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Initial Application of Selected-Ion Flow-Tube Mass Spectrometry to Real-Time Product Detection in Electrochemical CO_2 Reduction

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Abstract: Electrochemical CO_2 reduction (EC-CO2R) has seen a resurgence in interest over the past several years; however, the means of analyzing catalytically produced products continues to rely on decades-old methods such as gas chromatography, high performance liquid chromatography, and nuclear magnetic resonance. Real-time analysis of the gaseous and liquid products of this reaction is highly desirable; however, few analytical techniques have been developed thus far to meet this need. Here we demonstrate the first use of selected-ion flow-tube mass spectrometry (SIFT-MS) as an analytical tool capable of measuring in real time both the gas and liquid phase products of EC-CO2R in aqueous solution. SIFT-MS uses well understood ion molecule reactions to enable the analysis of similar multi-component mixtures by preventing substantial fragmentation of the analyte. We lay out the framework in which to evaluate the tool's capabilities and show that the C_1-C_3 hydrocarbon,
alcohol, and aldehyde products of CO2R should be quantitatively detectable.

Introduction

The quantification of multicomponent liquid and gaseous mixtures has been well established for decades and is especially important when studying CO2R catalysts.[1] Metals like copper (Cu) have been shown to simultaneously produce up to 16 different chemicals.[2] For the gaseous products, gas chromatography (GC) is typically used and for the liquid products, nuclear magnetic resonance (NMR) or high performance liquid chromatography (HPLC) are typical. All three of these techniques can reliably provide quantitative and reproducible results.

Online GC analysis is often utilized to detect the gaseous products of CO2R.[2–9] In this type of set up, gas flowing through the electrochemical cell is sampled by the GC periodically. Due to the GC's reliance on product separation before detection, most literature reports obtain data points only every 10 to 20 minutes. Liquid products are typically only analyzed once per run, at the conclusion. It is conceivable to take liquid aliquots every 10 to 20 minutes to be analyzed, although this is rarely done.[10,11] Liquids tend to be generated at very low rates and thus more time is needed for them to accumulate in the electrolyte before they can be detected. Thus, the traditional analytical techniques, while reliable, are not applicable if real-time analysis of CO2R products is desired.

The time dependent behavior of CO2R electrocatalysts has been shown to be a subject of great importance. It was critically studied by Hori and co-workers in the context of catalyst deactivation, although over fairly long times.[12] More recently, real-time data acquired by Koper and co-workers has provided insight into the CO2R mechanism,[13,14] including the voltage dependent pathways for ethylene formation.[15–17] These studies illustrate how real-time product analysis can provide new insights; however, there could be many more. For example, the dynamics of liquid product formation during CO2R are almost entirely unexplored. In general, the working assumption of most reports is that liquid products are being generated at a constant partial current density throughout the run. Using the information a GC provides, the faradaic efficiency loop can be closed assuming that liquids account for all the missing current. Although this is not a rigorous approach, it can be used to estimate if the magnitude of all liquid products being produced is constant (or not) throughout a run. However, the assumption that every liquid product (of which there can be as many as 14) is generated at a constant rate has limited experimental validation. To confirm this hypothesis,

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an experimental technique which can detect quantitatively and simultaneously all the gaseous and liquid products of CO2R would be required.

In addition, the real-time data provided by such a technique would greatly accelerate catalyst exploration by reducing the time needed to evaluate a catalyst from days to potentially a few hours. This could also enable the use of high throughput material library approaches to catalyst discovery.[18]   This high through-put catalyst screening has already been successfully implemented to catalyst discovery for the oxygen evolution reaction[19–23] and the hydrogen evolution reaction (HER).[23–25] However, the task of identifying a more active catalyst is simplified for these reactions because only one product is made (namely oxygen or hydrogen). Thus only current or the production of that one product needs to be monitored to identify a "hit" (i.e. a catalyst for further investigation).   Screening CO2R catalysts is more complicated due to the production of multiple products and the competing HER reaction.   Thus monitoring current alone will not provide the necessary information to identify a hit and detailed product detection is necessary. As of yet, there has only been one implementation of high through-put screening in CO2R which is due, in part, to the lack of a suitable real-time analytical tool.[26,27]

For all the aforementioned reasons, considerable effort has been put into developing systems which can acquire real-time data.   Historically, in electrochemistry, this effort has been focused on differential electrochemical mass spectrometry (DEMS),[28–32] which has seen both historic[33–37] and more recent specific adaptation to CO2R systems.[27,38–40] In these systems, electron ionization mass spectrometry (EI-MS) is typically coupled to a specialized electrochemical cell or sample collection tip.   Of particular note are the systems developed by Koper and co-workers[39] and Bell and co-workers[38] for CO2R.   Koper's online electrochemical mass spectrometer (OLEMS) places a porous tip very close to the electrochemical surface, where it collects both gaseous and liquid products.   While this approach is not quantitative, it has shown the ability to detect hydrogen, methane, ethylene, ethane, methanol, acetaldehyde, and ethanol in specific situations.   Bell's DEMS system relies on an innovative electrochemical flow cell, which enables quantitative product analysis.   This system extracts liquid and gaseous products through a membrane and can quantify hydrogen, methane, ethylene, and ethane, as well as 1-propanol and ethanol with some assistance from ex-situ HPLC analysis.

Detection and quantification of the products of a reaction can be broken down into three levels of detail.   At the first level, the analytical system can simply identify whether or not a group of chemicals is present.   For example, a detection system could identify if alcohols are being produced, but not which ones or how much of each.   At the second level, the system can identify each chemical individually.   Thus, which specific alcohol is being produced is known.   At the third and most detailed level, the detection system can identify each chemical individually as well as how much of that chemical is being produced, allowing for full quantifiable analysis of each product.   An ideal real-time product detection system for CO2R would be able to detect and quantify (level 3) all the products that have been observed.   In addition, the system would be able to do this on a relevant time scale,

where sub-second resolution would be ideal. Here we explore the first application of selective-ion flow-tube mass spectrometry (SIFT-MS) to the *in-situ* detection of the volatile products of CO2R. SIFT-MS uses the products of ion-molecule reactions to detect analytes and in this way is more adept at analyzing complex multi-component mixtures like that of the 20 potential liquid and gaseous products of CO2R.

Limitations of Electron Ionization Mass Spectrometry

The main reason current DEMS systems have trouble delineating all the products of CO2R (level 1 analytical system) is that they depend on electron ionization mass spectrometry (EI-MS).   Electron ionization is a relatively harsh process in which sample molecules are not only ionized but often broken down into many constituent fragments.   The reason so much fragmentation occurs is due to the high energy (~10 eV) required to ionize a molecule in comparison to the typical energy required to cleave bonds (~3 eV).[41,42] This so-called fragmentation pattern is a fingerprint for the molecule; however, the high degree of fragmentation complicates the analysis of multi-component mixtures, if the components produce many of the same fragments. This is the case with the products of CO2R which are all small molecule hydrocarbons, alcohols, or aldehydes.   This is further complicated because the primary constituent of gaseous samples, making up 99% of the sample, is CO_2 while the remaining gases and entrained liquid vapors, to be detected, represent only a very small fraction of the sample.   Thus when the sample is injected onto an electron ionization source, the CO_2 ionization fragments produce a large background signal at masses that would be monitored to detect the other chemicals.   This issue can be easily avoided by the separation that is achieved with gas chromatography mass spectrometry, but then the real-time capability of the analysis is lost.

Table S1 shows a list of all the products that have been reported for CO2R on copper.[2] Formaldehyde, methanol, ethane, and propene have also been included as these have been reported as CO2R products on other catalysts and would be of particular interest as fuels.[14,43–50] The table shows a heat map of what ionization fragments (*m/z*) are produced for each molecule, from green being abundantly produced to gray being scarcely produced.[51] Furthermore the *m/z* patterns for water and CO_2 are shown, as these components will make up the bulk of a sample being injected.[51] *m/z* values highlighted in red indicate masses where water or CO_2 will make major contributions and thus no other component will be detectable at these masses.   These masses have been crossed out across the table as a result.

With such a map it is possible to identify which compounds can be detected and quantified if an unknown mixture is sampled. For this analysis it was assumed that any secondary fragment less than 25% in intensity of the primary *m/z* could be ignored. This resulted in identifying unique *m/z* values for hydrogen, ethylene, propylene, formic acid, methanol, acetic acid, ethylene glycol, and allyl alcohol. A unique *m/z* means that this compound could be directly quantified by calibrating just one mass fragment. Further analysis showed methane, ethane, and ethanol could be quantified by subtraction.   All other compounds which contributed

significantly to the identified *m/z* could be subtracted away leaving only the contribution of the one remaining compound. Thus as long as the contributions to a specific *m/z* are a linear sum of the parts, which it should be for electron ionization MS, compounds can be reliably identified by subtraction. However, this analysis shows that the remaining products (carbon monoxide, formaldehyde, glyoxal, glycolaldehyde, acetaldehyde, hydroxyacetone, acetone, propionaldehyde, and 1-propanol) cannot be deconvoluted from each other and thus are unquantifiable, preventing level 3 analytical detection.

EI-MS is an extremely sensitive analytical technique, which has been regularly shown to be capable of quantifiably detecting picogram amounts of analyte.[42] However, this high level of sensitivity does not resolve the above mentioned issues with mass overlap when analyzing a complex mixture of similar compounds. If a more selective ionization technique could be coupled to the extremely sensitive detection method of MS, then it may be possible to overcome some of the detection issues EI-MS faces, as outlined above. Here, SIFT ionization, as an alternative to EI, is explored as one possibility. The advantage of SIFT-MS is that it uses a gentler chemical ionization technique, which, in principle, produces a far simpler fragmentation pattern where molecules only produce several characteristic ions instead of dozens.[52] In addition the technique does not ionize CO_2, as will be explained in more detail below, thus avoiding the large background issue. Thus, level 3 analytical detection of a more complex multi-component system should be possible.

Brief History and Applications of SIFT-MS

The selected ion flow tube (SIFT) technique was developed in 1976[52] where it was used for further study in the well-established ion-molecule reaction kinetics field.[53,54] It was then adapted in 1996 to use the well-established ion-molecule reaction data to quantify unknown samples injected into the flow tube.[55] Combining the two yields a technique for doing spectrometry and was thus renamed selected-ion flow-tub mass spectrometry (SIFT-MS). The details of the technique have been summarized in a series of review articles.[56–58] Essentially, the method consists of feeding an unknown gas mixture into the reaction flow tube where it undergoes "soft" chemical ionization by reaction with injected reagent ions. These reagent ions are typically H_3O^+, NO^+, and O_2^+ and the flow tube contains fast flowing carrier gas (typically He or N_2) at ~1 Torr such the the residence time of analyte molecules in the tube is short, simplifying the reaction chemistry. The combined mixture of now ionized unknown molecules in the carrier gas is sampled at a downstream quadrupole mass spectrometer. Utilizing the known reaction product library, the unknown samples can be identified in a way similar to electron-ionization mass spectrometry. A schematic of a SIFT-MS system is shown in Figure 1.

SIFT-MS utilizes multiple reagent ions, as compared to proton transfer reaction mass spectrometry (PTR-MS) in which only H_3O^+ is used as the reagent ion.[59] The reagent ions in SIFT-MS are selected by an upstream quadrupole such that only one is injected at a time into the flow tube. Each reagent ion has unique reactions with an analyte molecule, thus allowing for multiple avenues to confirm the identity of an unknown species. This is particularly useful when trying to analyze complicated mixtures of similar molecules like that produced by CO2R. Furthermore, because the chemical ionization is not strong enough to ionize O_2, N_2, Ar, or CO_2 but is very reactive with most volatile organics, SIFT-MS has routinely shown ppb level detection of analytes without separation from their makeup gas.[57,60] However, the soft nature of this ionization also has the drawback of not ionizing two important products of CO2R, hydrogen and carbon monoxide. In addition, because the reaction rates of many molecules with these reagent ions have been well studied,[61–65] it is claimed that SIFT-MS does not require external calibration. The makeup of the analyte can simply be back calculated using the known reagent ion concentration, the known reaction rate, and the measured products of the reaction. Thus obtaining quantitative information should be much simpler than the rigorous calibration process typically required of a GC or EI-MS analytical system.

SIFT-MS has been utilized mainly for environmental impact studies, analyzing trace gases in atmospheric air, and for
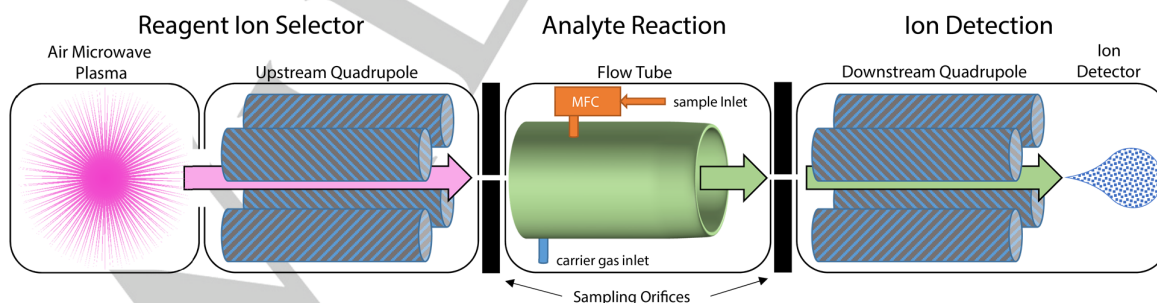

Reagent Ion Selector   Analyte Reaction   Ion Detection

Figure 1. Schematic of SIFT-MS: A schematic of the different sections of a SIFT-MS are shown. In the first section, the reagent ions H_3O^+, NO^+, and O_2^+ are generated from air and then selected by the upstream quadrupole. The reagent ions are injected into the flow tube where they can react with the sample. The product ions of this reaction are then detected by a downstream mass spectrometer.

biological studies, analyzing the metabolites in exhaled breath. In these applications, hydrocarbon and volatile organic compounds (VOCs), respectively, are the main target analytes.[56,66,67] Real-time detection is important due to VOCs' tendency to adsorb onto storage container walls, preventing accurate quantification. With SIFT-MS the samples are taken directly from the atmosphere, without the need for storage, eliminating this issue. The real-time detection is also important for environmental applications, where improper release of chemicals in the air can be detected immediately and addressed.

Three potentially important attributes of SIFT-MS can be observed from these previous applications which may make it well-suited for CO2R.

1. SIFT-MS has already been used to detect the types of chemicals that are relevant to CO2R, with a high degree of sensitivity.
2. SIFT-MS can readily detect products in real-time with sub-second time resolution.
3. SIFT-MS can detect VOCs simply from the vapor released by these liquids. Thus it may be possible to eliminate direct sampling of the liquid to identify the liquid products of CO2R.

Prospective Outlook on the use of SIFT-MS with CO2R

In order to understand if SIFT-MS can provide any advantages over traditional analytical techniques, the first step is to use the literature to determine if all the CO2R products can be uniquely identified if injected together. The method of injection is by sampling a stream of CO_2 flowing through an electrochemical cell which will entrain the generated hydrocarbon gases and the vapor of the alcohol and aldehyde liquid products accumulating in the electrolyte. The CO2R products are the analytes to be detected by reaction with the SIFT-MS reagent ions. These reactions will create product ions that are detected by the MS. The molecular chemistry involved in these reaction is briefly reviewed in the supplementary information and has been reviewed in much greater detail by Smith and Španěl.[57]

The literature was surveyed to build a library of expected product ions for the same products of CO2R listed in Table S1.[61–

65] This information is summarized in Table 1. For several CO2R products, no data was available (glycolaldehyde, hydroxyacetone, allyl alcohol). For these chemicals the ionization energy (IE)[68] and proton affinity (PA)[69] were obtained from the literature, if available, and then the appropriate reaction was applied from those summarized in the SI and an expected m/z was hypothesized. For example, the IE of both hydroxyacetone and ally alcohol were found to be less than that of O_2, thus it is expected that these molecules will undergo a charge transfer reaction with O_2^+ producing m/z 74 and 58 respectively. Because this data only represents an educated guess, it was not included in the further analysis below. Data was available for formic acid and acetic acid; however, these compounds were neglected from further analysis because at the pH of a typical CO2R experiment (~7) they are mostly deprotonated and ions have no vapor pressure through which they could be detected in a gaseous stream.

It can be observed from Table 1 that many of the target analytes would produce the same m/z fragments (highlighted cells with bolded m/z's). However, due to the multiple reagent ions and the limited fragmentation patterns it is possible to deconvolute these overlaps and hypothesize a scheme in which all the target analytes can be identified. Table 2 summarizes which m/z values can be used to identify which analytes for each reagent ion. In green text are masses which are unique identifiers for their specific analyte; no other analyte produces this m/z value. In orange text are the masses which can be used to identify the target analyte but require deconvolution first. Multiple analytes contribute at this m/z but the contributions of all the other analytes, other than the target molecule, can be subtracted away. Finally there are several reagent ion/analyte combinations which produced a highly convoluted m/z value which could not be used to identify any individual analyte. Such combinations were labelled as "no usable reaction" and highlighted in red. Despite the presence of several of these combinations, it is still possible to find at least one reagent ion m/z which can be used to identify each product of CO2R. In this way, it is hypothesized that SIFT-MS can be used to identify and quantify methane, ethylene, ethane, propylene, formaldehyde, methanol, glyoxal, acetaldehyde, ethylene glycol, ethanol, acetone, propionaldehyde, and 1-propanol; a substantial improvement over previous real-time analytical techniques.

Table 1. Prospective Outlook on SIFT-MS: The expected product ion mass numbers are tabulated for each compound to be detected using SIFT-MS. The duplicate masses ion are highlighted in a different color for each reagent ion and bolded indicating where overlap and deconvolution may be necessary.

	REAGENT IONS								
	H_3O^+			NO^+			O_2^+		
Mass of Reactant Ions	19 (37, 55)			30 (48)			32 (50)		
Analyte	m/z Products			m/z Products			m/z Products		
Hydrogen	NR			NR			NR		
Carbon Monoxide	NR			NR			NR		
Methane	NR			NR			47		
Ethylene	29	**47**		58				**28**	
Ethane	NR			NR			29	30	28
Propylene		**43**		72				42	
Formic Acid	ND			ND			ND		
Formaldehyde	31	49	**61**	NR			29	30	31
Methanol	33	51	**65**	62			31		32
Glyoxal		**59**		**88**			29	30	58
Acetic Acid	ND			ND			ND		
Glycolaldehyde	UNK			UNK			UNK		
Acetaldehyde	**45**	**63**	**81**	43	**61**		43		44
Ethylene Glycol	**45**	**63**	**81**	**61**	92		31	33	62
Ethanol	**47**	**65**	83	45	63		45	46	63
Hydroxyacetone	UNK			UNK			74*		
Acetone	**59**	77	117	**88**			43		58
Allyl Alcohol	UNK			UNK			58*		
Propionaldehyde		59		57			57		**58**
1-Propanol	43	61	79	59			31		42

Duplicate m/z are highlighted and bold	Duplicate m/z are highlighted and bold	Duplicate m/z are highlighted and bold

NR = No Reaction   ND = Not Detectable   UNK = Unknown Reaction

* = estimated m/z product based off hypothesized reaction

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Table 2. Prospective Outlook on SIFT-MS: The mass library was analyzed to identify which masses can be used to specifically identify each compound. Those masses listed in green and italicized are unique to that chemical and require no deconvolution to use. The masses listed in orange and underlined would require deconvolution with other compounds that produce that mass, but those contributions can be subtracted away. Masses listed in red and double underlined cannot be deconvoluted or used.

Analyte	REAGENT IONS		
	H_3O^+	NO^+	O_2^+
Hydrogen	NR	NR	NR
Carbon Monoxide	NR	NR	NR
Methane	NR	NR	*47*
Ethylene	*29*	*58*	NUR
Ethane	NR	NR	28
Propylene	43	*72*	NUR
Formic Acid	ND	ND	ND
Formaldehyde	*31/49*	NR	*30/29*
Methanol	*33*	*62*	NUR
Glyoxal	NUR	NUR	58
Acetic Acid	ND	ND	ND
Glycolaldehyde	UNK	UNK	UNK
Acetaldehyde	NUR	*43*	*44*
Ethylene Glycol	NUR	*92*	*33/62*
Ethanol	47	*45*	*45/46*
Hydroxyacetone	UNK	UNK	UNK
Acetone	*77*	NUR	43
Allyl Alcohol	UNK	UNK	UNK
Propionaldehyde	NUR	*57*	*57*
1-Propanol	61	*59*	NUR

Green = Unique Mass   Orange = Deconvolution Required
Red / NUR = No Usable Reaction, Deconvolution Not Possible
NR = No Reaction ND = Not Detectable UNK = Unknown Reaction

Tables 1 and 2 also show that SIFT-MS cannot be used to detect hydrogen or carbon monoxide.[57] Thus it would not be possible to completely close the faradaic efficiency loop without additional analytical equipment. The inability to detect hydrogen in particular is a failing of SIFT-MS in comparison to EI-MS. Neither EI-MS nor SIFT-MS can detect carbon monoxide. It would be possible to add a real-time hydrogen detector to the system in the form of an in-line thermal conductivity detector; however, the accuracy of such a system has not yet been proven. There are also potential optical detectors which could be used to detect CO in real-time;[70] however, the effectiveness of such an addition has not yet been validated either. While this is a drawback of SIFT-MS, coupling the system to a GC would provide periodic information to help close this information gap.

With this strong framework supporting the investigation of SIFT-MS as an analytical tool for detecting the products of CO2R, the remainder of this paper is dedicated to exploring the practical implementation of this technique for CO2R experiments. The analytical framework suggests that almost all the expected products can be quantified; however, this hypothesis needs to be experimentally validated.

Results and Discussion

Complications Arising from the Presence of Water Vapor

Initially, the literature built product ion library was used to attempt to calibrate the SIFT-MS. A quick investigation revealed however that the SIFT reactions were not proceeding as suggested in the literature. Table S2 shows the results of individually injecting the three most commonly detected hydrocarbon gases: methane, ethylene, and ethane. It was found that the reagent ions H_3O^+ (m/z = 19) and $H_3O^+(H_2O)$ (m/z = 37) were present in the NO^+ and O_2^+ channels in significant concentrations. As a result of this channel contamination (the source of which is discussed in more detail in the SI), the product ions being produced for each gas were not always those which were expected. For example, from Table 1, it is expected that only ethylene will produce counts at 29 and 47 when reacting with H_3O^+ (hereafter shortened to H_3O^+(29) and H_3O^+(47) respectively), and indeed those two masses did increase when ethylene was injected and not when methane or ethane was injected (Table S2). However, masses O_2^+(28), O_2^+(29), and O_2^+(47) also responded to the injection of ethylene, when only O_2^+(28) was expected. The response of O_2^+(29) and O_2^+(47) for ethylene can be explained by the high counts of the unexpected reagent ion H_3O^+ in the O_2^+ channel. Clearly the H_3O^+ must be reacting with ethylene to create these masses in the O_2^+ channel where they otherwise would not be expected to be made. The additional unexpected masses, due to the presence of water vapor in the sample gas, seriously undermines the analytical framework that was established earlier to quantify the different products of CO2R. As one example, the observed production of O_2^+(47) by ethylene and ethane directly conflicts with the ability to detect methane which only produces O_2^+(47). The results of this initial investigation clarified the need for a more complete investigation of the product ions produced by SIFT-MS for humidified samples like those found in CO2R experiments.

To be sure that entrained water vapor in the sampled gas was the cause of the high H_3O^+ counts in the O_2^+ channel, attempts were made to dry the gas before entering the SIFT-MS. In this way the water vapor which is converted into the reactive H_3O^+ ion is eliminated. Several different methods were investigated to dry the gas, including chemical drying agents like magnesium sulfate and a low temperature moisture trap. These were found to be capable of removing the water vapor from gas taken directly from the cylinder; however, none of these were capable of removing the amount of water vapor that was picked up when bubbling the gas through water, as would be done in a CO2R experiment. Thus it was determined that it would be impractical to calibrate the tool for a condition that was incompatible with the final experimental procedure and no further attempts were made to precondition the gas for the SIFT-MS.

Building a New Product Ion Library

To build a new product ion library, a full mass SIM scan was made to monitor all the masses from 19 to 150 for all three reagent

Table 3. New Mass Library for SIFT-MS: Using the full mass survey, all the masses which responded to each injected compound were recorded. Several more product ion masses were identified in this survey then were initially proposed by the literature review. The duplicate masses are highlighted in a different color for each reagent ion and bolded. Despite this, it is possible to identify masses that allow for the unique identification of each compound tested here. The unique masses are in green text and italicized and the masses which require deconvolution are in orange text and underlined.

	REAGENT IONS		
	H_3O^+	NO^+	O_2^+
Mass of Reactant Ions	*19 (37, 55)*	*30 (48)*	*32 (50)*
Analyte	*m/z* Products	*m/z* Products	*m/z* Products
Methane	NR	NR	47
Ethylene	29 47 65 67 69	41 56	28 29 42 46 47 57 58
Ethane	28	28	20 21 26 27 28 29 47 51
Propylene	41 43 43 44 85	41 43 72	40 41 42 69
Formic Acid	ND	ND	ND
Formaldehyde	65	45 75	75
Methanol	33 51 52 53 69	33 51 52 62	31 49 51
Acetaldehyde	45 46 63 64 89	43 45 63 74	43 44 45 61 62 63
Ethanol	47 48 65 66	45 47 63 65 76	31 45 47 49 63 64 65
Propionaldehyde	41 58 59 60 77 78 117 118	29 57 58 59 60 75 76 77 133	29 40 48 57 58 59 75 76 77 116 117 118 133
1-Propanol	43 79 80	59 60 77	31 42 49 59 77
	Duplicate *m/z* are highlighted and bold	Duplicate *m/z* are highlighted and bold	Duplicate *m/z* are highlighted and bold

NR = No Reaction   ND = Not Detectable   *Green = Usable Unique Mass*   Orange = Usable Mass but Deconvolution Required

ion channels. The four hydrocarbon gases, formic acid, and the C_1-C_3 aldehydes and alcohols were reviewed in this initial study The other minor liquid products, like glyoxal and hydroxyacetone, have not yet been investigated and will be the subject of future study. The resulting mass spectra were then reviewed to determine which masses were responding for each analyte. Fairly high concentrations of each analyte were used in this analysis to ensure that all possible product ions responded regardless of reaction rate. Table 3 shows the results of this investigation. Highlighted cells with bolded masses represent those masses which have contributions from more than one analyte.

When compared to Table 1, it is observed that many more masses are responding for each analyte than the literature predicted. However, this investigation also shows that it should still be possible to deconvolute and quantify all of these chemicals. The masses with the largest response factors for each analyte were analyzed and a new framework was hypothesized. In Table 3, the masses which should provide the most sensitive unique detection of their corresponding analyte are in green text and italicized. In orange text and underlined are the masses which can also be used to detect certain analytes but require deconvolution due to the contribution of multiple chemicals to that mass. It can be seen that there is at least one mass that can be used to detect every hydrocarbon, aldehyde, and alcohol. Experiments were run to see if formic acid could be detected; however, it was found that no mass responded. This reinforces the earlier hypothesis that formic acid and acetic acid vapor entrained in the CO_2 flowing through the cell cannot be detected because they are fully deprotonated at typical CO2R electrolyte pHs.

Using the green and orange masses as the new detection framework, the response factors of all the analytes were compared (Table 4). In doing this, it can be seen which masses may have conflicts which need to be deconvoluted and which masses are truly unique. The response factor (RF) was calculated as,

$$RF = (PIC - BC) / BC \qquad (1)$$

Where the product ion counts (PIC) are the number of counts per second obtained at a given *m/z* that responds to the analyte and the background counts (BC) are the counts per second obtained at the same *m/z* when pure CO_2 is injected into the SIFT-MS. The PIC will be a function of the kinetics of the SIFT reaction and the concentration of the analyte in the sampled stream. For liquid products, the concentration of the liquid's vapor in the gaseous stream will be a function of it's concentration in the liquid and its vapor pressure.

Analyzing Table 4, response factors greater than 1 are highlighted in purple for the masses of each analyte. For each *m/z*, the highest response factor is in green text or in some cases orange text. These highest response factors correspond to the masses for each analyte identified in Table 3 which are to be used to quantify the analyte. In some situations it is clear that for a given mass, more than one analyte has a comparable RF, and in these situations deconvolution will need to be applied, thus the use of orange text. For example with mass $NO^+(59)$ (*m/z* 59+ in the NO^+ channel), there are comparable contributions of both propionaldehyde and 1-propanol. However, using the unique mass $NO^+(57)$ to quantify propionaldehyde, propionaldehyde's contribution to $NO^+(59)$ can be subtracted away, leaving just the contribution of 1-propanol.

Table 4. Response Factor of CO2R Products in SIFT-MS: Selecting only the masses that will be used to identify the various products of CO2R, the response factors of every chemical is calculated. From these response factors it can be seen how sensitively the SIFT-MS can detect these various products. Masses that will require deconvolution in order to identify just one product of CO2R also become apparent. Response factors greater than one are highlighted in purple and bolded. Response factors that uniquely identify a compound are in green text and italicized and response factors that require deconvolution to be used for a compound are in orange text and underlined.

	RESPONSE FACTOR												
	Methane	Ethylene*	Ethane	Propylene	Formic Acid	Form-aldehyde	Methanol	Acet-aldehyde	Ethanol	Propion-aldehyde	1-Propanol		
m/z	1000 ppm	1600 ppm	1000 ppm	100 ppm	1 mM	1 mM	1 mM	1 mM	1 mM	1 mM	1 mM	m/z Assignment	Comments
29+ (19+)	0.05	*18.4*	**1.26**	**1.02**	-0.27	-0.22	-0.26	-0.12	**1.13**	-0.26	-0.21	Ethylene	Not very sensative
45+ (19+)	-0.07	-0.54	-0.11	-0.11	0.04	**2.21**	-0.04	*177*	-0.14	-0.35	-0.11	Acetaldehyde	Unique, negligble contribution from other components
79+ (19+)	-0.08	-0.42	-0.34	**1.39**	0.11	-0.44	-0.24	-0.28	-0.09	0.41	*12.9*	1-Propanol	Not very sensative
80+ (19+)	0.17		0.08	0.83	0.21	-0.38	-0.25	-0.30	-0.36	0.77	*12.4*	1-Propanol	Not very sensative
56+ (30+)	-0.33	*14.8*	0.36	**3.60**	0.36	0.04	-0.19	-0.40	0.18	-0.10	0.38	Ethylene	More unique than 29+ (19+) but lower sensativity
57+ (30+)	-0.41	-0.77	-0.51	-0.40	-0.34	-0.14	-0.60	-0.57	-0.56	*621*	-0.55	Propionaldeyde	Unique
59+ (30+)	-0.71	-0.87	-0.75	-0.47	0.48	-0.76	-0.26	-0.78	-0.76	**11.7**	<u>58.1</u>	1-Propanol	More sensative but requires propionaldehyde subtraction
62+ (30+)	-0.59	0.40	-0.76	-0.44	-0.50	**1.50**	*64.5*	0.17	-0.22	-0.40	-0.18	Methanol	Unique, negligble contribution from other components
65+ (30+)	-0.08		-0.31	-0.92	0.11	**1.25**	0.14	-0.01	*13.8*	-0.33	-0.17	Ethanol	Unique but not very sensative
21+ (32+)	0.28		**18.1**	0.20	-0.01	-0.42	-0.06	0.66	-0.07	0.09	-0.25	Ethane	Unique but not as sensative 28+ (32+) or 29+ (32+)
28+ (32+)	-0.36	<u>**2676**</u>	<u>**322**</u>	0.00	-0.48	-0.43	-0.65	-0.61	-0.51	**6.70**	-0.43	Ethane/Ethylene	Requires subtraction
29+ (32+)	0.20	<u>**327**</u>	<u>**541**</u>	**2.08**	-0.81	-0.77	-0.81	-0.16	-0.70	**10.7**	-0.74	Ethane/Ethylene	Requires subtraction
41+ (32+)	-0.13		**2.02**	*481*	0.08	-0.74	-0.42	-0.44	0.14	**7.99**	**1.81**	Propylene	Unique, negligble contribution from other components
47+ (32+)	<u>55.8</u>	**16.32**	**34.29**	-0.19	-0.02	-0.08	0.03	0.31	**7.17**	0.37	-0.08	Methane	Requires subtraction
75+ (32+)	0.20		0.58	0.22	0.24	<u>73.7</u>	0.34	-0.59	-0.16	**5.00**	0.15	Formaldehyde	Requires propionaldehyde Subtraction

Response Factors Greater than 1   *Green = Unique Product Ion*   <u>Orange = Product Ion Requiring Deconvolution</u>

Testing the New SIFT-MS Analytical Framework

With this new framework in place test cases were run to confirm that individual components could be identified in multiple component systems (Table 5). It should be noted here that only the *m/z*'s listed in Table 4 and the reagent ion masses were monitored for these experiments. With this streamlined SIM scan method, the relevant masses could be measured every ~5 seconds instead of every ~90 seconds, which was required when doing the full mass range scan used for library development. Thus the time resolution of the experiments is within an agreeable range. This time resolution could be further improved if needed by focusing the method on only two compounds instead of the full set.

Table 5. Cross Sensitivity Response Factor Analysis of CO2R Products in SIFT-MS: Several case studies were taken to see if the RFs for a mixture would be the same as the sum of the two individual components of that mixture. For each set of 3 columns, the 1st and 2nd column contain the individual component data and the 3rd column contains the mixture data. It can be seen that in systems that require deconvolution (formaldehyde + propionaldehyde & 1-propanol + propionaldehyde) and those that don't (ethane + propionaldehyde & propylene + propionaldehyde), the RF's for the mixture are measured to be close to the sum of the individual components. The relevant chemicals to monitor are highlighted and bolded for each test case.

Mass Assignment	m/z	Ethane	Propion-aldehyde	Ethane + Propionaldehyde	Propylene	Propion-aldehyde	Propylene + Propionaldehyde	Form-aldehyde	Propion-aldehyde	Formaldehyde + Propionaldehyde	1-Propanol	Propion-aldehyde	1-Propanol + Propionaldehyde
		1000 ppm	1 mM	1000 ppm + 1 mM	100 ppm	1 mM	100 ppm + 1 mM	1 mM	1 mM	1 mM + 1 mM	1 mM	1 mM	1 mM + 1 mM
1-Propanol	79+ (19+)	-0.47	0.95	1.14	0.36	1.01	1.44	-0.22	1.01	0.88	**18.4**	**1.01**	**17.2**
Propionaldeyde	57+ (30+)	-0.83	262	271	-0.40	230	212	-0.66	230	232	**-0.82**	**230**	**268**
1-Propanol	59+ (30+)	-0.77	25.03	25.66	-0.54	20.7	17.1	-0.56	20.7	23.8	**110**	**20.7**	**137**
Ethane	21+ (32+)	**12.06**	**0.54**	**11.4**	-0.10	-0.20	-0.04	-0.38	-0.20	-0.02	-0.19	-0.20	-0.02
Propylene	41+ (32+)	0.60	1.17	2.92	**366**	**15.3**	**358**	-0.73	15.33	0.77	1.90	15.3	3.35
Formaldehyde	75+ (32+)	3.22	9.80	18.08	0.05	6.49	6.57	**113**	**6.49**	**125**	0.76	6.49	14.5

In the first two test cases, unique systems were combined. First ethane at 1000 ppm and 1 mM propionaldehyde were tested. The response factors of the individual components and then the response factors of their mixture are shown in Table 5. It can be seen that neither component was expected to contribute significantly to the other and the mixture showed that as well. Both $NO^+(57)$ (propionaldehyde) and $O_2^+(21)$ (ethane) deviated less than 10% from the value obtained for the individual component. The second test was combining 100 ppm propylene and 1 mM propionaldehyde. Like the first test, neither component contributed significantly to the other. Furthermore, the test of the mixture gave response factors very similar to that of the individual components.

In the second two cases, mixtures that required subtraction were combined. The first was a combination of 1 mM formaldehyde and 1 mM propionaldehyde. From the individual component data, the propionaldehyde m/z ($NO^+(57)$) is expected to be unique while the formaldehyde m/z ($O_2^+(75)$) has a small contribution from propionaldehyde. Appropriately, the mixture of the two at the $O_2^+(75)$ mass has a higher RF than the individual components and the sum of the two individual component's RFs comes within 10% of the mixture. The second combination tested was 1 mM 1-propanol and 1 mM propionaldehyde. Here two masses for 1-propanol are shown, $H_3O^+(79)$ which is not very sensitive but is mostly unique for 1-propanol, and $NO^+(59)$ which is more sensitive but convoluted with propionaldehyde. This experiment shows that either mass could be used for 1-propanol. $NO^+(59)$ is a combination of the two individual RFs within 10% and $H_3O^+(79)$ is within 10% of the individual component response of 1-propanol.

To further test this new analytical framework, a CO2R experiment was run using copper foil as a catalyst. In this simple experiment, 0.1M KHCO$_3$ was used as the electrolyte and -1.0 V vs. RHE was applied to the Cu. The unique masses $H_3O^+(45)$, $NO^+(57)$, and $H_3O^+(79)$ were measured to investigate the time evolution of acetaldehyde, propionaldehyde, and 1-propanol respectively. Figure 2a shows the raw counts produced by the SIFT-MS for each m/z being watched. Before time 0, there is a very low baseline of counts at each of these masses. Then at time 0, the potential is applied to the electrode and it can be observed that the masses start to rise immediately. This data can be further analyzed and converted into response factors, like was done above (Fig. 2b). The final step to analyze this data is to convert the response factors into concentrations (Fig. 2c). As an example, this was done here with the single concentration calibration point taken above, creating a 1-point calibration curve and assuming the response is linear as concentration increases. This is not a completely rigorous approach but it is instructive to show that different products have different response factors. Looking at the raw data alone can be misleading as it can be seen from the Figure 2c that 1-propanol and acetaldehyde are being produced at close to the same rates, a point that is not obvious from examining the response factors or raw counts. This is due mainly to the largely different vapor pressures of these two liquids which is convoluted in the conversion of counts to concentration. The conclusion from this experiment is that all three of these

liquids onset together and are produced at a fairly constant rate throughout the experiment. This kind of real-time information about the production rate of liquids from CO2R has not been readily available thus far and it is a strong motivation for further development of this SIFT-MS analytical technology. Details about the gaseous products (namely methane and ethylene) which were also monitored during this experiment are presented in the SI.
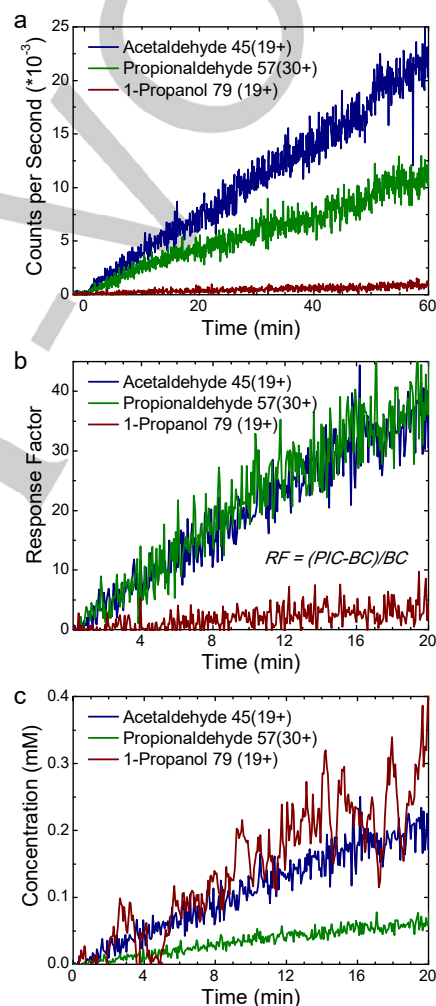

Figure 2. SIFT-MS Analysis of Cu for CO2R: Cu foil was used as a CO2R catalyst at ~-1.0V vs. RHE in 0.1M KHCO$_3$. SIFT-MS was used to analyze the production of acetaldehyde, using mass 45(19+), propionaldehyde, using mass 57(30+), and 1-propanol, using mass 79(19+). (a) The raw counts over the 60 minute run are shown and it can be seen the counts steadily rise, corresponding to the expected rise in liquid product concentration in the electrolyte over time. (b) The raw counts are converted to a response factor, focusing on the first 20 minutes of the run. (c) The raw counts are converted to concentration using a rough 1-point calibration curve.

Outlook

An initial analysis of SIFT-MS to detect the products of CO2R has shown some promise and a partial library of the product ions produced by the SIFT reagent ion reactions in a humid environment has been assembled. The analysis shows that SIFT-MS compares well to the other real-time CO2R product detection systems. The results of the investigation here show that SIFT-MS is clearly capable of at least level 2 detection and with additional study, is likely capable of level 3 detection, for many if not all of the compounds studied here, excluding importantly hydrogen and carbon monoxide. This puts SIFT-MS on par with the system developed by Koper, unable to detect hydrogen but capable of detecting far more aldehydes and alcohols. With additional study on the calibration of the *m/z* response factors, it should be possible to match the level 3 detection developed by Bell with the ability to detect additional products as well. There is the additional advantage that a highly specialized electrochemical cell is not required when coupling to the SIFT-MS as is required with Bell's DEMS setup. This comparison has been summarized in Table 6.

Table 6. Comparison of Real-Time CO2R Analytical Tools: A comparison of SIFT-MS to the state of the art real-time CO2R product detection systems of Bell[38] and Koper[39] is given. The compounds that each system can detect are checked and highlighted in green. The analytical level is given of 1, 2, or 3 with 3 being the highest fully quantifiable detection level.

	H_2	CO	CH_4	C_2H_4	C_2H_6	C_3H_6	HCOOH	CH_3OH	CH_3CHO	C_2H_5OH	C_2H_5CHO	C_3H_7OH	Analytical Level	Comments
Koper	✓		✓	✓	✓				✓	✓	✓		Level 2	Can't be quantitative
Bell	✓		✓	✓	✓					✓		✓	Level 3	
SIFT-MS			✓	✓	✓	✓		✓	✓	✓	✓	✓	Level 2 – Level 3 with additional study	Additional compounds may be detectable with further study

In the future, the product ion library developed here will need to be completed with the remaining CO2R products which were not reviewed: glyoxal, glycolaldehyde, acetic acid, ethylene glycol, hydroxyacetone, acetone, and allyl alcohol. In light of this completed library, the analytical framework to select which *m/z* values can be used to identify each product will need to be reevaluated. This library will also need to be extended to include the testing of these chemicals at multiple concentration levels to ensure the product ion fingerprint does not change. This data can then be used to generate calibration curves to make this analytical technique quantitative.

Some promising initial tests performed here confirm that the chemicals, which were mostly detected as individual components, can still be detected in a mixture as a sum of the mixture's parts. Table 5 summarized a few experiments supporting this conclusion; however, additional tests are needed in this area, utilizing increasingly complex mixtures. The end goal would be to establish a reference table for 16 individual components' RFs and then identifying a mixture of all 16 components showing the resulting RFs are a summation of the individual components. This

procedure would show that all the products from a potentially new CO2R catalyst can be correctly identified with SIFT-MS (level 3 analytical system). Once the SIFT-MS analytical capabilities have been completely understood, the dynamics of liquid product generation on CO2R catalysts, in particular Cu and Cu based catalysts, can be studied in depth.

Conclusions

The application of SIFT-MS to the detection of the products of CO2R was explored. Hypothetically, there are many advantages to using SIFT-MS as an analytical tool over other real-time analysis tools like electron ionization MS. In particular, examination of the literature suggested that the soft chemical ionization utilized in SIFT-MS would allow for the simultaneous detection of most of the CO2R products. When the SIFT-MS was tested in a real experimental setting, it was found that the presence of water vapor in the sample stream dramatically changed the reaction chemistry and thus changed which product ions to expect for an injected analyte. Nevertheless, thorough investigation of a subset of the CO2R products showed that these chemicals could all still be uniquely identified using SIFT-MS. Several sample product combination experiments confirmed the capability of the SIFT-MS to successfully detect, in real-time, the individual components of a mixture qualitatively. Additionally, there is a strong indication that this can be converted in the future to a quantitative analysis. Finally a preliminary examination of the production of acetaldehyde, propionaldehyde, and 1-propanol on Cu CO2R was performed. It was found that all three of these chemicals appear to onset at the same time and are produced at a constant rate throughout the reaction.

Further scrutiny still remains to fully confirm the capability of SIFT-MS to be used as a quantitative, real-time, analytical technique for detecting the products of CO2R; however, the promising results reported here provide a compelling proof of concept.

Experimental Section

SIFT-MS Experiments

The SIFT-MS used in this study was a Voice 200, a commercial tool manufactured by SYFT Technologies. 99.999% pure nitrogen gas was used as the flow tube carrier gas and 99.99% CO_2 was used in some of the experiments (Air Products). The tool uses lab air to create the air plasma that supplied the reagent ions. To control the inlet flow of gas into the flow tube, a mass flow controller (MFC, Alicat Scientific) with a 0.5 – 100 sccm range was used. For all the experiments presented here, an inlet flow rate of 1 sccm was used. The low pressure in the flow tube drove the flow of gas through the MFC, allowing the gas coming from the CO2R reaction cell to remain at atmospheric pressure. The flow of gas from the cell in excess of the 1 sccm inlet to the SYFT was vented. A schematic representation of the setup is shown in Fig. S1.

In order to confirm and quantify the ionization patterns of the product ion library described above for the various products of CO2R, these chemicals were injected into the SIFT-MS one by one. For the gaseous products (methane, ethylene, ethane, propylene), gas cylinders with 100-

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3000 ppm of a single gas were used (Air Products). The cylinders were balanced with carbon dioxide. The concentrations of the gases were selected according to the expected range of concentrations that each gas would reach in the outlet flow of an actual CO2R electrochemical reactor. It was important to purchase these calibration cylinders as single component mixtures, unlike those which are typically used to calibrate a GC, which contain all the gaseous species of interest. The single component mixtures allowed an unconvoluted examination of what masses were produced by each gas in SIFT-MS.

To measure the SIFT-MS response to these gaseous products, the gas first needed to be hydrated. The gas needed to be hydrated as the presence of water vapor in the analyte gas had a large effect on which product ions were observed. To accomplish this, one half of an electrochemical cell (pictured in Figure S1, and described in more detail below) was used, filled with water. Teflon plates were used in place of the electrode and membrane for the half-cell being used. Gas flow into the electrochemical cell was controlled by an MFC. The outlet flow of the half-cell was connected to a mass flow meter (MFM, Alicat Scientific), to ensure there were no leaks in the cell, and then to a T-union. One connection of the T went to the MFC that controlled the inlet flow of gas into the SIFT-MS and the other connection went to some tubing that was open to the atmosphere. It is important to ensure that the flow of gas from the cell remains greater than the gas sampling rate of the SIFT-MS, so that the SIFT-MS will not sample the ambient atmosphere. This was confirmed by the observance of methane (which is present in the atmosphere at ~3 ppm) when the inlet was open to atmosphere and the disappearance of this signal when only pure CO_2 was flown past the inlet in the configuration just described. Furthermore, all metal tubing after the electrochemical cell was wrapped in heating tape to prevent the adsorption of water or other chemicals to the walls. In order to calibrate the SIFT-MS at multiple concentration points per gas, the calibration gas was diluted by co-flowing CO_2 into the electrochemical half-cell using a second MFC.

In order to calibrate the SIFT-MS response to the liquid products of CO2R, formic acid, formaldehyde, methanol, acetaldehyde, ethanol, propionaldehyde, and 1-propanol of the highest available purity were acquired (Sigma-Aldrich). 1 mM standard solutions of these chemicals were made in water, except for formic acid which was made in 0.1 M potassium bicarbonate. These solutions were then placed in the half-cell and CO_2 was bubbled through at 5 sccm, the same flow rate which would be used in a real CO2R experiment. The SIFT-MS sampled the effluent gas from the cell in the same way as described above for the gaseous product measurements. In between measurements, the electrochemical cell was cleaned in 1 M nitric acid to ensure there was no cross contamination.

To build the library of product ions, a selected ion monitoring (SIM) program was used on the SIFT-MS to monitor all masses from 19 to 150 for each of the three reagent ions. With this program it took ~90 seconds to complete one cycle of all the masses, thus each experiment was run for 15 minutes to allow the acquisition of 10 data points per *m/z*. This was enough data to confirm that the effluent being sampled was at steady state. In between sample runs, the inlet of the SIFT-MS was connected to a pure CO_2 flow and the baseline was monitored to ensure it returned to the expected state before continuing

CO2R Experiments

The electrochemical cell used here has been described in detail previously;[71] however, some minor modifications were made for this work (Fig. S2). The cell is composed of an anode and cathode chamber, separated by an anion-conducting membrane, Selemion AMV (AGC Engineering Co.). A 1 mm OD Ag/AgCl reference electrode (Innovative Instruments) was inserted into the cathode chamber to monitor the working electrode potential. This reference electrode was calibrated against an ideal reversible hydrogen electrode. The cell used here differed from the previous design in that it was machined out of polyether ether ketone (PEEK) instead of polycarbonate. PEEK is a more chemically-resistant material, in comparison with polycarbonate, which allowed for the use of strong acids in the cleaning procedures. This lead to more reproducible experimental results (due to the improved cleaning procedure). In addition, a small glass sheath was added to the reference electrode port, which prevented the accumulation of bubbles on the electrode and produced more stable chronoamperometry data. The cell was sealed by compressing the stack of counter electrode, anode chamber, membrane, cathode chamber, and working electrode between two outer plates secured with bolts. The seals were made with FEP-coated Viton O-rings (McMaster Carr).

99.995% base metal pure potassium carbonate (K_2CO_3) (Sigma-Aldrich) was used as the precursor salt for making the 0.1 M potassium bicarbonate ($KHCO_3$) electrolyte used in this study. The conversion of carbonate to bicarbonate electrolyte is achieved by sparging the carbonate electrolyte with 1 atmosphere of CO_2. The complete conversion of the electrolyte was confirmed by measuring the pH of the solution to be less than 6.82.

The cell was assembled with a new Cu foil as the working electrode, a platinum foil counter electrode, and a piece of Selemion membrane. Before each experiment, 2 ml of electrolyte was injected into each compartment of the cell and CO_2 was bubbled through the cell at 5 sccm and 1 atmosphere. A Biologic VSP-300 potentiostat with electrochemical impedance package was used to measure the electrochemical impedance of the cell in order to enable *in-situ* iR compensation. 85% compensation was used to correct for the cell resistance (the uncompensated resistance was ~60 ohms). The remaining 15% of the uncompensated resistance was corrected for *ex-situ*. A constant voltage was applied versus the Ag/AgCl reference electrode for 70 minutes and the gas exiting the cathode compartment was directed to the SIFT-MS, as described previously, for product analysis.

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Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

Here we demonstrate the first use of selected-ion flow-tube mass spectrometry (SIFT-MS) as an analytical tool capable of measuring in real time both the gaseous and liquid products of electrochemical CO_2 reduction in aqueous solution. We lay out the framework in which to evaluate the tools capabilities and show that the C_1-C_3 hydrocarbon, alcohol, and aldehyde products of CO2R can be quantitatively detected.
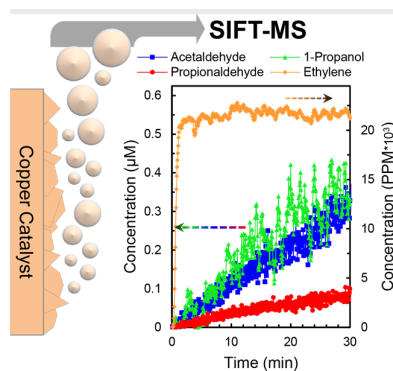
Peter Lobaccaro, Lily Mandal, Mallikarjuna Rao Motapothula, Matthew Sherburne, Jens Martin, T. Venkatesan, and Joel W. Ager*

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Initial Application of Selected-Ion Flow-Tube Mass Spectrometry to Real-Time Product Detection in Electrochemical CO_2 Reduction