SIFT-MS FOR CARBON DIOXIDE REDUCTION REACTION

# APPLICATION OF SELECTED-ION-FLOW-TUBE MASS SPECTROMETRY FOR REAL-TIME OPERANDO QUANTITATIVE MEASUREMENT OF PRODUCT FORMATION FOR ELECTROCHEMICAL REDUCTION OF CARBON DIOXIDE

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A Thesis Submitted to the School of Graduate Studies in the Partial Fulfillment of the Requirements for the Degree Master of Applied Science

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## Lay Abstract

The electrochemical reduction of carbon dioxide can be used within electrolyzer devices to help mitigate greenhouse gas emissions to combat global warming. The process is when carbon dioxide is extracted from sources such as industrial plants and undergoes electrochemical reduction to be converted into 16 or more products that can be then sold within the market for profit. The common analysis methods currently used to analyze how much of each product is produced from an electrolyzer device does not reveal all the information needed to best design electrolyzer devices. This has led way to new analysis methods that are being explored that can find all the information needed for product analysis that leads to optimal electrolyzer design. This work investigated uses a special type of mass spectrometry that will allow for the full information to be found on the products from electrochemical carbon dioxide reduction leading to enhanced electrolyzer designs.

### Abstract

Electrochemical  $CO_2$  reduction reaction ( $CO_2R$ ) is a promising route to help reduce greenhouse gas emissions and reach carbon dioxide net zero emissions to combat global warming. Currently, in order to investigate catalytically produced products from CO<sub>2</sub>R offline methods such as gas chromatography (GC) and nuclear magnetic resonance (NMR) are used. These offline methods have a time resolution on the minutes to hours scale which leads to uncertainty of evaluating how products are produced from CO<sub>2</sub>R, such as knowing if a product is produced from electrochemical means or chemical conversion, and if a product is being produced in a linear rate of production or a different rate. This is where the ability to have real-time analysis of the products generated from CO<sub>2</sub>R is desirable, as it can more definitively answer many of these questions. Yet few analytical techniques have been developed in detail so far to achieve real-time analysis. Herein, we show the use of selected-ion flow-tube mass spectrometry (SIFT-MS) that quantitatively measures in realtime an array of 10 C<sub>1</sub>, C<sub>2</sub>, and C<sub>3</sub> products from CO<sub>2</sub>R such as ethanol, ethylene or methane. The custom-developed SIFT-MS selected ion mode scan measures the concentration of gas and liquid-phase products of CO<sub>2</sub>R at the same time and is compatible with any electrolyzer cell. We demonstrate that the SIFT-MS technique can reliably and accurately determine product concentration in real-time through the evaluation of Cu foil and its comparison to traditional techniques. Considering the narrow range of developed and deployed techniques for real-time quantitative product analysis for CO<sub>2</sub>R, this study

on SIFT-MS is a critical tool for future research in accelerating and optimizing catalyst design for electrochemical CO<sub>2</sub>R applications.

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# List of Abbreviations and Symbols

Ag	Silver
C1	Chemistry of one-carbon molecules
C <sub>2</sub>	Chemistry of two-carbon molecules
$C_2^+$	Chemistry of two or more carbon molecules
C <sub>3</sub>	Chemistry of three-carbon molecules
C4	Chemistry of four-carbon molecules
CA	Chronoamperometry
Cl	Chloride
СМ	Centimeters
СО	Carbon Monoxide
CO <sub>2</sub>	Carbon Dioxide
$CO_2R$	Carbon Dioxide Reduction Reaction
Cu	Copper
CV	Cyclic Voltammetry
DEMS	Differential Electrochemical Mass Spectrometry
EC-MS	Electrochemical Mass Spectrometry
EIS	Electrochemical Impedance Spectroscopy
FE	Faradaic Efficiency
GC	Gas Chromatography
HER	Hydrogen Evolution Reaction

H <sub>2</sub> O	Water
HPLC	High-Performance Liquid Chromatography
iR	Voltage Loss or Voltage Compensation
KHCO <sub>3</sub>	Potassium Bicarbonate
КОН	Potassium Hydroxide
MEA	Membrane Electrode Assembly
m/z	Mass-to-Charge Ratio
NMR	Nuclear Magnetic Resonance
OER	Oxygen Evolution Reaction
PPM	Parts Per Million
Pt	Platinum
PTR-TOF-MS	Proton-Transfer-Reaction Time-of-Flight Mass Spectrometry
RHE	Reversible Hydrogen Electrode
S	Seconds
SIFT-MS	Selected-Ion-Flow-Tube Mass Spectrometry
SIM	Selected Ion Mode
VOC	Volatile Organic Compound

# **Declaration of Academic Achievement**

I, Timothy Matthew Gibson, declare that this thesis titled, "Application of Selected-Ion-Flow-Tube-Mass Spectrometry for real-time operando quantitative measurement of product formation for electrochemical reduction of carbon dioxide" and the work presented in it are my own.

# **1. Introduction**

### **1.1 Carbon Dioxide Induced Climate Change**

Climate change represents one of the most significant and extensively debated environmental challenges of the present-day [1]. The progression of climate change is primarily driven by the increasing concentration of greenhouse gases in the atmosphere [1], [2]. This results in a range of detrimental environmental impacts, including intensifying storm severity, prolonged drought occurrences, rising sea levels, and loss of species [1], [3]. The recent surge in greenhouse gas emissions is attributable to human-caused activities, which in Canada, can be categorized into distinct economic sectors as illustrated in Figure 1 [2]. There exists no singular technology or solution capable of mitigating greenhouse gas emissions across all sectors. Renewable energy technologies, such as wind and solar, contribute to emission reductions in the electricity sector [4], while advancements in electric vehicle technology can facilitate significant reductions in the transport sector [5], and development in carbon dioxide technology will reduce emissions from the oil and gas and heavy industry sectors [1], [3]. This thesis will specifically examine the carbon dioxide reduction reaction and the carbon electrolyzer technologies that have emerged from this research area [6], [7], [8]. This area of research will aid in the reduction of emissions across primarily the oil and gas industry, as well as heavy industry, which collectively account for approximately 40% of Canada's total carbon dioxide emissions [2].





change/services/environmental-indicators/greenhouse-gas-emissions.html [2].

### **1.2 CO<sub>2</sub>R Electrolyzer Economic Analysis**

Carbon dioxide reduction reaction (CO<sub>2</sub>R) electrolyzer technologies consists of the operation of facilitating the conversion of carbon dioxide either stored or typically emitted from industrial sources into valuable fuels and chemicals [6], [7]. When coupled with renewable energy sources, this establishes a carbon-neutral process, delivering value while mitigating CO<sub>2</sub> emissions [6]. However, the technology is impeded by prominent challenges that hinder its commercialization and industrial application. One of these challenges is CO<sub>2</sub>R produces over 18 diverse carbon products, including C<sub>1</sub>, C<sub>2</sub>, and C<sub>3</sub>, in the form of hydrocarbons, aldehydes, and alcohols [8]. This creates an issue as it can be expensive and energy intensive to have a separation process that comes after the production of products from CO<sub>2</sub>R electrolyzer systems [6], [7]. Ideally the electrolyzer system will produce one major product, and with this in mind, economic analysis can be done to see which product can be the best target [6], [7]. From a techno-economic perspective, among the C<sub>1</sub> products, carbon monoxide and formate emerge as the most viable production candidates [6], [7]. Electrolyzer technology could be installed to produce carbon monoxide and formic acid at production costs below the existing market rates, specifically at \$0.44 kg<sup>-1</sup> and \$0.59 kg<sup>-1</sup> respectively, as depicted in Figure 2, in contrast to the market prices of  $0.80 \text{ kg}^{-1}$  for carbon monoxide and  $0.50 \text{ kg}^{-1}$  for formic acid [7].



Figure 2. Production cost changes for various parameters in both an optimistic and pessimistic situation a) carbon monoxide b) formic acid. The neutral baseline production cost of carbon monoxide is \$0.44 kg<sup>-1</sup> and formic acid is \$0.59 kg<sup>-1</sup>, Reproduced with permission from Springer Nature, H. Shin, K. U. Hansen, and F. Jiao, "Techno-economic assessment of low-temperature carbon dioxide electrolysis," Nat. Sustain., vol. 4, no. 10, pp. 911–919, 2021, doi: 10.1038/s41893-021-00739-x [7].

The primary challenge with C<sub>1</sub> products lies in their considerably smaller market size compared to C<sub>2</sub> product markets. Specifically, carbon monoxide and formic acid

possess market sizes of \$3 billion and \$6 billion respectively, whereas the most promising C<sub>2</sub> products, ethylene and ethanol, exhibit market sizes of \$230 billion and \$75 billion respectively [7]. Although C<sub>1</sub> products are closer to commercialization, C<sub>2</sub> products are significantly more attractive [6], [7]. The C<sub>2</sub> products nearest to industrialization are ethylene and ethanol [7]. Both of these products require substantially higher faradaic efficiency (FE) selectivity, stability, and numerous other factors, as illustrated in Figure 3, in order to achieve profitability [6], [7]. When examining one of the critical parameters, it is evident that stability presents the biggest challenge confronting the field, with an industry target set at achieving a duration of 20,000 hours [6]. Stability being the electrolyzer holding its performance characteristics for a set amount of time before noticeably degrading such as selectivity towards a product, or current density. For C<sub>1</sub> products, stability exceeding 1,000 hours has been attained; where in contrast, C<sub>2</sub> products have only demonstrated stability for 100 hours [6]. Despite some advancements in enhancing stability and notable progress being made in other important metrics such as current density, and faradaic efficiency in recent years, considerable improvement is still necessary before these electrolyzer technologies become viable for C<sub>2</sub> products [6], [7]. Therefore, extensive research is being conducted on CO<sub>2</sub>R to gain comprehensive insights into the CO<sub>2</sub>R reaction, which can subsequently be applied to develop commercial electrolyzer systems [6], [7].



**Figure 3.** Highlights the roadmap to the parameters needed for reducing the product cost of a) ethylene and b) ethanol to a target production price that is cost-relevant, Reproduced with permission from Springer Nature, H. Shin, K. U. Hansen, and F. Jiao, "Technoeconomic assessment of low-temperature carbon dioxide electrolysis," Nat. Sustain., vol.

4, no. 10, pp. 911–919, 2021, doi: 10.1038/s41893-021-00739-x [7].

#### **1.3 Electrochemical CO<sub>2</sub> Reduction Fundamentals**

In electrochemical redox reactions reduction is the transfer of electrons when they are gained by a molecule or a decrease in oxidation state and always accompanied by an oxidation process, which is the transfer of electrons when they are lost by a molecule or an increase in oxidation state [9]. The conversion of carbon dioxide to a more reduced chemical species through the application of electrical energy, known as CO<sub>2</sub>R, represents the reduction part of a redox reaction. Hence each CO<sub>2</sub>R reaction is required to couple with an oxidation reaction, typically the oxygen evolution reaction, which is a well-established area of research utilizing water as a plentiful resource and catalysts that are thoroughly documented [6]. When CO<sub>2</sub>R is combined with the oxygen evolution reaction, it constitutes a nonspontaneous reaction necessitating the application of a voltage to progress the reaction [6]. The application of an electric potential is necessary for CO<sub>2</sub>R to overcome activation energy barriers, thereby allowing the reaction products to be kinetically favorable under room temperature and standard atmospheric pressure [6], [9]. There are over 18 distinct products reported for CO<sub>2</sub>R, all of which are similar in nature but exhibit varying standard electrode potentials, as depicted in Table 1 [8]. The standard electrode potentials of CO<sub>2</sub>R products lie in close proximity to the thermodynamic potential of the hydrogen evolution reaction (0 V vs reversible hydrogen electrode (RHE)). As illustrated in **Table 1**, the standard potentials of possible products produced from CO<sub>2</sub>R range from 0.21 V vs RHE to -0.26 V vs RHE [8]. This requires the design of materials for the cathode and catalyst in CO<sub>2</sub>R to be precisely designed to avoid the competitive hydrogen evolution reaction (HER) reaction and to optimize CO<sub>2</sub>R [6], [9].

 Table 1. Products of CO<sub>2</sub>R that shows the # e<sup>-</sup> needed to produce each product and the standard reduction potential (V vs RHE) of each product at a pH of 6.8, reproduced from [8]. Used with permission of Timothy Matthew Gibson, from Energy and Environment Science, New Insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces, Kuhl, Kendra, Cave,

Etosha, Abram, David, Jaramillo, Thomas, 5, 2012; permission conveyed through Copyright

Product	# e <sup>-</sup>	E	Product	# e <sup>-</sup>	Е
Formate O	2	-0.02	Acetaldehyde	10	0.05
Carbon monoxide	2	-0.10	Ethanol	12	0.09
Methanol CH <sub>3</sub> OH	6	0.03	Ethylene	12	0.08
Glyoxal	6	-0.16	Hydroxyacetone	14	0.46
Methane	8	0.17	Acetone	16	-0.14
Acetate	8	-0.26	Allyl alcohol	16	0.11
Glycolaldehyde	8	-0.03	Propionaldehyde	16	0.14
Ethylene glycol	10	0.20	1-Propanol	18	0.21

CO<sub>2</sub>R is a very complex reaction with many different pathways and also competing reactions as previously mentioned with HER. It is a complex process to design a catalyst for a specific product as one has to minimize HER, while maximizing selectivity for one CO<sub>2</sub>R product which varies upon a lot of operating factors such as properties of the catalyst, pH of the system, applied potential or voltage, surface chemistry, and morphology of the catalyst [6], [9]. See **Figure 4** for a visual representation of the complexity of the mechanism pathways for electrochemical CO<sub>2</sub>R [9]. One overall rule is that lower overpotentials closer to the standard reduction potential of these products lead to a high selectivity towards the HER as at these levels it is difficult for CO<sub>2</sub> activation to occur [9]. As the applied potential gets pushed towards more negative values it leads to increased CO-CO coupling or CO hydrogenation, which leads to C<sub>1</sub> and C<sub>2</sub> hydrocarbons starting to form [9]. Eventually, the applied potential will get too high of a value where the proton and electron transfers are accelerated which leads to reduced production of C<sub>2</sub><sup>+</sup> products and an increase of methane and hydrogen [6], [9]. There is a potential sweet spot for CO<sub>2</sub>R to produce the desired  $C_2^+$  products, which will vary for each catalyst material depending on a multitude of factors as previously discussed (pH, morphology etc.).



Figure 4. Highlights the different complex reaction pathways for CO<sub>2</sub>R, Reprinted with permission from T. Yan *et al.*, "Multiscale CO2 Electrocatalysis to C2+ Products:
Reaction Mechanisms, Catalyst Design, and Device Fabrication," *Chem. Rev.*, vol. 123, no. 17, pp. 10530–10583, 2023, doi: 10.1021/acs.chemrev.2c00514. Copyright 2024 American Chemical Society [9].

CO<sub>2</sub>R catalysts for the cathode can essentially be split up into three main categories based on their behaviour and selectivity towards specific products. The first class is formate-producing catalysts [6]. These catalysts are prone to adsorb an atom bound to \*HCOO (\* denotes an atom bound to the catalyst) which is the prominent intermediate in the formation of formate [6]. The most common CO<sub>2</sub>R catalysts that fall under this class are bismuth, cadmium, tin, indium, and lead [6]. The second class is catalysts that have an affinity for CO production. These catalysts have a tendency to start the CO<sub>2</sub>R process by binding the atom bound to the \*COOH species on the surface which will lead to a weakly bound \*CO intermediate [6]. This \*CO intermediate will eventually desorb from the catalyst surface as CO. The most common catalysts that fall under the second class are silver, gold, and nickel [6]. The third and final class produces various  $C_2^+$  hydrocarbons such as ethanol, ethylene and acetaldehyde. This is done by binding the \*CO with enough strength to continue the reaction and facilitate the production of an array of products [6]. There is only one catalyst material of relevance currently in this class which is Cu [6], [8]. Cu based catalysts have been tested in many different types such as copper nanoparticle catalysts, bimetallic catalysts where one of the metals is always copper (i.e. Cu-Ag), copper nanowires, oxide derived copper catalysts, and many other types. The research field continues to grow and adapt over time and the discovery of catalysts is a never-ending front. There could be development of a new material one day that can match copper in being able to produce  $C_2^+$  products within CO<sub>2</sub>R electrolyzers, and cells [6].

### **1.4 CO<sub>2</sub>R Electrolyzers and Cell types**

An electrolyzer is a device made up of an anode, and cathode that are connected through an electrolyte to complete an electrical circuit [6]. An electrical current (electrical energy) is applied to electrolyzer devices to drive a non-spontaneous chemical reaction. In the case of CO<sub>2</sub>R it is applying electrical energy to drive the conversion of carbon dioxide into products as discussed in **Section 1.3** and seen in **Table 1** [6], [8]. There are a few fundamental principles that make up the basis of how electrolyzers function that will be discussed which are the reversible voltage, operating voltage, overpotential and electrolyzer efficiency or energy efficiency [6], [10]. Then a very general approach for electrolyzer design will be discussed that briefly touches on a surface level what factors go into designing an electrolyzer. Finally, the common electrolyzer cells used within CO<sub>2</sub>R will be highlighted.

Reversible voltage is the theoretical minimum amount of voltage needed to drive the electrochemical reaction forward between the anode and cathode within an electrolyzer device [6], [10], [11]. It is calculated by taking the reduction potential occurring at the cathode and subtracting it from the reduction potential occurring at the anode as seen in **Equation 1** [6], [10], [11].

$$E_{reversible} = E_{cathode} - E_{anode} (1)$$

For CO<sub>2</sub>R there will be a unique reversible voltage or potential for each product produced during the electrochemical reaction as each product has its own unique standard reduction potential as seen from **Table 1** that would correlate to the E<sub>cathode</sub> [6], [8], [10],

[11]. For essentially all current CO<sub>2</sub>R electrolyzer devices OER occurs at anode and would correlate to the Eanode. If carbon monoxide was the product being produced from CO<sub>2</sub>R in an electrolyzer device its reversible potential would be the following where E<sub>cathode</sub> is taken from **Table 1** and  $E_{anode}$  is OER which has a standard reduction potential of +1.23 V in the same reference system from **Table 1** [6], [8], [11].  $E_{reversible} = -0.10 V - 1.23 V = -1.33 V$ (in reference to an RHE reference system, -1.33 V vs RHE) [8], [11]. This same process can be applied to each product that is produced electrochemically from the CO<sub>2</sub>R reaction. Reversible potential as noted earlier only covers the theoretical potential at which the reduction potential should occur at, when the electrolyzer device is actually used in practice overpotential and operating voltage need to be discussed [6], [10], [11]. Overpotential is the extra voltage needed to drive that electrochemical reaction forward past its reversible potential to which the electrochemical reaction will start in an experiment [6]. Mainly its due to reaction kinetics and it is the extra energy that needs to be applied to overcome the activation barrier for the reaction to occur at the surface of the electrode [6], [10]. Ohmic losses and mass transfer can also contribute to overpotential [6], [11]. Ohmic overpotential is occurring from the voltage loss due to the resistance of the electrolyte in the electrolyzer system [10], [11]. Mass transfer can contribute to the overpotential if the product being produced at the electrode surface has mass transfer rate (movement of ions through the solution) that is slower than the rate of the production of the product at the electrode surface (electrochemical reduction of CO<sub>2</sub>) [6], [10]. The calculation of overpotential is the net difference of potential required to drive the electrochemical reaction forward compared to its reversible potential. This leads into what operating voltage is, where its simply the actual voltage required to drive an electrochemical reaction for an actual electrolyzer experiment [10], [11]. The operating voltage can be calculated through taking the standard reversible potential and adding the overpotentials from kinetics (activation energy), ohmic factors, and mass transfer factors [6], [10]. Considering the principles discussed above overall electrolyzer efficiency can be analyzed. Electrolyzer efficiency or perhaps more commonly called energy efficiency aims to calculate the efficiency of energy used within the electrolyzer device. It is calculated through taking the fraction of electrical current that contributes to the production of a desired product and multiplying it by the theoretical potential at which the product is supposed to be produced and then divided by the potential at which the product is actually produced at. It can be calculated as seen in **Equation 2** [6], [10]. Where FE is faradaic efficiency of a specific product,  $E^{\circ}$  is the reversible potential of a specific product from electrochemical CO<sub>2</sub>R and E<sub>applied</sub> is the operating voltage of a specific product.

$$EE = FE * \left(\frac{E^{\circ}}{E_{applied}}\right)(2)$$

All of these principles, and factors discussed play a big part when making the design of an electrolyzer cell device and analyzing its industrial viability. Now a general surface level approach will be discussed for electrolyzer cell design of CO<sub>2</sub>R. It first starts where there is an industry agreeance that for an electrolyzer system designed for CO<sub>2</sub>R needs to have an operating voltage that is less than 2 V [6], [10]. The 2 V value comes from energy analysis done that looks at taking energy cost target for products produced from CO<sub>2</sub>R such as carbon monoxide or ethylene, and then multiplying an energy efficiency value to the energy target cost of the target product where the resulting value can be used to find the operating cell voltage needed to reach that target [6], [10]. Broadly looking at CO<sub>2</sub>R electrolyzer devices from the calculation done earlier and applying that to all the products produced from CO<sub>2</sub>R its known that most reversible potentials of products lie in the range of  $\sim 1.06$  V – 1.43 V (this is assuming OER is the anodic reaction) [6], [10]. However, the actual operating voltage always ends up being anywhere from 2 to 3 V higher due to overpotential which means the operating voltage is  $\sim$ 3.06 V - 4.43 V, which is well above the 2 V industry recommended maximum [6], [10]. From this a clear design goal for electrolyzer system becomes apparent, the cell voltage needs to be lowered. The best way to decrease cell voltage to reach the 2 V target comes from looking at which components of the electrolyzer device can be modified (cathode, anode and electrolyte) to decrease the overpotential [6], [10]. A lot of the overpotential comes from the cathode for  $CO_2R$ electrolyzer devices. Strategies to lower this overpotential lie in better catalyst design that can reduce the activation energy needed to drive the electrochemical reaction forward, or choosing a different electrolyte can also help reduce activation energy [10], [11]. Another portion of the overpotential also occurs from the anode and appropriate selection of anode material is also important to lower operating cell voltage. For the OER reaction occurring at the anode of these  $CO_2R$  electrolyzer devices depending on what pH the system is operating at plays a big role to determine what anode material is best appropriate [6], [10]. Perhaps the biggest improvement that can be made to reduce cell voltage on the anode side of CO<sub>2</sub>R electrolyzers is replacing OER with organic oxidation reaction such as glycerol oxidation reaction as they occur at much lower reversible potentials than OER, leading to decreased cell voltages [6]. These are the factors on a surface level that need to be considered when looking at CO<sub>2</sub>R electrolyzer design for industrially viability.

Within CO<sub>2</sub>R, there are two primary types of electrolyzer cells. The first electrolyzer cell type is the three-electrode cell setups, including H-cells or twocompartment cells, which have similar functionalities [6], [8]. Three-electrode cells are comprised of a cathode side and an anode side, distinctly separated by a membrane. The cathode side contains the working electrode and reference electrode, whereas the anode side comprises of the counter electrode [6], [8]. The catalyst or cathode material is within the cathode section, where catalysts are typically deposited on substrates such as carbon paper or a glassy carbon electrode. These substrates are used for many reasons, to highlight a few important reasons include their high electrical conductivity, and chemical stability [6], [8]. Various deposition techniques are utilized for the catalyst, including spray coating, drop casting, or electrodeposition [6]. Generally, the anode side features a Pt foil or iridium oxide as they possess high OER activity and stability [6]. The procedure for operating a CO<sub>2</sub>R reaction is fairly simple: once all electrodes are appropriately prepared and positioned within the three-electrode cell setup, the system is filled with an electrolyte, typically 0.1 M potassium bicarbonate or 1M KOH as the electrolyte enables the movement of ions between the cathode and anode completing the electrical circuit in the electrolyzer cell [6], [8]. The next step is where CO<sub>2</sub> gas is bubbled through to dissolve into the electrolyte within the cathode side, which serves as the CO<sub>2</sub> source for conducting the reduction reaction at the cathode electrode. The principal advantage of the three-electrode cell setup is the inclusion of a reference electrode, which enables extensive control of the system, thus proving beneficial for distinct studies of CO<sub>2</sub>R pathways and mechanisms [6], [8]. However, a disadvantage exists as the CO<sub>2</sub> must be bubbled into water, encountering mass limitation challenges due to the low solubility of CO<sub>2</sub> in aqueous electrolytes [6]. This limitation results in very low current densities, rendering them nonviable for industrial applications and restricting the three-electrode cell setups primarily to research applications [6]. The work in this thesis only uses three-electrode cell setups, particularly a twocompartment cell illustrated in **Figure 10**.

The second electrolyzer cell type is the membrane electrode assembly (MEA), which will be discussed briefly, as it is not the primary focus of this thesis but remains important to discuss. The MEA possesses a layered sandwich structure where the ion-exchange membrane is positioned directly between the cathode and anode, with virtually no separation between these three components, as depicted in **Figure 5** [6], [12]. In the MEA configuration, both the cathode and anode are constituted by flow plates. Carbon dioxide gas is introduced directly into the cell via the gas diffusion electrode located on the cathode side, while the anode side serves as the liquid flow channel for the liquid electrolyte [6], [12]. An advantage of the MEA configuration is that the zero-gap design mitigates the CO<sub>2</sub> solubility issue by feeding it directly through the cathode via the gas diffusion electrode [6]. This arrangement facilitates the achievement of elevated current densities at values significant to industrial applications, and the MEA structure accommodates stacking technology, rendering it viable for scaling processes and commercialization [6], [12].



Figure 5. MEA Cell Configuration, Reproduced with permission from John Wiley and Sons, Z. Zhang *et al.*, "Membrane Electrode Assembly for Electrocatalytic CO2 Reduction: Principle and Application," *Angew. Chem. Int. Ed.*, vol. 62, no. 28, p.

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GmbH [12].
#### **1.5 Different Characterization Techniques**

Two distinct categories of characterization techniques are available to quantify the products generated during the electrochemical conversion of  $CO_2R$ . These include offline characterization methods and online characterization methods or also commonly referred to as real-time methods, as illustrated in **Figure 6**.



**Figure 6.** Highlights the most common CO<sub>2</sub>R product quantification techniques for realtime and offline methods.

The offline characterization methods typically used include gas chromatography (GC) and nuclear magnetic resonance spectroscopy (NMR), where high performance

liquid chromatography (HPLC) is also sometimes utilized [8], [13], [14], [15], [16]. GC is used to quantify gaseous products for the CO<sub>2</sub>R reaction, whereas NMR or HPLC is utilized for quantifying liquid products. Since the inception of the field, these methods have been used extensively to quantify CO<sub>2</sub>R products and are well-documented in the literature for providing reliable quantitative and reproducible results [8], [13], [14], [15], [16]. The principal limitations of these offline characterization methods are their high time resolution, which ranges from 5 to 20 minutes for GC [17] and potentially up to days for NMR, resulting in merely a snapshot of the elapsed product detection, hindering real-time monitoring of product formation [8], [13], [14], [15], [16], [17], [18]. These traditional methods can only quantify either liquid or gas products from the CO<sub>2</sub>R reaction, but not both simultaneously [8]. These limitations have driven the field to explore and develop real-time characterization techniques for CO<sub>2</sub>R [17]. The main advantage of real-time techniques is they offer a significantly reduced time resolution, as they can measure products in seconds rather than minutes or days [17], [19], [20], [21]. Various groups in the literature have developed real-time characterization techniques, including proton-transfer time-of-flight mass spectrometry (PTR-TOF-MS), electrochemical mass spectrometry (EC-MS), selected-ion-flow-tube mass spectrometry (SIFT-MS), and differential electrochemical mass spectrometry (DEMS) [17], [19], [20], [21]. Clark et al. successfully employed DEMS as the first quantitative method to monitor the production of hydrogen and various common CO<sub>2</sub>R gas and liquid products such as ethylene and ethanol [21]. However, the range of products that DEMS can quantify is limited due to its nature as a hard ionization mass spectrometry method, which causes significant overlap in

fragmentation patterns, rendering many CO<sub>2</sub>R products, like propionaldehyde and allyl alcohol, unquantifiable [17], [21]. This issue has prompted the use of various soft ionization mass spectrometry techniques, as it results in substantially less fragmentation overlap, enabling the quantification of more products. Lobaccaro et al. created a framework using SIFT-MS to quantify CO<sub>2</sub>R products in real-time [17]. Ren et al. showed the use of PTR-TOF-MS for real-time CO<sub>2</sub>R measurements, while Loffler et al. did the same for EC-MS; where both groups successfully quantified products for CO<sub>2</sub>R, assisting in the study of reaction pathways and mechanisms [19], [20]. The advantage of real-time techniques can be seen in their ability to monitor product formation continuously, which provides valuable insights into reaction pathways and mechanisms, as well as having the capability of measuring both liquid and gas products at the same time [17], [19], [20]. However, the limitations of real-time techniques vary depending on the characterization method employed; common drawbacks include the inability to measure carbon monoxide or hydrogen and incompatibility with common cells used in the CO<sub>2</sub>R field, such as MEA cells [17], [19], [20], [21].

#### **1.6 Selected-Ion-Flow-Tube Mass Spectrometry**

Selected-ion-flow-tube mass spectrometry is a form of soft ionization direct mass spectrometry [17]. The term soft ionization denotes the capability of SIFT-MS to produce simplified mass spectra, resulting in reduced deconvolution challenges among products compared to mass spectrometry techniques utilizing hard ionization methods, such as DEMS [21], [22]. Simplified mass spectra refers to SIFT-MS producing significantly fewer mass fragments measured at the detector compared to hard ionization methods such as electrospray ionization in DEMS that produce significantly more mass fragments. SIFT-MS employs specific chemical ionization reactions to precisely quantify and identify trace quantities of volatile organic compounds within atmospheric samples. It facilitates realtime analytical characterization, achieving detection limits in the realm of the part-pertrillion by volume [22]. This capability is realized through the utilization of positive reagent ions, predominantly  $H_3O^+$ ,  $NO^+$ , and  $O_2^+$ , which react exclusively with trace organic compounds, while remaining inert to the air itself [22]. SIFT-MS also accommodates the deployment of negative reagent ions, including OH<sup>-</sup>, O<sup>-</sup>, O<sub>2</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, and NO<sub>3</sub><sup>-</sup>, for specific applications [22]. Typically, SIFT-MS does not require any sample pretreatment to accomplish product detection. SIFT-MS operates on the foundation of three principal regions, reagent ion selection, ionization and quantitation[20]. The initial region involves reagent ion selection, whereby SIFT-MS creates ions from an ion mixture produced via plasma microwave discharge in moist air [17], [22]. This selection process is conducted through a quadrupole mass filter that discerns the target ion based on its mass-to-charge ratio. Upon completion of the reagent ion selection, only the chosen ion persists to engage with the sample [22]. Progressing to the second region, ion-molecule reactions between the selected reagent ion and sample occur, contingent on the ionization of the reagent ion with a compound within the sample. This procedure transpires within the flow tube, wherein the selected reagent ion is introduced into a stream of carrier gas (e.g., Helium, CO<sub>2</sub>, Nitrogen) within the tube [22]. The reagent ion subsequently encounters the sample gas, introduced at a predetermined rate through a calibrated flow inlet. Consequently, reaction products are formed, leading to the final region. In this third region, the resultant product ions and unreacted reagent ions are subjected to filtration via another quadrupole mass filter and then quantified by a particle multiplier detector, contingent on count rates at selected mass-to-charge ratio metrics [22]. Finally, associated software employs the depicted formula to calculate the real-time concentration of targeted analytes, using established values within the SIFT-MS library [22].

#### **1.7 Research Motivation**

GC and NMR have traditionally been used as the main methods for the quantification of products in CO<sub>2</sub>R. These offline techniques have many disadvantages as discussed in the previous section so various real-time techniques have been introduced and used within research, but have not achieved common use in the field of  $CO_2R$  due to specific limitations unique to each method. To give an example of one PTR-TOF-MS is restricted by its high cost and limited compatibility with common CO<sub>2</sub>R cells [23]. SIFT-MS in comparison is compatible with any common cell within the CO<sub>2</sub>R field, allowing for immediate real-time measurement. This presents a compelling reason to develop a comprehensive scan using the SIFT-MS technique for CO<sub>2</sub>R product detection. Prior research on SIFT-MS has demonstrated its potential in analyzing specific CO<sub>2</sub>R products; however, the studies stop before exploring SIFT-MS applicability across a wider spectrum of products [17]. Thus, this project aims to advance SIFT-MS towards its full capability, enabling the quantification of a wide range of CO<sub>2</sub>R products. The aim of this project is to develop a reliable and reproducible characterization method using SIFT-MS for CO<sub>2</sub>R which will be done through benchmarking and validation against established methods such as GC and NMR, as documented in the literature. This thesis seeks to formulate a detailed SIFT-MS scan as an initial phase that can be extended in future research to leverage realtime analysis and enhance understanding of reaction pathways and mechanisms in CO<sub>2</sub>R, which will lead to faster analysis and optimized catalyst design within the CO<sub>2</sub>R research field.

#### **1.8 Research Objectives**

1) Produce a characterization method using SIFT-MS that quantitatively measures 8+ gas and liquid CO<sub>2</sub>R products at once from either the cathode or anode stream

- The main desire of this project is to create a SIFT-MS selected ion mode scan that accurately quantifies the production of at least 8+ gas and liquid products from electrochemical CO<sub>2</sub>R
- In order to achieve this, it is necessary to ensure all the mass scans, calibration curves, and deconvolution/concentration formulas are properly conducted and applied (As seen in section 3)

2) Validate the accuracy of the SIFT-MS selected ion mode quantitative scan through comparing benchmarking and validation tests to NMR and GC characterization techniques

- In order to be confident, that the selected ion mode scan from SIFT-MS developed gives accurate and expected results, Cu foil benchmarking must be done to see if performance characteristic values such as faradaic efficiency obtained from the SIFT-MS selected ion mode scan match to what is expected for a Cu foil system where measurements were conducted by GC and NMR characterization
- The final step is setting up SIFT-MS, GC and NMR in unison from the same reaction to compare the liquid and gas products for accuracy to ensure the selected ion mode scan gives results that are accurate for an entire full scope product analysis, where GC and NMR measurements will be used to fill in

the gap of products SIFT-MS cannot measure, along with ensuring the products that SIFT-MS selected ion mode scan measured that overlap with the GC and NMR technique are similar in value

## 2. Experimental Methodology 2.1 SIFT-MS: Mass Scan

Mass scans are primarily conducted within SIFT-MS to facilitate the identification of unknown compounds. These scans consecutively apply the three positive SIFT-MS reagent ions within milliseconds. Mass scans investigate a continuous mass range in increments of 1 atomic mass unit and in a range from a lower limit of 15 atomic mass units to an upper limit of 400 atomic mass units [22]. An illustration of a mass scan for allyl alcohol is provided in Figure 7 [24]. The data obtained from mass scans can subsequently be matched against the compound library for compound identification and concentration determination [22]. Mass scans generate a signal intensity in counts per second or counts per hertz versus mass-to-charge ratio, rather than displaying product concentration; as product concentration measurement is used within a selected ion mode (SIM) scan. There are several reasons for using counts per second instead of concentration for mass scans. Primarily, it is inaccurate to apply a singular reaction rate coefficient to an individual mass scan result [22]. Given that the mass scan is a signal response collection of all compounds within the sample, not all compounds react at identical rates with any given reagent ion. This is critically important as the rate coefficient for each compound significantly influences the response count observed in the mass spectrum [22]. For instance, consider two compounds within a sample that are present at the same concentration but possess different rate coefficients. The compound with the higher or faster reaction rate coefficient will elicit a higher counts per second signal from the detector, whereas the compound with the slower reaction rate coefficient will yield a lower counts per second signal [22]. Employing a single rate coefficient to convert raw data to concentration would incorrectly represent one compound at a higher concentration. Another rationale for utilizing counts per second rather than concentration as the measurement in mass scans is that the signal at a single mass-to-charge ratio does not exclusively belong to one compound [22]. Often, the mass-to-charge ratio value signal may be shared by multiple compounds within the sample, necessitating deconvolution to determine the concentration, if applicable. The use of multiple reagent ions in SIFT-MS frequently resolves shared mass-to-charge values between compounds, as a different reagent ion can provide an individual quantitative measurement for overlapping compounds [22].



Figure 7. SIFT-MS full mass scan spectra for allyl alcohol in the range of 15 to 200 mass

to charge ratio for the reagent ions  $H_3O^+$ ,  $NO^+$  and  $O_2^+$ .

#### 2.2 SIFT-MS: SIM Scan

SIM scans have a similar base nature to mass scans, but SIM scans have a calculation step and output the concentration of a product as a function of time versus a counts per second of specific mass-to-charge ratio for a mass scan [22]. To show an example of a SIM scan that would be seen directly from the SIFT-MS software is seen in Figure 8. During a SIM scan, a predetermined mass-to-charge ratio from the SIFT-MS library corresponding to the target compound is selected, and the concentration of the target product is assessed based solely on the specific signals chosen by the user [22]. For instance, if acetaldehyde is the analyte of interest in a given sample, it exhibits the following mass-to-charge (m/z) values with positive reagent ions: for  $H_3O^+$ : 45, 63, 81; for  $NO^+$ : 43, 61; and for  $O_2^+$ : 43, 44 [17], [22]. In the quantification of acetaldehyde using a SIM scan, selecting only the NO<sup>+</sup> signals would enable the calculation of acetaldehyde concentration relying exclusively on the  $NO^+$  signals, excluding the H3O<sup>+</sup> or  $O2^+$  channels. This methodology is particularly advantageous when other products in the sample coincide with acetaldehyde on H3O<sup>+</sup> signals but not on NO<sup>+</sup> signals, thus allowing acetaldehyde to present a distinct quantifiable signal [22].



**Figure 8.** SIFT-MS raw data SIM Scan, showing an example of what a SIM scan directly from the SIFT-MS characterization technique will look like, where concentration reading of products is on the y-axis (each colour is a different product) and time is on the x-axis

The concentration of a SIM scan is calculated by the SIFT-MS software in real-time from three main factors. The first one is the known constant flow rate of the sample gas into the instrument which is controlled from the instruments flow restrictor inlet [22]. Another factor is the ratio of reagent ions and sample product ions counts at the detector. The last major factor is the reaction rate coefficient for the specific target compound with the reagent ion that is being used. Based on these factors the following **Equation 3** is used within a SIM scan to calculate the concentration of the sample analyte [22]. **Equation 3** calculates analyte concentration, where [A] is analyte concentration, [P<sup>+</sup>] product ions as counts per second, [I<sup>+</sup>] unreacted reagent ions as counts per second, k is reaction rate coefficient, D<sub>r</sub> is the diffusion correction, t<sub>r</sub> is the reaction time [22].

$$[A] = \frac{[P^+]}{kD_r t_r [I^+]} (3)$$

#### **2.3 SIFT-MS: Adding New Product to Ion Library**

SIFT-MS boasts a comprehensive library comprised of an extensive array of volatile compounds, which is adept at accurately quantifying target compounds. This library does not cover every chemical species measurable by SIFT-MS, so there exists a procedure for incorporating new products, contingent upon their reactivity with one of the reagent ions. Initially, the procedure necessitates the preparation of a diluted sample of the compound, with concentrations ranging from 10 to 30 ppm (parts per million) by volume [22]. A complete mass scan of this diluted sample is then conducted, employing all three reagent ions, covering a mass range from 15 to 200 atomic mass units, with a resolution of 5 steps per atomic mass unit, at a scanning interval of 100 milliseconds, and two repetitions [22]. In the case of compounds with significant mass, it is imperative that the scan extends at least 40 atomic mass units beyond the compound's neutral mass to ensure proper signal acquisition [22]. The suggested upper limit of 200 atomic mass units is a general guideline. For a product to qualify for inclusion in the product ion library, it should exhibit a response signal ranging from 5,000 to 10,000 counts per second for the product ion. Should the count signal exceed these thresholds, further dilution and subsequent mass scanning are warranted; conversely, if the signal is inadequate, it is crucial to verify the sample's compatibility with SIFT-MS standards [22]. To ascertain the origin of the signal as being from the product, it is advisable to conduct a reference mass scan using only the carrier gas, allowing for comparative analysis. Upon completion of the scan, analysis should focus on identifying the mass-to-charge ratio values corresponding to the product-derived signal [22]. The subsequent step involves the assignment of rate coefficients for each reagent ion. These coefficients can be deduced theoretically or estimated, contingent upon the product being analyzed. In the absence of a calculable or estimable rate coefficient, a baseline rate coefficient of  $3.0*10^{-9}$  cm<sup>3</sup>s<sup>-1</sup> is recommended, given its applicability across a diverse spectrum of compounds [22]. Once rate coefficients are established, branching ratios can be computed for the primary and secondary chemistry of the interactions between the reagent ion and the sample. The final step entails the systematic entry of the new compound and all pertinent data into the system, which includes the compound name, reaction rate coefficients, product ion signals corresponding to each reagent ion, branching ratios, and any observed secondary chemistries [22].

#### 2.4 Chronoamperometry

Chronoamperometry is an analytical technique employed by a potentiostat wherein an electric potential is applied across the working and reference electrodes at a specified value, resulting in a current that is monitored as a function of time [25]. The potential of the working electrode is adjusted from an initial potential to a subsequent potential, and this step difference value between the two potentials is inputted by the user. Based on the materials and potential step involved, this applied potential step will induce a redox reaction [25]. Generally, if the second potential exceeds the first, an oxidation reaction will occur, resulting in the concentration of the reduction nearing zero at the electrode's surface. Conversely, if the second potential is lower than the first, a reduction reaction will ensue, bringing the concentration of the oxidation to near zero [25]. As a result, it is understood that the current generated by the applied potential is governed by diffusion, making it typical for chronoamperometry (CA) curves to diminish over time. These phenomena are depicted in **Figure 9** [25].



Figure 9. a) Applied potential of a CA experiment highlighting the potential step applied b) Results from a) which show a common CA output c) Chronocoulogram highlighting the oxidation of a redox-active sample d) Double-step CA highlighting a negative and positive step application e) Resulting CA from d) highlighting the oxidation and reduction of a sample. Used with permission of Timothy Matthew Gibson, from Chemical Society Reviews, Cyclic voltammetry and chronoamperometry: mechanistic tools for organic electrosynthesis, Rafiee, Mohammad, Abrams, Dylan, Cardinale, Luana, Goss, Zachary, Romero-Arenas, Antonio, Stahl, Shannon, 53, 2024; permission conveyed through Copyright Clearance Center, Inc [25].

## 2.5 Electrochemical Impedance Spectroscopy & iR Compensation

Electrochemical impedance spectroscopy constitutes a minor component in the scope of this thesis, specifically employed to determine resistance and subsequently compute the potential of the three-electrode, two-compartment cell [26], [27]. While representing a minor segment, it is essential to briefly discuss a few aspects of electrochemical impedance spectroscopy (EIS). EIS is a complex electrochemical test applied by a potentiostat that can be used to find valuable kinetic data and mechanistic understanding into electrochemical systems through using alternative current to adjust the electrode potential at different frequencies to measure the response of the setup [27]. EIS can be viewed as a transfer function where it is a technique that will model the output signal to the input signal across a large array of frequencies [27]. EIS can be used to find the resistance of electrochemical cell setups, specifically a 3-electrode configuration.

A common issue that can occur during electrochemical experiments using 3electrode configurations during a CA test is voltage loss [26]. A technique known as iR compensation was developed to correct for this which employs the use of EIS. The voltage loss happens from the electrolyte solution between the working electrode and the reference electrode [26]. Between the working electrode and reference electrode there is an electrical double-layer capacitance on the surface of the working electrode that will have a potential drop. There is also the bulk electrolyte that lies between the electrical double-layer capacitance and reference electrode where another potential drop will occur [26]. Operationally the potential applied to the working electrode is controlled by changing the charge on the electrical double-layer [26]. As in accordance with Ohm's law, there is also current flowing through the bulk electrolyte causing a resistance within the solution. In order to find the actual potential being applied within a system, it can be done through taking the potential inputted into the CA and subtracting the iR compensation occurring within the electrolyte, where that resistance can be found through EIS measurements. In order to evaluate this three-electrode system properly and know what potential is being applied, iR compensation can be done through an on-the-fly correction to account for this voltage loss [26]. Where 85% of the iR compensation is automatically corrected by the potentiostat instrument and the CA scan is briefly interrupted during the experiment to take an EIS measurement which will be used to account for the other 15% of the iR compensation and to avoid potentiostat oscillations and overcorrected results [26].

#### **3. Project Investigation**

The following is a copy of a manuscript in preparation that examines the research project within this thesis. The supporting information of this manuscript has been incorporated into the main body of this thesis. The same title within the manuscript has been used for this thesis and is currently still under revision and considered a private document. Once a modified version has been submitted to a journal for publication in the future it will no longer be a private document. This manuscript is referenced as *Private Communication from Timothy Matthew Gibson: Dept of Chemical Engineering, McMaster University 2024*.

Application of Selected-Ion Flow-Tube Mass Spectrometry for real-time operando quantitative measurement of product formation for electrochemical reduction of carbon dioxide

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#### **3.1 Abstract**

Electrochemical CO<sub>2</sub> reduction reaction is a promising route to help reduce greenhouse gas emissions and reach carbon dioxide net zero emissions to combat global warming. Currently, the means of analyzing catalytically produced products from CO<sub>2</sub>R relies on older methods such as gas chromatography and nuclear magnetic resonance. The ability to have real-time analysis of the products generated from CO<sub>2</sub>R is desirable. Yet few analytical techniques have been developed in detail so far to achieve real-time analysis. Herein, we show the use of selected-ion flow-tube mass spectrometry that quantitatively measures in real-time an array of 10 C<sub>1</sub>, C<sub>2</sub>, and C<sub>3</sub> products from CO<sub>2</sub>R such as ethanol, ethylene or methane. The custom-developed SIFT-MS scan measures the concentration of gas and liquid-phase products of  $CO_2R$  at the same time and is compatible with any electrolyzer cell. We demonstrate that the SIFT-MS technique can reliably and accurately determine product concentration in real-time through the evaluation of Cu foil and its comparison to traditional techniques. Considering the narrow range of developed and deployed techniques for real-time quantitative product analysis for CO<sub>2</sub>R, this study on SIFT-MS is a critical tool for future research in accelerating and optimizing catalyst design for electrochemical CO<sub>2</sub>R applications.

#### **3.2 Introduction**

The development of an electrochemical CO<sub>2</sub> reduction reaction for a cost-effective electrolyzer process to convert CO<sub>2</sub> into fuels and chemicals would help the world shift towards a sustainable energy future [1], [7], [8]. Currently, there is still a rising global temperature of the earth which has led to severe heat waves that have created record-high temperatures [1]. A way to help combat the  $CO_2$  and global warming issues is through continuing to develop and commercialize the technology of electrochemical CO<sub>2</sub> reduction, as this can lead to a sustainable renewable industry [7], [28], [29], [30]. When CO<sub>2</sub> electrolysis is coupled with a renewable energy source such as solar or wind, this can create carbon-neutral fuels or chemicals that are useful for the economy through a sustainable avenue [7], [28], [30]. Currently, copper is required for the economic conversion of  $CO_2$ to  $C_2^+$  products, as it is the only electrocatalyst that can reduce  $CO_2$  to as many as 18+ products of C<sub>1</sub>, C<sub>2</sub> and many higher-order hydrocarbons, aldehydes, and alcohols [8]. It does so, however, with minimal selectivity unless specific measures are taken to modify and adjust the catalyst to favor the production of highly valuable chemicals [7], [31]. Economic analysis on high-value chemicals has been done which showed that 1-propanol, ethanol, and ethylene show the greatest promise for profitability for high-value chemicals in the near future [31]. Given the sensitivity of the reaction to various operating conditions, it is critical to be able to not only accurately quantify the gaseous and liquid products being formed, but also have a high degree of time-dependence to properly capture propertyperformance relationships. Thus, making it is vital to find viable characterization techniques that can quantify the products produced from CO<sub>2</sub>R and gain valuable insight into the reaction mechanisms.

Currently, methods for the quantification of electrochemical CO<sub>2</sub>R reaction products are gas chromatography for gaseous products, and nuclear magnetic resonance spectroscopy or high-performance liquid chromatography for liquid products [8], [13], [14], [15], [16], [18]. These methods have been proven to provide reliable quantitative and reproducible results, and have been used reliably by the community over the last decade [17]. One limitation of these methods is their poor time-sensitive resolution, and ability to capture product quantification in real-time. While GC has a time resolution which is in the minutes range [17], the typical GC scan will obtain a singular data point per product once every 10-20 minutes. Liquid products, in particular those of low vapor pressure, are typically measured only once per run [8], [13], [14], [15], [16], [17], [18]. In theory, it is possible to aliquot a portion of the electrolyte out and have a liquid product detection data point every 5-20 minutes, but this is rarely done as NMR is an offline technique. Not only does this remove real-time quantification, but products such as acetaldehyde will undergo Cannizzaro reactions within the vials before the measurement and convert to ethanol and acetate [32], [33]. This may lead to erroneous quantification of the actual products produced during the electrochemical reaction, and in particular, limiting the quantification of important reaction intermediates. Real-time analysis is advantageous for unravelling important information pertaining to the reaction mechanisms during the electrochemical reduction of CO<sub>2</sub>.

Real-time characterization for CO<sub>2</sub>R although underutilized within this field still has been studied, one of the first in-depth reports was done by Hori et al. in the context of catalyst deactivation [34]. This led to future studies starting to build off this and gaseous real-time product detection studies were then done by Koper et al. and Clark et al. providing insight into the CO<sub>2</sub>R mechanism, mainly looking at voltage-dependent pathways for the production of ethylene [16], [21], [35], [36], [37]. They used a custom differential electrochemical mass spectrometry cell that works in a highly specific window of parameters. Specialty hardware is also required, requiring the use of pervaporation membranes, limitations to specific flow rates, and transfer capillaries to connect electrodes and electrolyte holding chambers [21]. Recently there have been real-time product detection studies done by Qiao et al. that have provided intriguing new insight into the liquid product CO<sub>2</sub>R mechanism, looking at the acetaldehyde to ethanol ratio and pathways for ethanol formation [38]. Loffler et al. also showed pathways for ethanol formation from real-time characterization techniques [19]. Ren et al. used real-time product detection to show how formaldehyde which was recently thought to be an intermediate to methanol formation, is likely not [20]. From these findings, it can be seen that real-time characterization techniques are discovering valuable information for the complex reaction mechanism of CO<sub>2</sub>R that traditional characterization techniques cannot. Along with reaction mechanisms, real-time techniques will also accelerate the ability to analyze a catalyst for CO<sub>2</sub>R by reducing the time needed to fully evaluate catalyst performanceproduct relationships from days to as low as a few hours. This is highly beneficial for highthroughput testing and material library approaches to find optimized catalysts in a

significantly faster period than what is currently possible – a rapidly advancing field [39]. While this high-throughput testing has been done in fields similar to CO<sub>2</sub>R such as water electrolysis with the hydrogen evolution reaction [40], [41], [42], electrochemical CO<sub>2</sub>R has yet to meet the same throughput due to the nature of the current characterization methods. Being able to apply this for CO<sub>2</sub>R catalysts could be an extreme advantage in speeding up catalyst design and optimization, and real-time product detection could allow for high-throughput testing to become a reality for CO<sub>2</sub>R in the near future.

In terms of real-time characterization methods used for  $CO_2R$ , the first tests included electron ionization mass spectrometry and differential electrochemical mass spectrometry systems coupled with a custom electrochemical cell or a sample collection tip [21], [43]. Koper et al developed an online electrochemical mass spectrometry system using a porous tip close to the surface of the reaction to collect both gaseous and liquid products to qualitatively measure the products formed [44]. These systems use hard ionization mass spectrometry which results in large overlapping fragmentation patterns that make it difficult to accurately quantify the array of products produced during CO<sub>2</sub>R as there is intense overlap of the products that are not possible to deconvolute. This led the way to the use of soft ionization mass spectrometry techniques that utilize soft ionization methods that produce less intense mass fragmentation patterns making it possible to deconvolute all the products of CO<sub>2</sub>R easier and quantify more products. Ren et al. have used proton-transferreaction time-of-flight mass spectrometry to quantitatively find the onset potentials of reaction mechanisms [20]. Loffler et al used electrochemical real-time mass spectrometry (EC-RTMS) to find the faradaic efficiency through cyclic voltammetry (CV) curves for CO<sub>2</sub>R [19]. Lobaccaro et al used SIFT-MS to quantify a few gas and liquid products for CO<sub>2</sub>R [17]. Two of the more promising real-time detection techniques are PTR-TOF-MS and SIFT-MS. PTR-TOF-MS has a better limit of detection compared to SIFT-MS but is a more expensive technique and only has one reagent ion for analysis of products. Whereas SIFT-MS is a cheaper more accessible technique that has multiple reagent ions allowing for a more robust analysis of solution mixtures which is useful for CO<sub>2</sub>R as it produces an array of products [45].

This paper will focus on the SIFT-MS characterization technique. SIFT-MS offers the ability to quantitatively measure the product detection for the electrochemical reduction of CO<sub>2</sub>R for any experimental setup whether it is a two-compartment cell, H-cell or MEA. Lobaccaro et al. laid the framework for SIFT-MS and showed its promise in how SIFT-MS is a powerful technique to use for CO<sub>2</sub>R to monitor gaseous and liquid products in realtime [17]. The next step is to utilize SIFT-MS to create a method that can quantitatively measure both gaseous and liquid products all at once. This paper looks at the creation of a SIFT-MS library scan that quantifies 10 liquid and gaseous products of CO<sub>2</sub>R reaction at once for operando real-time measurements and experimentally validates the scan framework through a Cu Foil electrochemical CO<sub>2</sub>R case study, and direct comparison to common techniques.

#### **3.3 Materials and Methods**

#### **3.3.1 Electrode Preparation**

Copper Foil (thickness 0.1 mm, Sigma-Aldrich, 99.99%) was used as the material for the working electrode. For copper foil the surface before each experiment was mechanically polished (sandpaper, 3M) and rinsed with Millipore water to remove as much discoloration as possible. The copper foil then underwent electropolishing in phosphoric acid (85% in H<sub>2</sub>O, Sigma-Aldrich) at 2.1 V vs graphite rod acting as the counter electrode that was 1.5 cm away from the copper foil for a time of 5 minutes [8]. This was to strip away and remove any contaminants on the surface of the copper foil.

#### **3.3.2 Electrochemical Cell and Setup**

A custom two-compartment cell was used for all experiments which was made by a 3d printer with a material of polypropylene and then fitted with silicon O-rings (McMaster Carr), see **Figure 10** for a representation of the cell. A membrane is placed between the working and counter electrode compartments to separate and prevent the oxidation of the reduced CO<sub>2</sub> products. For these specific experiments, an anion exchange membrane (Selemion) was used. The cell has an electrode area of 5.94 cm<sup>2</sup> (1.8 cm x 3.3 cm) and an electrolyte volume of 50 mL in both the working and counter electrode compartments. During the electrolysis experiments, CO<sub>2</sub> (Linde, 99.99%) regulated by a mass flow controller (Sierra, Smart trak 100) at 40 sccm flowed through the cell. 40 sccm was chosen as it minimized the formation of gas bubbles while also being an optimal flow for SIFT- MS detection. Each experiment had copper foil as the working electrode and iridium oxide (Dioxide Materials) as the counter electrode. For the reference electrode an Ag/AgCl (Pine Research) was used. A 0.1 M solution of KHCO<sub>3</sub> (Sigma-Aldrich, 99.99%) was used as the electrolyte for all experiments and was prepared with Millipore water. The pH of the electrolyte purged with CO<sub>2</sub> was 6.8.



Figure 10. Schematic of the two-compartment electrochemical cell used for all the CO<sub>2</sub>R electrochemical reduction measurements

For the overall setup, the two-compartment cell is separated into two flow streams classified as the catholyte and anolyte streams. Both streams went into separate electrolyte holders that were set to a separate peristaltic pump (NE-9000G, Pump Systems Inc.) flowing at 40 ml/min. This created a closed flow cell system where from each electrolyte holder there is an outlet stream that can be connected to the SIFT-MS or any characterization technique for product detection, where the full experimental setup can be seen in **Figure 11**.



Figure 11. Full schematic setup of the flow cell for performing electrochemical measurements.

#### **3.3.3 Electrolysis**

Electrochemistry measurements were done with a Biologic VSP150 potentiostat. All of the electrochemical data was generated with the use of an Ag/AgCl reference electrode and then converted to a reversible hydrogen electrode (RHE) scale through the following formula  $V_{vs RHE} = V_{measured vs Ag/AgCl} + 0.197 + 0.059*6.8_{(pH)} + 0.15*R_{avg}$  [8]. The potentiostat compensated for 85% of  $R_{avg}$  and the last 15% was corrected in post calculations as seen in the above formula  $0.15*R_{avg}$  to find accurate potentials. EC-Lab software was employed for the electrochemical experiments. The next step was applying chronoamperometry of the desired potential interrupting the CA briefly to measure the  $R_u$ value that will be used for the 15% correction in post calculations.

#### 3.3.4 Measurement Stability Current vs. Potential

Figure 12 shows the electrolysis experiments current versus the time profile at each voltage. The current remained relatively stable over the time it was applied to the twocompartment cell at lower potentials for the Cu foil. At the more negative potentials, there is a decline in the value of the current as time progresses. There are a few reasons why stability is lost at higher potentials. At higher current densities, the current data starts to have increased instability and fluctuations, and this is likely from the increased bubbles that are forming on the electrode surface. These bubbles will cover the areas of the electrode until they grow large enough and then eventually get released, and this leads to the instability and variance seen in the current at lower potentials and becomes more noticeable at higher potentials. The iR compensation could also contribute to the changes in current as the bubbles make it challenging for the potentiostat to maintain a constant voltage. Efforts were made to minimize the bubble formation as much as possible by tilting the cell at a 45-degree angle to minimize the surface area to which the bubble formed on the surface of the electrode. The angle also allowed the bubbles to break off and release at a smaller size. The anode material was switched from platinum foil to iridium oxide to have greater stability at higher potentials. Greater stability was observed with the iridium oxide anode due to iridium having improved desired properties for the counter electrode material such as higher corrosion resistance [46], [47].



**Figure 12.** Current density of the Cu Foil CO<sub>2</sub>R experiment as a function of time at 5 varying voltages ranging from -0.77 V vs RHE to -1.08 V vs RHE.

#### **3.3.5 Characterization Techniques**

SIFT-MS is a real-time technique, that has the capability to record a singular data point in periods of 50ms or less when a fast response is required, which is generally used for instances such as analysis of breath samples [22]. For situations such as CO<sub>2</sub>R electrolysis where accuracy and improved data quality are of importance product sampling periods are 100 ms or more, depending on the total number of target products for the scan [22]. The more products there are within the scan, the longer the sampling period will be, for this specific application the scan had a total of 10 products to measure and a sampling period of ~2 seconds. The SIFT-MS was used to determine the concentration of the following gaseous and liquid products: allyl alcohol, acetaldehyde, acetone, ethane, ethanol, ethene, methanol, methane, propionaldehyde, and n-propanol. The following products were selected as they are the most common CO<sub>2</sub>R products seen within the literature that SIFT-MS can quantify [8], [16], [19], [32], [45], [48]. The faradaic efficiency was determined by calculating the number of coulombs needed to produce the measured amount of each product and then dividing by the total charge, for detailed information see Section 3.3.6. To determine whether SIFT-MS can be used in isolation from other techniques, the quantification results when possible were directly compared to common CO<sub>2</sub> characterization techniques. For nuclear magnetic resonance spectroscopy, all of the 7 liquid products measured from SIFT-MS (allyl alcohol, acetaldehyde, acetone, ethanol, methanol, propionaldehyde, n-propanol) were compared directly to NMR results. Gas chromatography (GC, SRI)) was also used to quantify the faradaic efficiency of gaseous products. The GC collected samples from the cathode liquid electrolyte holder once every 18 minutes a total of 4 times to determine the concentration of hydrogen, and CO. The final calculated faradaic efficiency value was the average of the 4 measurements collected at the specific potential. Lastly, liquid-phase products were also measured using NMR. An internal standard of dimethyl sulfoxide and phenol was used in 0.1 M KHCO<sub>3</sub>. Once the electrochemical experiment was completed the catholyte electrolyte would be deposited into an airtight 20 mL vial. 700  $\mu$ L of the catholyte electrolyte will be mixed into a solution containing the internal standard with 35 µL of 10 mM dimethyl sulfoxide and 50 mM of phenol for NMR analysis. The ratio of the area of product peak areas to the internal

standards was recorded and used to quantify the concentrations of the products and then determine the faradaic efficiency.

# 3.3.6 Faradaic Efficiency Calculation for CO<sub>2</sub>R on SIFT-MS

There are separate faradaic efficiency calculations for gas versus liquid products [49]. This stems from that liquid and gas products are produced through different manners within the system. Gas products are constantly being produced and also exiting through the exit tubing connected to the SIFT-MS from the flow cell setup. For gases, there is essentially a 100% collection efficiency as soon as the gas was produced from the CO<sub>2</sub>R electrochemical reaction. Eventually, the gas being produced will equal the amount of gas exiting and reach a relative steady state of production within the system. Specifically, for this SIFT-MS setup, it was found it takes around 12 minutes to reach this steady state. As the potential increases to higher negative values the time to reach a steady state also slightly increases, which is likely due to at more negative potentials there is a greater buildup of gas leading to mass transfer limitations that cause the system to take longer to reach steady state. For SIFT-MS gas faradaic efficiency calculations the formulas derived from the literature can be applied and used with no modification needed [49]. Equation 4 was used to find faradaic efficiency for gas products [49]. Calculation of faradaic efficiency for gas products produced by SIFT-MS, where ne is the number of moles of electrons needed to produce 1 molecule of product, x is ppm of gaseous product produced measured by SIFT-MS, P is ambient pressure from the setup, T is ambient temperature from the setup, F is faradays constant, R is gas constant, I is average current during the sampling time and flowrate is the measured value of gas flow going into the SIFT-MS by the flow meter [47].

$$FE_{g} = \frac{n_{e} * x * F * flowrate * P}{R * T * I} * 100\% (4)$$

Calculations for liquid products faradaic efficiencies have to use different formulas as they accumulate in a different manner within the system than gas products. Liquid products dissolve within the electrolyte and accumulate over time during the reaction. The product produced during the CO<sub>2</sub>R reaction never exits the system whereas gas products do. As SIFT-MS is a real-time technique the pre-existing liquid faradaic efficiency calculations used for NMR and HPLC offer a good starting point but need to be altered to be used for the SIFT-MS technique [49]. Faradaic efficiency is the measurement of the selectivity of a product produced during CO<sub>2</sub>R and is calculated as the production of charge consumed for the generation of a specific product divided by the total charge passed during a specific timeframe [49]. To calculate faradaic efficiency for SIFT-MS the selectivity of the product produced is found through measuring the rate of production of a specific product and multiplying by the volume of electrolyte within the solution to get the mol/min of that product being produced. To find the total charge produced during that timeframe it can be done through taking the current passed and dividing it by the ne and faradays constant to get the total theoretical mol/min overall. This can be seen in Equation 5 and this was how faradaic efficiency can be found for liquid products being measured by SIFT-MS. Calculation of faradaic efficiency for liquid products produced by SIFT-MS, where x is the rate of production of a specific liquid product, volume is the total volume of electrolyte,  $I_{avg}$  is the average current applied over a single SIFT-MS data point (~2 seconds), n<sub>e</sub> is the number of moles of electrons needed to produce 1 molecule of product, and F is faradays constant.

$$FE_{l} = \frac{x_{rate} * volume}{I_{avg} * \frac{1}{n_{e}} * \frac{1}{F}} * 100\% (5)$$

#### 3.4 Results & Discussion

### **3.4.1 Methodology Development - Creating the Product** Library

Prior to analysis, a product library of the desired electrochemical CO<sub>2</sub>R products had to be created. We chose to focus on ten products of interest: 1-propanol, acetaldehyde, acetone, allyl alcohol, ethanol, ethane, ethylene, methanol, methane, and propionaldehyde. These were selected based on desired quantification as an important CO<sub>2</sub>R product and/or intermediate. A majority of these compounds have known ionization products, but for some, we had to generate our own product library. This was done for allyl alcohol see **Section 3.4.2**, for full details on how allyl alcohol was added to the library. A full mass scan was made to quantify and monitor all the target products above, confirming their ionization patterns. Other common CO<sub>2</sub>R products that are absent from the above library include formate and glycolaldehyde – such products will require additional conditions and processing to be detected by the SIFT-MS see **Section 3.4.3**, for extended details on additional products.

With a focus on the above ten products, we needed to ensure that each product could be isolated and measured with enough sensitivity in the presence of all other products. Peak and product deconvolution is necessary. This practice is quite common when using mass spectrometry, and was required with previous CO<sub>2</sub>R studies that utilized any form of mass spectrometry [17], [21]. One benefit of the SIFT-MS, compared to other techniques such as EI-MS and PTR-MS is the three available regent ions –  $H_3O^+$ , NO, and  $O_2^+$  - which can be used either independently or together to quantify and deconvolute typical overlapping products. From this exercise, we were able to identify 6 of the 10 target products have unique m/z response factors that require zero deconvolution when calculating the concentration. The following 4 products require deconvolution ethanol, methane, 1propanol and allyl alcohol as they have overlapping m/z values with other products and see **Section 3.4.4**, for detailed information on deconvolution and concentration formulas.
Product	<i>H</i> <sub>3</sub> <i>O</i> <sup>+</sup>	<b>NO</b> <sup>+</sup>	<b>O</b> 2 <sup>+</sup>	Detection Limit (ppm)
1-Propanol		59		0.02
Acetaldehyde	45			0.30
Acetone		88		0.01
Allyl Alcohol		57		0.05
Ethane			29	
Ethanol			45	0.05
Ethylene			28	0.20
Methane			47	10
Methanol	33			0.05
Propionaldehyde	60			0.05

**Table 2.** SIM scan highlighting each product ion mass number for each compound to be detectedusing SIFT-MS with  $H_3O^+$ ,  $NO^+$ , and  $O_2^+$  as reagent ions.

#### **3.4.2 Addition of Allyl Alcohol into SIFT-MS Library**

Allyl alcohol was not in the SIFT-MS natural library so it had to be manually added. The protocols outlined by SYFT to add new products to the library were followed [22]. A dilute sample of allyl alcohol between 10-30 ppm was made and run under the experimental CO<sub>2</sub>R conditions and the recommended default rate coefficient of  $3.0*10^{-9}$  cm<sup>3</sup>s<sup>-1</sup> was used. A mass scan of the product is conducted with 2 repetitions and then from there, the top response count m/z fragmentation patterns from each reagent ion can be found. The needed branching ratios were calculated and added into the library with any secondary chemistry observed. The mass scan used can be seen in **Figure 13** and from this process, it was found that Allyl Alcohol has a noticeable response count to the following m/z values from each reagent ion H<sub>3</sub>O<sup>+</sup>: 41, 59, 77, O<sub>2</sub><sup>+</sup>: 57, 58, 59 and NO<sup>+</sup>: 57, 75.



Figure 13. Mass Scan of Allyl Alcohol for SIFT-MS under humid conditions

# **3.4.3 Additional Products of CO<sub>2</sub>R that could be added** to SIFT-MS

A few other liquid products were looked at to be included within the scan that is commonly measured for CO<sub>2</sub>R with the NMR technique. Glycolaldehyde was looked at, however, the vapor pressure of this product at room temperature is too low for SIFT-MS to detect, despite the chemical being within the library of SIFT-MS. In order to measure glycolaldehyde the solution would have to be heated to increase the vapor pressure of the glycolaldehyde making it detectable for the SIFT-MS. Formate and acetate were looked at as well. Formic acid and acetic acid do have a high enough vapor pressure that could be measured and quantified by SIFT-MS. The pH of the electrolyte system with potassium bicarbonate is 6.8 which results in formic acid and acetic acid being in its deprotonated base form of formate and acetate. The deprotonated base form does not have vapor pressure high enough for SIFT-MS to quantify these products. In order to measure these products in real-time for CO<sub>2</sub>R and SIFT-MS a more acidic electrolyte would have to be used which is uncommon for CO<sub>2</sub>R as it generally leads to worse performance. The other option is to take the solution once the reaction is complete and change the pH to a lower level converting the formate and acetate to formic acid and acetic acid and then using SIFT-MS to quantify the product. Although this loses the real-time aspect, it still eliminates the need to run further NMR tests, cutting down analysis time and could be worth looking at the validity of this approach in the future.

#### **3.4.4 Deconvolution and Concentration Formula**

For four products within the SIM scan: ethanol, methane, allyl alcohol and 1propanol they did not have an ideal unique m/z value that could be used to quantify the product. To accurately determine the concentration of these products deconvolution formulas were used. These equations are seen in Equation 6-9. which show the deconvolution formula for liquid products where Product<sub>calibration</sub> is the slope calibration value from Figure 14 that converts ppm SIM scan reading into mM concentration, [Product]<sub>exp</sub> is the ppm concentration reading recorded by SIFT-MS, [Product]<sub>real</sub> is the concentration of product in mM after Equation 10 has been applied for unique signals, Product<sub>calibration</sub> is the calibration value to which that product contributes to that signal, and Methane<sub>ppm</sub> is the ppm reading of methane from SIFT-MS. The m/z value at which one of these products is being quantified also has other products contributing to that signal of known amounts. In order to find the true signal of the target product the amount that the other products are contributing to the m/z value must be subtracted. The deconvolution formulas for the 4 products that require them are seen below. One non-deconvolution formula is shown in **Equation 10** which is used for any product that has a unique signal to determine concentration.

To give an example case to explain how deconvolution works ethanol was quantified by the m/z value of NO+ (45). Acetaldehyde also has a high response factor at the same m/z value that contributes to the signal. In order to accurately determine the concentration of ethanol it requires a subtraction of the amount of acetaldehyde signal that

contributes to the ethanol signal leaving only the response count from the ethanol. Once the acetaldehyde signal from the NO+ (45) is removed the response count left is only ethanol and not a combination of acetaldehyde and ethanol. This deconvoluted product response count value can now be used to find an accurate value of ethanol concertation.

$$[Ethanol] = Ethanol_{calibration} * \left( [Ethanol]_{exp} - \left( \frac{[Acetaldehyde]_{real}}{Acetaldehyde_{calibration}} \right) \right) (6)$$

[1 - Propanol]

 $= 1 - Propanol_{calibration}$   $* \left( [1 - Propanol]_{ern} - \left( \frac{[Acetone]_{real}}{1 - Propanol} \right) \right)$ 

$$-\left(\frac{[Allyl Alcohol]_{real}}{Allyl Alcohol_{calibration}}\right) - \left(\frac{[Propionaldehyde]_{real}}{Propionaldehdye_{calibration}}\right)\right) (7)$$

[Allyl Alcohol]

$$= Allyl Alcohol_{calibration}$$

$$* \left( [Allyl Alcohol]_{exp} - \left( \frac{[Propionaldehyde]_{real}}{Propionaldehyde_{calibration}} \right) \right) (8)$$

$$[Methane] = Methane_{ppm} - \left( \frac{[Ethanol]_{real}}{Ethanol_{calibration}} \right) - \left( \frac{[Ethylene]_{real}}{Ethylene_{calibration}} \right) (9)$$

$$[Product_x] = Product_{calibration} * [Product]_{exp} (10)$$

# **3.4.5 Methodology Development – Considerations for Calibration**

To properly quantify the products for CO2R using SIFT-MS the environment must be taken into account due to the presence of humidity, which was originally identified by Lobaccaro et al. [17]. In particular, the presence of high moisture would cause the generation of  $H_3O^+$  reagent ions within the analyte, and thus one can expect  $H_3O^+$  reagent products also in the product spectra of those produced from NO<sup>+</sup> and O<sub>2</sub><sup>+</sup> reagent ions. This is observed within our measurements due to the direct collection of product signals from the anolyte and catholyte chambers. An example is propionaldehyde is expected to have m/z product values on the H<sub>3</sub>O<sup>+</sup> reagent ion of 59,77,95 and in the NO<sup>+</sup> channel of 57 and the  $O_2^+$  channel of 57,58 [17]. Within our system, other peaks are present – for example, significant peaks at m/z = 59,76 and 77 are also present in the  $O_2^+$  channel, caused by the presence of high H<sub>3</sub>O<sup>+</sup> ions in the channel as well, this is illustrated and further explained in Section 3.4.6. This phenomenon occurs with not just propional dehyde but every product being quantified, as many of the CO<sub>2</sub>R products are highly active towards the H<sub>3</sub>O<sup>+</sup> reagent ions. Although there are methods to dry the gas and remove the water vapor such as chemical drying agents, dehumidifiers, and low-temperature moist traps, none of these were found to be capable of removing the water vapor from the system when the CO<sub>2</sub> gas is bubbled into the electrolyte solution [17]. Given the nature of electrochemical CO<sub>2</sub>R experiments water vapor is always present and must be accounted for with careful external calibration. In fact, we consider this a benefit versus other quantitative techniques as no

preconditioning or treatment of the input line is needed, further exemplifying the real-time capabilities of SIFT-MS.

With this in mind, to properly quantify the liquid products formed during electrochemical CO<sub>2</sub>R, measured via the setup shown in **Figure 14**, external calibration methods are necessary to properly convert SIFT-MS product (m/z) ion counts to a true concentration (ppm). This was performed using both single products in isolation, and mixture product calibration curves of our products of interest, performed under the same experimental conditions as the electrochemical CO<sub>2</sub>R experiments. A 3-point calibration curve for each product or mixture was made of 0.1 mM, 0.3 mM, and 0.6 mM. As expected, each product calibration can be fit to a linear fit, with the slope used to convert the signal count recorded from CO<sub>2</sub>R experiments and find the true concentration of the product produced and accumulating in the analyte chamber.

A mixture calibration curve was used to obtain all slope values needed to convert the product signal into concentration. This was done as during CO<sub>2</sub>R the products formed within the electrolyte were an array of different products so mixture calibration curves best model true experimental conditions. According to Raoult's law, the vapor pressure of a solvent within a solution will be equal to the vapor pressure of that solvent scaled by the mole fraction of the solvent present [50]. The vapor pressure of each product within the solution is a mole-weighted mean of the individual vapor pressures. Ethanol has a vapor pressure of 54.68 mmHg at 25 °C, and according to Raoult's law the vapor pressure of Ethanol will be lower within a mixture solution, hence this decrease in vapor pressure is assuming ideal behaviour, which may not be the case during the electrochemical reduction of CO<sub>2</sub>R experiments – another reason that external calibration is required. As there are many products being formed during CO<sub>2</sub>R if the calibration values are also taken from a mixture, it will provide a more accurate value that best represents the experimental conditions. Overall, the trend observed in the single and mixture calibration curves trended as expected with Raoult's law.



Figure 14. SIFT-MS external 3-point liquid calibration curve where 0.1 mM, 0.3 mM, and 0.6 mM of the product were used for true solution concentration and the corresponding SIFT-MS product response count is measured.

#### **3.4.6 Water Vapor Contamination Phenomenon**

The CO<sub>2</sub>R reaction environment is an extremely humid environment from the presence of water vapor from the electrolyte solution. This humid environment causes H<sub>3</sub>O<sup>+</sup> reagent ions to leak into the O<sub>2</sub><sup>+</sup> and NO<sup>+</sup> channels for SIFT-MS when measurements are occurring. The contamination and humid environment results in an array of m/z values that are not expected for all 3 reagent ion channels within SIFT-MS. Looking at propionaldehyde as an example, the  $O_2^+$  reagent ion to m/z values of 57 and 58. A blank electrolyte solution with no propionaldehyde was run as a baseline and compared to an electrolyte solution containing propionaldehyde to measure all the m/z fragmentation values seen in the humid CO<sub>2</sub>R environment. The values found are seen in Figure 15 and show that for the  $O_2^+$  reagent ion, the following m/z values have a noticeable response count that was due to the humid environment that were not expected: 76, 77. As previously stated these unexpected values arise from the presence of  $H_3O^+$  in the other reagent ion chambers and this is seen in the mass scan as well from elevated m/z values of 19 which is due to the presence of  $H_3O^+$  ions leaking into these streams. This environment can lead to an array of reactions that are not expected resulting in the new fragmentation patterns observed.



Figure 15. Mass scan of Propionaldehyde for SIFT-MS under humid conditions

#### 3.4.7 Case Study on Cu Foil

Cu foil was used as the case study as it has been extensively studied for  $CO_2R$  [8] and was the best candidate to evaluate the accuracy and repeatability of SIFT-MS for CO<sub>2</sub>R. For CO<sub>2</sub>R in previous Cu foil studies done by Kuhl et al. it shows that at negative potentials from 0 V vs RHE to around -0.75 V vs RHE, only major products are seen such as hydrogen, carbon monoxide and formate which SIFT-MS cannot detect [8]. Over time as the potential grows increasingly negative other major products start to be seen such as ethylene and methane which are the first products SIFT-MS can detect and then an array of liquid products at even more negative potentials [8]. Figure 16 plots the faradaic efficiency of each product and its evolution over time and at each of the five potentials during electrolysis. The Cu Foil results closely match the expected profile, based on reported literature data [8]. At the lowest applied potential of -0.77 V vs RHE, only ethylene is quantifiable in small amounts as expected. No methane is observed, despite literature supporting that it could be produced at these potentials low potentials [8]. This comes down to an issue of the reaction coefficient of the target product with the reagent ions. Ethylene is nearly one thousand times more reactive with reagent ions and hence has magnitudes greater sensitivity than methane. As such, trace amounts of ethylene are quantifiable (subppm level), whereas methane is required in greater abundance (~10 ppm) before proper quantification can be made with respect to the baseline. Table 2 has detection limits for all compounds we plan to measure. Detailed information for detection limits and SIFT-MS can be found in Section 3.4.8. For methane, this does not occur until -0.95 V vs RHE. As the potential was raised the amount of ethylene and methane being produced steadily rose to

comparable faradaic efficiency values for each potential as reported within the literature [8], showing SIFT-MS can accurately quantify gases for CO<sub>2</sub>R.

For liquid product production from Cu foil, we are able to detect and quantify 1propanol, acetaldehyde, acetone, allyl alcohol, ethanol, and propionaldehyde at -0.95 V vs RHE. This is due to the production of these liquids passing the limit of detection for SIFT-MS at this potential, and it also closely aligns with the limit of detection of the NMR technique for these products within the literature [8]. -1.04 V vs RHE is where methanol quantification is detected. Relative to the NMR limit of detection for methanol, SIFT-MS is slightly worse as NMR can pick up methanol at around -0.95 V vs RHE [8]. For liquid products and reaching the limit of detection for SIFT-MS it will vary from product to product with the two biggest factors being the vapor pressure of the liquid and reaction rate coefficient (discussed previously). Methanol at room temperature has a vapor pressure of 90 mm Hg which is relatively on the lower side of the spectrum compared to the other products being quantified. Other products within this scan at room temperature such as acetaldehyde has a vapor pressure of 760 mm Hg, acetone has one of 190 mm Hg and propanal has one of 235 mm Hg. Methanol has a very low ionization reaction rate coefficient relative to other liquid products as its reaction rate coefficient is 2.7\*10<sup>-9</sup> while other products such as acetone has a reaction rate coefficient of  $3.9*10^{-9}$  and propionaldehyde 3.6\*10<sup>-9</sup>. The limit of detection for all the liquid products except methanol for SIFT-MS matches the conventional methods such as NMR [8]. The faradaic efficiency trend and values for liquid products from Cu Foil and the SIFT-MS scan match the general trends seen within the field as they increase in selectivity as the potential decreases and start to plateau at -1.08 V vs RHE. Our two-compartment cell system was limited to -1.08 V vs RHE as this was the highest potential that could be measured that remained stable for enough time without overloading the potentiostat. This was due to the bubbles forming at higher potentials and there was not enough surface area for the potentiostat to supply current between the working electrode and counter electrode to reach the desired potential causing the potentiostat to overload.



Figure 16. SIFT-MS Analysis of Cu Foil for CO2R at varying potentials from -0.77 V vs RHE to -1.08 V vs RHE a) Major, intermediate and minor products faradaic efficiency mapped as a function of time at varying potentials vs RHE b) Major, intermediate and minor products faradaic efficiency mapped to potential.

To properly evaluate the use of SIFT-MS as a real-time quantification method, the results were compared to GC and NMR, traditional product characterization methods, to ensure agreement among product measurement. For this measurement, we chose to apply a voltage of 1.04 V vs. RHE and collect aliquots from the catholyte chamber to evaluate with GC and NMR, while concurrently monitoring product formation in real-time. One of the weaknesses of SIFT-MS is it cannot measure CO or H<sub>2</sub> as these product ions do not react with any of the reagent ions. These products are major products being produced within the CO<sub>2</sub>R reaction. Formic acid is another major product produced that SIFT-MS could potentially measure, but as this system uses potassium bicarbonate as an electrolyte and has a 6.8 pH the formic acid is in the base conjugate form which does not have a high enough vapor pressure to effectively measure. To look at the full picture of the total faradaic efficiency and further analyze how accurate the SIFT-MS scan is, SIFT-MS, NMR and GC characterization was done for the same electrochemical reduction of CO<sub>2</sub>R using copper foil -1.04 V vs RHE. At -1.04 V vs RHE the SIFT-MS scan measured the 9 products as seen in Figure 17 c) NMR measured the rest of the liquid products shown and GC measured the rest of the gas products as seen in Figure 17 c). From Figure 17 c) it was seen that there was a total faradaic efficiency of 93% combining all the characterization methods, which is an acceptable value within the community indicating the SIFT-MS scan can be used to accurately quantify products.

There is strong agreement among products with SIFT-MS compared to GC & NMR, with the exception of acetaldehyde and ethanol [19], [38]. Acetaldehyde faradaic efficiency is roughly a factor of 10 greater than expected, and the ethanol faradaic efficiency is lower

when using real-time detection techniques compared to traditional NMR measurements. This observation demonstrates one of the critical aspects of measuring product formation in *real-time*, as we are observing here the formation of a CO to ethylene intermediate that cannot be captured using traditional *offline* liquid measurement techniques. Acetaldehyde undergoes chemical conversion via the Cannizzaro reaction to ethanol post-reaction.[32], [33]. This can be extended to other catalysts, where there could be further situations from other chemical conversions such as the Aldol reaction, Tishchenko reaction, self-condensation and polymerization converting various CO<sub>2</sub>R products to other products from non-electrochemical means that SIFT-MS can identify and quantify which other techniques cannot [38]. This will be a focus of further studies, to see if modification of the product delivery to the SIFT-MS to can capture the presence of potential intermediates.

A comparison of the remaining liquid product comparison from this electrochemical reduction reaction ran at -1.04 V vs RHE was conducted that shows the difference in faradaic efficiency for liquid products that both SIFT-MS and NMR can quantify as seen in **Figure 17 a**) & b). Looking at all the products except acetaldehyde, and ethanol both techniques gave relatively close quantification values that are within the expected range of experimental error of each technique. This confirms that the SIFT-MS scan accurately quantifies liquid product formation in *real-time*, reducing the analysis time for what would typically be days or hours down to minutes.



Figure 17. a) & b) Shows the faradaic efficiency difference between SIFT-MS and NMR for the same liquid product at a potential of -1.04 V vs RHE for Cu foil CO<sub>2</sub>R experiment a) Intermediate liquid products b) Minor liquid products c) Total faradaic efficiency for Cu Foil CO<sub>2</sub>R experiment at -1.04 V vs RHE Shows the total faradaic efficiency using SIFT-MS, GC and NMR characterization techniques.

#### **3.4.8 Limit of Detection SIFT-MS**

The limit of detection for each product analyzed using SIFT-MS is influenced by several key properties, which vary based on whether the target product is gaseous or liquid. For gaseous substances, the primary determinants of the limit of detection are the reaction rate coefficient and the branching ratio. An elevated reaction rate coefficient coupled with a higher branching ratio results in a decreased limit of detection due to the production of a more stable, low-fluctuation signal by SIFT-MS. As illustrated in Table 3, ethylene exhibits a notably higher limit of detection compared to methane, attributable to a higher reaction rate coefficient. In contrast, for liquid products, while the limit of detection also depends on the reaction rate coefficient and branching ratio, it is significantly impacted by vapor pressure. The strength of a liquid product's response is observable from its calibration curves. For instance, a concentration of 0.1 mM 1-propanol does not yield an equivalent ppm reading in SIFT-MS as does 0.1 mM propionaldehyde, as depicted in Figure 14, despite being of equal concentration. This disparity is primarily driven by vapor pressure. A higher vapor pressure is strongly correlated with enhanced product response strength, given that vapor pressure measures a material's tendency to transition into the gaseous state, and increased vapor pressure leads to the generation of more gaseous molecules of the specific product, which SIFT-MS quantifies. The reaction rate coefficient and branching ratio influence the baseline of the liquid product. A product with a lower reaction rate coefficient and branching ratio will exhibit greater variance in its SIFT-MS readings, producing a noisier baseline that necessitates a higher concentration of product to distinguish whether the SIFT-MS response is attributable to product generation or merely noise. Another influencing factor of the limit of detection is contamination. SIFT-MS is capable of detecting products in the ppb range, rendering it a highly sensitive analytical technique. Comprehensive measures were undertaken to minimize contamination throughout the experiments, including thorough cleaning and the utilization of new tubing connections. It was discovered that ethanol could leach into the connection tubing, resulting in an elevated SIFT-MS baseline for ethanol, thereby substantially increasing its limit of detection. This issue was resolved by replacing the tubing. A parallel issue was identified for acetaldehyde, which manifested a higher baseline due to undetermined contamination. Despite attempts with new tubing and cleaning strategies, no changes fixed this issue. Although acetaldehyde was anticipated to possess a low limit of detection based on its vapor pressure, reaction rate coefficient, and branching ratio, contamination contributed to it having one of the poorest detection limits. The limit of detection for liquid products using SIFT-MS is predominantly dependent on vapor pressure, branching ratio, reaction rate coefficient, and contamination status. A higher vapor pressure, reaction rate coefficient, and branching ratio correlate with a lower limit of detection, whereas significant contamination substantially elevates the limit of detection.

 Table 3. Displays the factors that affect the detection limit for SIFT-MS. Product response strength is ranked on a scale of 1-3 where 3 is the strongest response strength. Baseline level strength is ranked on a scale of 1-3 where 3 is a high baseline response.

Product	Vapor Pressure (mm Hg)	Reaction Rate Coefficient	Branching Ratio	Product Response Strength	Baseline	Detection Limit (ppm)
1-Propanol	18	2.3 E-9	1	1	3	0.02
Acetaldehyde	760	3.7 E-9	1	2	1	0.30
Acetone	190	3.9 E-9	1	2	3	0.01
Allyl Alcohol	19	3.0 E-9	0.30	1	3	0.05
Ethane						
Ethanol	40	2.3 E-9	0.75	1	2	0.05
Ethylene		1.0 E-9	1			0.20
Methane		5.0 E-12	1			10
Methanol	90	2.7 E-9	1	0.5	2.5	0.05
Propionaldehyde	235	3.6 E-9	0.10	3	2	0.05

#### **3.4.9 Partial Current Density and Rate of Production**

Product concentrations, and by extension faradaic efficiency, is a valuable metric to understand CO<sub>2</sub> reduction selectivity, but other metrics also provide additional insight into CO<sub>2</sub> reduction such as partial current density in which real-time analysis can provide new information. Partial current density can provide a clearer insight into the kinetics of the reaction. Figure 18 a) shows how partial current density increases for each product as the potential is driven to further negative values, indicative of a greater turnover frequency. The evolving partial current density over time for gas products can be seen in Figure 18 b) highlighting an advantage of how real-time analysis can provide a more detailed insight as traditional techniques are not capable of finding real-time measurements for partial current density. Figure 19 displays the rate of production for the liquid products and it further validates that the liquid products' partial current density and faradaic efficiency increase was a result of the increasing negative potential having a higher affinity towards  $C_2^+$ products. In Figure 20 it is seen that the liquid product rate of formation increases at a constant linear production rate as the potential is applied, and it can be confirmed. In the past for offline techniques a linear rate of production was theorized but difficult to prove with experimental evidence due to lack of real-time measurements. From these results, the SIFT-MS scan was accurately quantifying many important performance characteristics for catalyst materials for CO<sub>2</sub>R electrochemical reduction and can be utilized to confirm and find out new information in regards to reaction kinetics and the CO<sub>2</sub>R pathways.



**Figure 18.** Highlights the partial current density for Cu Foil CO<sub>2</sub>R experiment a) Shows the partial current density of each product at varying potentials from -0.77 V vs RHE to -

1.08 V vs RHE b) Shows the real-time evolution of partial current density for gas products measured by SIFT-MS at varying potentials from -0.77 V vs RHE to -1.08 V vs

RHE.



Figure 19. Shows the rate of production of liquid products for Cu Foil of CO<sub>2</sub> reduction

as a function of varying potentials from -0.95 V vs RHE to -1.08 V vs RHE.



Figure 20. Liquid concentration accumulation of 1-propanol at -1.04 V vs RHE as a

function of time.

### **3.5 Conclusions and Outlook**

New insight into the use of SIFT-MS to quantify *real-time* product detection for the electrochemical reduction of CO<sub>2</sub> into fuels and chemicals has been demonstrated in this work. A new experimental quantitative analysis to analyze 10 products using a SIM scan from SIFT-MS was created that allowed for accurate quantification of the concentration of an array of CO<sub>2</sub>R products to find important catalyst performance characteristics such as faradaic efficiency, partial current density and rate of production. It was also further validated by running an experiment where SIFT-MS, NMR and GC were all conducted on the same electrochemical experiment to find the total faradaic efficiency and the liquid products were cross-referenced between the SIFT-MS and NMR results. It was found that the results were as expected where the total faradaic efficiency was within an acceptable complete range. The liquid product comparisons between NMR and SIFT-MS matched up aside from the differences expected to be seen with acetaldehyde and ethanol where the advantages of real-time measurements to acquire new knowledge were on display. Overall, a successful quantitative SIFT-MS SIM scan was created that can be further used to find out valuable real-time product information about catalysts within the CO<sub>2</sub>R field to generate new knowledge about reaction pathways and mechanisms.

The framework for a quantitative analysis that can be used for CO<sub>2</sub>R has been laid out, but there are still many ways in which this can be utilized to further catalyst studies and also improve the range of products detectable by SIFT-MS. This scan took around 90 minutes to fully analyze 5 different potentials, which would take offline techniques upwards of 6 hours for gas products and a day for liquid products. This opens the avenue for implementing automated high-throughput testing which could vastly decrease the time needed to study catalysts for CO<sub>2</sub>R and help design catalysts at a more efficient rate. The scan taking 90 minutes could potentially be optimized to be even quicker with future studies as well. Aside from high-throughput testing the real-time analysis also opens avenues for discovering new reaction pathways and mechanisms for CO<sub>2</sub>R catalysts such as looking at acetaldehyde to ethanol ratios, along with examining how pulsed electrolysis affects product detection. Overall SIFT-MS has a promising future to make significant steps towards advancing catalyst design and discovery for CO<sub>2</sub>R and helping progress this technology towards industrialization for a sustainable renewable energy future.

## 4. Conclusions and Future Work

The work outlined within this thesis showed new insight into the capability of how SIFT-MS can be utilized to quantify *real-time* product detection for the electrochemical reduction of CO2 into valuable chemicals and fuels. A new quantitative scan using SIFT-MS was created that analyzed 10 products from CO<sub>2</sub>R in an accurate and reproducible manner that aligns with literature values and common characterization techniques. The liquid product comparisons between SIFT-MS and NMR highlights an advantage to measuring in real-time as seen from the loss of acetaldehyde from the NMR technique compared to SIFT-MS results. This shows how SIFT-MS results depict a more accurate quantification of the electrochemical conversions taking place, compared to chemical conversions that can occur after the reaction, as in this case with acetaldehyde converting to ethanol showing how NMR results can have an inflated quantification of ethanol and deflated one of acetaldehyde. In summary, a successful quantitative SIFT-MS scan was created to detect an array of  $CO_2R$  products that can be used in the future to analyze catalysts within the CO<sub>2</sub>R field to find out valuable information on reaction pathways, mechanisms and also speed up analysis time.

With the SIFT-MS framework set, the leads way to interesting opportunities on how SIFT-MS can be used in future work. There are a few promising avenues to look at for how SIFT-MS can be used. The first one being optimizing reaction parameters within the SIFT-MS to develop the fastest possible analysis time of catalysts for CO<sub>2</sub>R. It is known from this study that the slowest SIFT-MS can analyze gas and liquid products is roughly around

5 to 10 minutes depending on the potential for a two-compartment cell. The biggest limiting factor to why it cannot be done quicker is due to the production rate of products teetering on the limit of detection limits of SIFT-MS itself. Replacing the two-compartment cell with an MEA cell that produces a significantly higher volume of product overall and analyzing and optimizing reaction parameters such as time needed to accurately quantify liquid products, carrier gas flow rate, liquid flow rate, capture technique, and number of products within the SIM scan leads to intriguing future avenues. Using the traditional characterization techniques, it will take upwards of 5 or more hours to a day to analyze a catalyst at 5 different potential values with little room to improve this time without sacrificing significant accuracy. SIFT-MS could bring the time down to analyze a catalyst of 5 different potentials to under an hour and potentially more. This leads the way to opening the door to widening the use of high-throughput testing for CO<sub>2</sub>R catalyst materials.

Another interesting avenue to look at is being able to see how pulsed electrolysis can be used with SIFT-MS to find out intriguing information about electrochemical CO<sub>2</sub>R and CO<sub>2</sub>R electrolyzer systems. Pulsed electrolysis has been shown to have an effect on the inhibition of catalyst poisoning, changing the surface of the catalyst via surface reconstruction which affects product distribution, and an effect on the mass transport limitation within the system [51]. SIFT-MS provides real-time product analysis capability which can be coupled with pulsed electrolysis to find the optimal pulse duration hold that maximizes selectivity towards a specific product. This can be used to see immediate changes to reaction pathway and mechanisms that are occurring to potentially unveil new information that can lead to better understanding of pathways and then this can be used to enhance catalyst design. It can also be used to look at minimizing overpotentials through allowing the catalyst on the electrode to recover during off-periods of the pulse which can be best monitored by the real-time capabilities of SIFT-MS. The off-time period can then be optimized to find the most efficient off-period pulse lengths that could correlate to catalyst recovery and lead way to improved mitigation of catalyst degradation in CO<sub>2</sub>R electrolyzer systems. All of these listed insights could pave way to knowledge on how a specific type of copper catalyst, morphology or surface characteristic coupled with pulsed electrolysis has enhanced selectivity towards a specific product, or leads to mitigated catalyst degradation improving stability of the overall electrolyzer device. In turn these improvements would translate to better energy efficiency of the electrolyzer CO<sub>2</sub>R cell systems that will drive this technology one step closer towards meeting the industry requirements for industrialization and commercialization of this technology.

Lastly, a perhaps ambitious goal would be seeing if SIFT-MS could be used to detect products from the glycerol oxidation reaction. As glycerol oxidation is potentially a replacement for the hydrogen evolution reaction on the anode side within a CO<sub>2</sub>R cell setup that leads to reduced operating cell voltage. Glycerol oxidation reaction also produces a wide range of volatile value-added products that SIFT-MS could potentially measure. In a future CO<sub>2</sub>R cell setup where CO<sub>2</sub>R is occurring on the cathode side and glycerol oxidation is occurring on the anode side SIFT-MS could be a prime characterization technique to use for product detection where it can detect both the CO<sub>2</sub>R products being generated on the cathode and also the glycerol oxidation products being generated on the anode as well. Overall, SIFT-MS has a promising future in being utilized to help advance catalyst design and discovery for CO<sub>2</sub>R technology and help progress the field towards commercialization.

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