enhanced reactant supply and thereby enhanced product formation.

In electrochemical detection integrated DEMS (chapter 4),\(^2\) a second electrochemical detector was integrated to DEMS and demonstrated. The electrochemical detector was deposited on a carbon fiber ring and press fitted to the membrane electrode in the ring disc configuration. Detection was made possible by enclosing this ring disc assembly in a thin layer formed by placing the ring disc assembly beside a teflon wall that has a nozzle at its center. This enabled transfer of products to the ring detector as they are formed. Hydroxylamine oxidation on Au electrode was performed to detect produced NO and demonstrate the working of the electrochemical detector.

The capabilities of the developed DEMS detection setup could be exploited in various electrochemical reactions. Catalyst exploratory work could be undertaken with ease in well-defined conditions. Strategies to overcome limitations posed by certain reactions or different detection methods need to be devised to effectively develop this detection setup as a versatile tool in electrocatalysis studies.
There is a continuous analytical need to detect the undetected products in exploratory CO₂ reduction research. Binary alloys have been explored. Multicomponent alloys could be pursued. Recently Kuhl et al.,³ used GC and NMR to study CO₂ reduction on copper and reported a total of 16 different products. It included ethanol, n-propanol, allyl alcohol, acetaldehyde, propionaldehyde, acetate, methanol, ethylene glycol, glycolaldehyde, hydroxyacetone, acetone, glyoxal in addition to the majorly reported methane, ethylene, CO and formate.

7.1 References


2. Venkatachalam, S.; Angelici, R. J.; Woo, L. K.; Hillier, A. C., Integration of electrochemical detection into differential electrochemical mass spectrometry using a thin layered wall jet ring disc electrode. (to be published soon).

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