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MASTER THESIS

Topic:

**Application of Fourier Transform Infrared (FTIR) Spectroscopy on the
electrochemical reduction of carbon dioxide**

Submitted by Amidu Bah

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Dedication

To my beloved parents:

Mr. Hassan Bah(late)

Ya Aminata Bundu.

To my lovely wife:

Fatou Jobe

To my elder brother:

Mr. Sheriff Bah

And my children:

Abdulrahman Bah

Mustapha Bah.

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ABSTRACT

The global challenge today is that of climate change which is mainly attributed to the excess emission of greenhouse gases, especially carbon dioxide produced from the burning of fossil fuels. The sources of carbon dioxide are anthropogenic and they include power generation, transport, industrial sources, chemical production, petroleum production and agricultural practices. Most of these sources burn coal, oil, and natural gas, which releases carbon dioxide as a by-product. One of the ways to reduce carbon dioxide emission is to use renewable energy resources. Photovoltaic technology which uses solar energy can generate enormous amounts of electricity whose excess can be used to electrochemically reduce carbon dioxide into fuels and other chemicals. Storing renewable energy into chemicals is a very important technique since renewable energy sources are intermittent which is due to seasonal variations. The ability to show what happens in the electrochemical reduction reaction of carbon dioxide to produce fuels and other valuable chemicals is a prerequisite for the development of electrochemical reactions. Fourier Transform Infrared (FTIR) spectroscopy techniques of transmittance and attenuated total reflectance are capable of revealing most of the functional groups of the important intermediate species and products of carbon dioxide reduction reactions. The choice for FTIR techniques over the other spectroscopic techniques such as, atomic, ultraviolet and visible, Raman NMR and mass spectroscopy is that, FTIR techniques are faster and reliable in sample analysis, and are not destructive to the samples. Having an insight into how the electrochemical reduction of carbon dioxide works and the ideal conditions of the reaction, is key towards the development and upscaling of carbon dioxide reduction technology. FTIR application on carbon dioxide reduction reaction identifies and profiles reaction species of reagents, intermediates, products and by-products of the reaction. This work looks at the application of FTIR techniques (transmittance and attenuated total reflectance) on the electrochemical reduction of carbon dioxide, so as to have an insight into the products formed using the ex-situ approach.

In this work, five samples of saturated carbon dioxide in potassium hydrogen carbonate, purged with various concentrations of folic acid were analyzed using the FTIR techniques of transmittance and attenuated total reflectance. The results from both techniques showed the functional group hydroxyl ion (OH^-) of carboxylic acid, carbon monoxide and carbon dioxide in all the samples analyzed. Similar results were also shown in a gas chromatography device with the same samples

analyzed in the FTIR. Hydrogen was not seen in the FTIR results but showed up in the gas chromatogram, and in addition, showed the concentration of the gas products in the samples. A combination of hydrogen and carbon monoxide (H_2 and CO) in the right ratio can be used to produce green fuel (syngas) in the Fischer-Tropsch process, with the use of photovoltaic technology as a source of electricity to power the reactions.

Keywords: Infrared (IR), Electrolytic Cell (EC), Fourier Transform Infrared (FTIR) spectroscopy, Carbon dioxide reduction reaction (CO_2RR), Potassium hydrogen carbonate ($KHCO_3$).

RÉSUMÉ

La capacité à montrer ce qui se passe dans la réaction de réduction électrochimique du dioxyde de carbone est une étape très importante dans la lutte contre les problèmes du changement climatique. Les techniques FTIR de transmittance et de réflectance totale atténuée sont tout à fait capables de révéler tous les groupes fonctionnels des espèces intermédiaires importantes et des produits des réactions de réduction du dioxyde de carbone. En plus de ces outils puissants, il est également possible d'approfondir la recherche sur la conception de catalyseurs pour la sélectivité des produits. J'ai étudié l'application des techniques FTIR (transmittance et réflectance totale atténuée) à la réduction électrochimique du dioxyde de carbone et, en plus de cette technique, la chromatographie en phase gazeuse a également été utilisée pour analyser les mêmes échantillons afin d'obtenir un résultat de référence avec lequel comparer les résultats des techniques FTIR. Dans ce travail, cinq échantillons ont été préparés : hydrogénocarbonate de potassium aqueux réduit ($KHCO_3$), $KHCO_3$ purgé avec trois concentrations différentes d'acide folique (AF) et $KHCO_3$ purgé avec du dioxyde de carbone. Les résultats des deux techniques ont montré clairement la présence d'acide carboxylique dans tous les échantillons analysés par les techniques FTIR et les résultats montrent également la présence de gaz d'hydrogène et de monoxyde de carbone. L'efficacité faradique du monoxyde de carbone était comprise entre 80 et 92 %, tandis que celle de l'hydrogène était comprise entre 8 et 21 %. Une combinaison de ces gaz (H_2 et CO) dans le bon rapport peut être utilisée pour produire du carburant vert (gaz de synthèse) dans le procédé Fis.

Mots clés : Infrarouge (IR), cellule électrolytique (EC), spectroscopie infrarouge à transformée de Fourier (FTIR), réaction de réduction du dioxyde de carbone (CO₂RR), hydrogénocarbonate de potassium (KHCO₃).

Acronyms and Abbreviations

ATR : Attenuated total reflectance

COP : conference of parties

CO₂RR : Carbon dioxide reduction reaction

EC : electrolytic cell

EPDM : Ethylene propylene diene monomer

FTIR : Fourier transform infrared

EPDM : Ethylene propylene diene monomer

PTFE : Polytetrafluorethylene

KHCO₃ : Potassium hydrogen carbonate

(aq) : aqueous

(g) : gas

(l) : liquid

GDL : gas diffusion layer

GDE : Gas diffusion electrode

SEIRAS : Surface enhanced infrared absorption spectroscopy

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Chapter I

INTRODUCTION

1.1 Problem statement

The emission of greenhouse gases at current levels is a threat to human existence. The transport sector and manufacturing industries, largely powered by fossil fuels, are the main sources of the increase of carbon dioxide (CO₂) concentration in the atmosphere. The molecule of carbon dioxide belongs to greenhouse gas which have led to the effects of climate change. The effects of climate change are so devastating that they are threatening the survival of every living thing on earth (<https://ourworldindata.org/co2-and-greenhouse-gas-emissions>), (<https://www.transportenvironment.org>).

Carbon dioxide sequestration and capture methods (post-combustion, pre-combustion and oxy-combustion, etc.) were initially developed to reduce the concentration of CO₂ in the atmosphere. However, these methods are limited by the risk of CO₂ leakage (Madejsk *et al.*, 2022 , Odunlami *et al.*, 2022).

New carbon dioxide reduction methods (thermochemical, photochemical, electrochemical) are moving towards more efficient processes for reducing CO₂ concentrations in the atmosphere. These methods involve transforming CO₂ into other more useful chemical compounds and will provide a means of renewable energy storage in such products (CH₄, C₂H₅OH, H₂ and other hydrocarbons.....). (Zheng, Y., et at., 2019)

To efficiently reduce the presence of CO₂ concentration in nature is to electrochemically reduce it into other chemical products that may have high economic benefits. It is important to be able to identify and analyze what is produced during the electrocatalytic reduction of carbon dioxide. Fourier transform infrared spectroscopy (FTIR) techniques can be used to analyze and identify the products formed from the electrochemical reduction reaction process of carbon dioxide.

FTIR techniques (transmittance and attenuated total reflectance infrared spectroscopy) are faster and more reliable compared to other analytic techniques, and should be quite useful in identifying the products of carbon dioxide reduction in order to ascertain that electrochemical reduction of carbon dioxide into fuels and other chemicals, is a useful and dependable technology. The

application of FTIR techniques will give an insight about the products of solar fuels formed, such as methane, ethane, ethene, alcohols and carboxylic acids.

1.2 Research Question

How suitable are FTIR techniques for the analysis of the products of carbon dioxide reduction reaction?

1.3 Research Hypothesis

If FTIR techniques (transmittance and attenuated total reflectance) can analyze and identify the products of the electrochemical reduction of carbon dioxide, such as methane, ethene, aldehydes, ketones and alcohols, then these techniques should be applicable in revealing the intermediate species and products of all chemical reactions.

1.4 Research Objectives

The aim of this thesis is to use Fourier transform infrared spectroscopy (FTIR) techniques (transmittance and attenuate total reflection-infrared) to enable us identify and analyze the products of carbon dioxide reduction in electrolytic cells. This work is looking at converting carbon dioxide into artificial fuels and other important chemicals that will help to reduce our dependency on fossil fuels.

The main objective of this thesis is to analyze the products of carbon dioxide reduction using FTIR techniques. This main objective will be achieved through these following specific objectives:

- ✓ To electrochemically reduce carbon dioxide with a silver catalyst in an alkaline electrolyte.
- ✓ To identify the products formed in the reduction of carbon dioxide using FTIR techniques.

1.5. Thesis' structure

This thesis is mainly consisted of three parts (literature review, methodology and results and discussion) preceded by an introduction and followed by a conclusion is proposed.

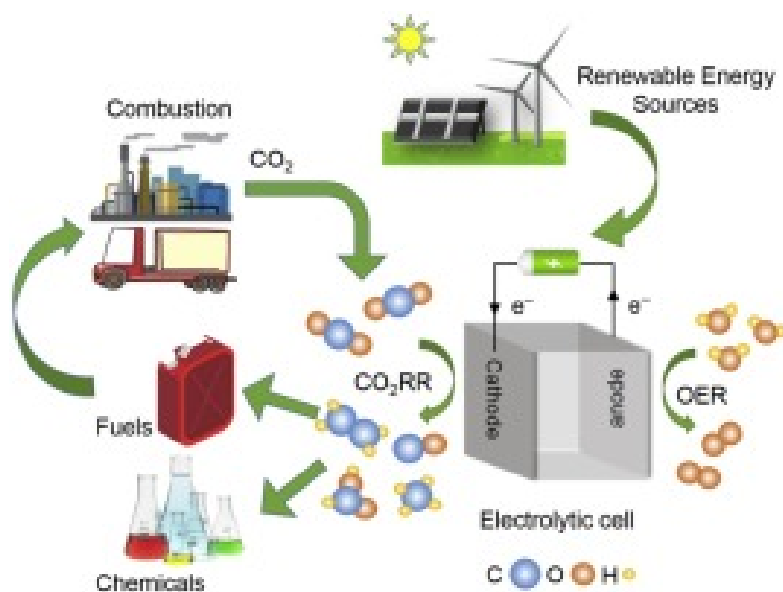


Figure 1: Coupling renewable energy sources to electrochemical cells and industries.
 (DOI:10.1016/j.jcou.2019.09.007)

Chapter II

Literature Review

One of the ways to control the concentration of carbon dioxide in the atmosphere is to electrochemically reduce it into other chemical products that may have high economic benefits, and will provide a means of renewable energy storage in such products. FTIR techniques can be used to analyze and identify the products formed from the electrochemical reduction reaction process of carbon dioxide.

A review of literature from several articles has outlined some of the challenges, solutions and future prospects on how carbon dioxide reduction can produce valuable products that can be identified and analyzed using FTIR techniques. The FTIR techniques used in this work were Transmittance and ATR-IR spectroscopy.

Kumar N., et al., (2023) : reported that carbon dioxide is the main raw material for plants to make their food through photosynthesis but on the other hand, too much concentration of it in the atmosphere can cause climate change , whose effects are very devastating ranging from floods, sea-level rise and drought. The removal of excess carbon dioxide from the atmosphere is therefore a very important process to save lives and properties. K, Namesh et al., examined methods that could be used to remove carbon dioxide from the atmosphere especially direct carbon capture through a chemical process of extraction and storage in a liquid or solid state. Air is drawn into a chamber and compressed. It is then made to react with sodium hydroxide to sodium carbonate. This is a way in which carbon dioxide is temporarily stored. Later , it will be heated to release the carbon dioxide, from where it is used as a raw material to produce valuable materials like solar fuels, carboxylic acids and alcohol.

Pawel M., et al.,(2022) discuss different techniques of carbon dioxide capture techniques that can be used to reduce its concentration from the atmosphere, and also to use it as a raw material to produce valuable products. The capture techniques consider combustion from chemical absorption, physical and membrane separation, chemical looping combustion, calcium looping process and oxy-combustion. The authors of this paper also reported that as at 2021, there were about 27 numerous projects developing to invest on carbon dioxide capture. If all these projects operated successfully, it is estimated that they will reduce about 150 Mt/ year of carbon dioxide.

Verma, S., & Yadav, A. (2023) wrote on the significance of photoelectrochemical conversion of carbon dioxide into solar fuels (methane, ethane, and ethylene), and other valuable chemical substances like alcohols and organic acids. The method of their research is mimicking photosynthesis. The document reviewed electrodes, species kinetics and modified the reactor designed for the photoelectrochemical conversion of carbon dioxide. This work utilized 2D/3D materials, carbon-based catalysts and biological molecules, and uses photovoltaic tandem cell technology as a source of green energy.

Odunlami O.A., et al., (2022): investigated advanced technologies of carbon dioxide capture in reference to already established ones. The aim is to remove excess carbon dioxide from the atmosphere in order to avert the effects of climate change. This paper looked at adsorption, absorption, cryogenic separation and a combination of several other techniques in order to determine the most suitable technique of carbon dioxide capture and storage. Though energy intensive and threat to vessel corrosion, the absorption technique of carbon dioxide capture is more efficient, according to this paper. The authors have highlighted advanced methods such as ionic liquids, zeolites, molten carbonate fuel cell and integration with several other components that enhance efficiency carbon dioxide capture. The authors finally concluded that molten carbonate fuel cells of the three advanced methods.

Perez, E.R., et al., (2005): In situ FT-IR and ex situ EPR (electron paramagnetic resonance) analysis have demonstrated the formation of free radicals in the absence of CO₂ and at potentials more negative than -1.8 V (SCE). This technique allows one to obtain information on the structure of active sites in catalysts and also to study the reaction dynamics of the reaction system where these free radicals are formed. FT-IR measurements using s-polarized light have proved that these radicals are in solution.

Wang, W., et al., (2021): Combining X-ray absorption technique with in situ FT-IR spectroscopy techniques (transmittance and attenuated total reflectance) reveal that, Cu catalyst mainly existed in the form of CuO when inside an electrolyte, while Cu⁺ which obtained from photocatalytic reaction, forms on the surface layer of the CuO matrix becoming the active site for the attachment of CO and for further C-C to form C₂H₄ (ethene).

The intermediates that resulted to the formation of these valuable products were first generated and observed by in situ FTIR during the photocatalytic process of carbon dioxide. This work uses

the method of photocatalysis to reduce carbon dioxide into formate and ethene with the application of in situ FTIR spectroscopy.

Cao, X., et al (2021): In situ and operando techniques with real-time monitoring are important to obtain deep insight into the electrocatalytic reaction to reveal the dynamic evolution of electrocatalysts' structure and composition under experimental conditions. In this paper, the reaction pathways for the CO₂ reduction reaction (CO₂RR) in the generation of various products (e.g., C₁ and C₂) was conducted and monitored in situ with FTIR techniques. *CO and *OOCH radicals were revealed that lead to the formation of formate, carbon monoxide and ethane. Moreover, recent advances in the development and applications of in situ and operando characterization techniques, from the basic working principles and in situ cell structure to detailed applications are discussed.

Iwasita, T., et al.,(1992) :Three different coordinated forms of CO adsorbed to the platinum surface were observed for methanol, formic acid and reduced carbon dioxide: linear-, bridge- and multi-bonded CO. Using new experimental approach absolute absorption bands are observed for the adsorption of methanol and reduced carbon dioxide. Sample spectra are computed with respect to a reference spectrum which is taken before adsorption. In this way the presence of a COH adsorbate is demonstrated.

Firet, N. J, & Smith, W.A (2017): In this work, studies were done on the reaction mechanism of silver as a CO₂ reduction catalyst using in situ attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) during the electrochemical cycling. Using ATR-FTIR, it is possible to observe the reaction intermediates on the surface of Ag thin films formed during the CO₂ electroreduction reaction.

At a moderate overpotential, a proton coupled electron transfer reaction mechanism is confirmed to be the dominant CO₂ reduction pathway. However, at a more negative applied potential, both the COO⁻ and the COOH intermediates are detected using ATR-FTIR, which indicates that individual proton and electron transfer steps occur, offering a different pathway than at lower potentials.

These results indicate that the CO₂ reduction reaction mechanism can be potential dependent and not always involving a concerted proton coupled electron transfer, opening alternative pathways to optimize efficient and selective catalysts for desired product formation.

M. Nur Hossain, *et al.*, (2017) reported that copper nanoparticles and reduced graphene oxide deposited on a glassy carbon electrode produced very good results, showing formate and carbon monoxide as the main products based on the gas chromatography (GC) and high-pressure liquid chromatography (HPLC) analysis. The study of this reduction reaction using ATR-FTIR technique on the Cu/rGO at in situ reveals the important intermediates of *COH and *OOCH at different cathodic potentials which gave rise to the products of formate and carbon monoxide. J. Li, *et al.* (2022) outlined that the high content of water (H₂O) in aqueous electrolyte of KHCO₃ interferes with spectral analysis that probes the concentration of CO₂ (aq) dissolved in the electrolyte. Water has the tendency to absorb IR spectrum and hence interferes with the carbon dioxide, and other products in the electrolyte in terms of their spectral peaks. The authors of this literature suggested the use of heavy water (D₂O) which form spectral peaks in the fingerprint region, away from the main products or their functional groups are formed.

Zhao, Y., *et al.*, (2022) argued that copper is an excellent catalyst and has the selective property of reducing CO₂ and water into C₁ and C₂ products based on properties of its morphology. Vibrational spectroscopic techniques such as Raman and FTIR reveals *COO and *CHO intermediates on the copper surface as the reaction proceeds.

Hori, Y., *et al.*, (1989) suggested that one of the ways to obtain higher order carbon compounds from carbon dioxide reduction is to design a Cu-Ag catalyst combination which will increase the active sites of the reaction and favors C₁ and C₂ products and will also provide a better understanding of the reaction mechanism with the help of FTIR in situ techniques that will show all the reaction intermediates such as, *HCOO⁻ and *OCH. These species will form the valuable products of solar fuels and acids.

Osawa, M., (1997) reported that the use of SEIRAS(surface enhance infrared spectroscopy) is quite helpful in understanding the reaction mechanism of CO₂RR because it showed the reaction intermediate molecules that appear in the process, and these intermediates determine which products will be formed at the end of the reduction process of carbon dioxide.

One of the most commonly formed intermediates is *CO. The *CO intermediate shows asymmetric peaks between 2100 – 1900 cm^{-1} at -0.4 V potential in CO_2 saturated $\text{KHCO}_3(\text{aq})$ electrolyte, using the most promising electrocatalyst, Cu, for the conversion of CO_2 to CO, HCOOH, CH_4 , C_2H_4 and $\text{C}_2\text{H}_5\text{OH}$.

Jiang, T. *et al.*, (2021) reported that CO_2RR to formate and/or carbon monoxide on Pd-based electrodes is mainly dependent on the electrode potential and the nature of the electrode. However, this assertion can only be proven with spectroscopic techniques such as FTIR-ATR-SEIRAS (Fourier transform infrared -attenuated total reflectance-surface enhanced infrared absorbance spectroscopy), DEMS (differential electrochemical mass spectroscopy), GC(gas chromatography), and NMR (nuclear magnetic resonance).

Xu, Z., *et al.*, (2021) explained that it is very important to include vibrational spectroscopic techniques such as, FTIR and Raman, in the carbon dioxide reduction reaction process so that the knowledge of the states of the catalysts will be known in order to be able to identify the most important reaction intermediates that determine the formation of the products under the prevailing reaction conditions.

Chen, S., & Chen, A. (2019) asserted that Au is an efficient electrocatalyst for carbon dioxide electrochemical reduction reaction. When this reaction is done in situ with the application of ATR-IR spectroscopic technique, the reaction kinetics and intermediates could be observed directly. ATR-IR peaks revealed COO^- as the main intermediate, CO and HCOO^- as the main products. This method has carbon monoxide and formate as the main products during CO_2RR when Au Nanoparticles are used as electrocatalyst on the cathode surface.

Zhu, S., *et al.*, (2019) designed an Au-Pd nanoparticles material in a 94:6 ratio respectively, and encapsulated this material in a thin film shell of Pd. The experiment was done in situ and the FTIR spectroscopic evidence showed the presence of *CO intermediate species being released from the balanced arrangement of *COOH/*CO adsorption on the surface of the Au-Pd core shell catalyst to form the required CO product.

Zhu, S., *et al.*, (2019) argued that the challenges faced by copper as an electrocatalyst to directly convert carbon dioxide to hydrocarbon products are based on the fact that Cu cannot produce evidence of reaction intermediates in the downstream of *CO even on well-prepared thin films. It

has short residual time of the $*\text{CO}$, $*\text{COO}^-$ and HCOO^- intermediates on its surface and weak adsorption of these intermediates, as revealed through SEIRAS- FTIR spectroscopy techniques.

Cu could do better as an electrocatalyst only when coupled with its oxide or alloyed with Ag, in which case, this combination will increase its active sites and activity. Also, the wavenumbers detected from the Silicon prism (below 1200 cm^{-1}) on the ATR-IR spectroscopic device pose another challenge for the proper identification of the products formed when Cu alone is used as electrocatalyst, as this wavenumber is in the finger print region.

Katayama, Y., *et al.*, (2018) also argued that although polycrystalline Cu surfaces have long been known for their unique characteristic property of catalyzing CO_2 to C_1 and C_2 products such as, CH_4 , C_2H_4 , etc., and alcohols, it is still challenged with low selectivity of products.

Even when SEIRAS in situ technique was applied, Cu is not able to produce the main intermediates that are required to produce hydrocarbon products. The authors of this literature stated that when alloy of Cu, Pt, and Au catalyst was used, there was an excellent yield of hydrocarbons, and the important intermediates the reaction were shown such as, COO^- , CHO and $*\text{CO}$ were revealed using the surface enhanced infrared adsorption spectroscopy (SEIRAS) technique. They also revealed that there is an affinity between metal-oxygen and metal-carbon which facilitates adsorption of C- and O- bound intermediates into the catalyst to produce the intermediates for C_1 and C_{2+} products.

Wang, G., *et al.*, (2021) explained that there are multiple advantages of the electrolytic carbon dioxide reduction reaction which gives a bright future to our planet. The authors of this literature focused on improving the selectivity properties of newly designed electrocatalysts by alloying Cu and Ag/Au/Pt, and also to design an electrolyzer that is compatible to in situ surface enhanced infrared absorption spectroscopic (SEIRAS) techniques in order to identify the important intermediates of the reduction reaction of carbon dioxide.

Xu, Z., *et al.*, (2021) also supported that the structure-activity relationship and reaction mechanism of a catalyst, coupled with vibrational spectroscopic techniques (SEIRAS, Raman and FTIR) applied during in situ operations of carbon dioxide electrochemical reduction, will reveal the state of the electrocatalyst and the important intermediates formed as the reduction reaction proceeds.

In addition, vibrational spectroscopic techniques can show the surface transformation, active sites and other interfacial intermediates under the reaction conditions. This information revealed by SEIRAS is very useful in determining the products formed and supports further research for the development of new catalysts.

Yi, J.D., *et al.*, (2020) reported that vibrational techniques (Raman and FTIR) reveal *CH_2O and *OCH_3 are the main intermediates species of carbon dioxide reduction needed for the formation of CH_4 selectivity in the electrochemical process.

The main issue discussed by researchers today is surrounded around the huge potentials presented by carbon dioxide reduction reaction to produce hydrocarbons using renewable energy as a clean source of energy and also a means of energy storage from the excess produced during favorable seasons. This technique is quite useful towards reducing the concentration of carbon dioxide from the atmosphere and help in the mitigation of the challenges of climate change.

In our quest to achieve our dream of attaining carbon neutrality using carbon dioxide reduction reaction technique, there is need to improve the efficiency of this technique and make it feasible for industrial applications. Achieving this dream is dependent to a large extent on our understanding about what happens in an electrolytic cell that will bring about the formation of the numerous valuable products such as, solar fuels (methane, ethane, propane, butane and alcohols), organic acids, aldehydes and ketones.

FTIR techniques (transmittance and attenuated total reflectance) provide the unique opportunity in providing us with the insight about the reaction intermediates and products of the reduction reaction that goes on in the electrolytic cell. Having a knowledge of what a chemical reaction is set to produce is quite interesting and motivating, particularly when such a reaction is intended to produce valuable products from carbon dioxide, a gas seen largely as a greenhouse gas pollutant. Nothing else good is expected to come from it other than its use by green plants to make their food from it through photosynthesis.

The vibrational spectroscopic FTIR techniques (ATR-IR and Transmittance) have proven to be a very powerful tool that is quite applicable to identify and analyze the surface transformation, active sites of electrocatalysts, and interfacial intermediates, of the liquid products under the reaction conditions of carbon dioxide reduction reaction.

However, the products of carbon dioxide reduction are many and they include liquids, gases and functional groups of intermediate species. In this thesis, the aim is to include gas chromatography technique in addition to the FTIR as a reference device to FTIR, and also to identify those species in the fingerprint region of the FTIR window that may not be easily and accurately identified by the FTIR device.

In addition, GC can easily quantify the concentration of the products directly. Methane, carbon monoxide, ethylene, ethene, hydrogen, alcohol and carboxylic acids are among the major products of carbon dioxide reduction reaction that can be seen through the FTIR techniques of transmittance and attenuate total reflectance.

Chapter III

Materials and Methods

3.1 Fourier Transform Infrared (FTIR) Spectroscopy Device

FTIR device consists of four major components which includes a light source, an interferometer, sample chamber and a detector. The chamber that is a path through which infrared light emitted from a source is passed through a sample holder to a detector. The sample holder component of this device is placed between the IR light source and the detector. As light always travel in a straight path, the sample holder is designed in a way that it attaches itself firmly in a bottom frame bracket along the chamber of the device through which the IR light passes.

In this way, the IR light will pass through the sample and the transmitted radiation produced from the sample is sent to the detector. The different molecules in an infrared-sensitive sample have different bond energies which is why they absorb light of different wavelengths and hence produce different signals in the detector which serve as a fingerprint in the identification of each molecule contained in the sample. The infrared light source is a broadband emitter of mid-IR ceramic source between $50 - 7800 \text{ cm}^{-1}$.

The interferometer splits the beam of IR light from the source into two paths. One light path goes to a fixed mirror, the other goes to a moving mirror which aids better illumination and interaction of light on the sample. The pyroelectric detector used with the FTIR spectrometer has two doped element-based elements, deuterated alanine doped triglycerine sulphate (DTGS). The IR light coming into the detector heats up the DTGS material and cause it to expand and change the dipole orientation of the material which generates a signal displayed as spectra. The chamber is the column where IR light passes from its source, through the sample into the detector.



Figure 2: FTIR apparatus for Transmittance Technique

(Source: <https://lotusgemology.com/index.php/2-uncategorised/294-ftir-in-gem-testing-ftir-intrigue-lotus-gemology>)

Figure 3 is a chart showing the electromagnetic radiation spectrum with all the energy levels of the lights, their wavelengths, energy and frequencies. The spectrum also shows the part of the spectrum that relates to FTIR techniques (mid-infrared) in the wavenumber range of 4000 to 400 cm^{-1} .

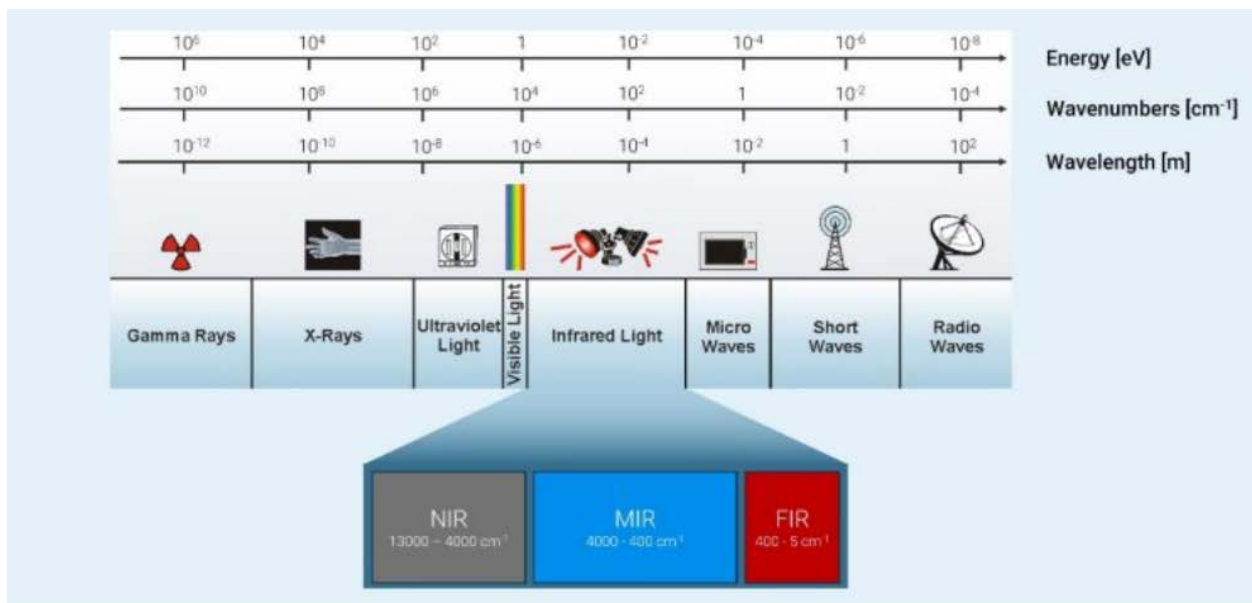


Figure 3: Electromagnetic spectrum

What is seen below in figure 3 are the various vibrational movements of infrared sensitive molecules. Each molecule vibrates according to the amount of IR light that it absorbs that will dislodge their bond energy and cause a change in their dipole charge. The new dipole arrangement is what cause to vibrational stretches, bending, twisting, wagging and rocking. Carbon dioxide molecules can vibrate by symmetric stretching, bending and asymmetric stretching. After stretching, the molecules then lose their excitation energy and emit the IR light they absorbed before and assume lower energy state.

Vibration resulting to changes in bond angle of a molecule cause deformation or bending. Vibration that leads to changes in bond length cause stretching. The wavenumber of C=O stretch is between $1760-1690\text{ cm}^{-1}$, while that of C-O stretch is between $1320-1210\text{ cm}^{-1}$. Bonds in molecules that stretch in-plane form symmetric stretching, while those that stretch out-of-plane form asymmetric stretching.

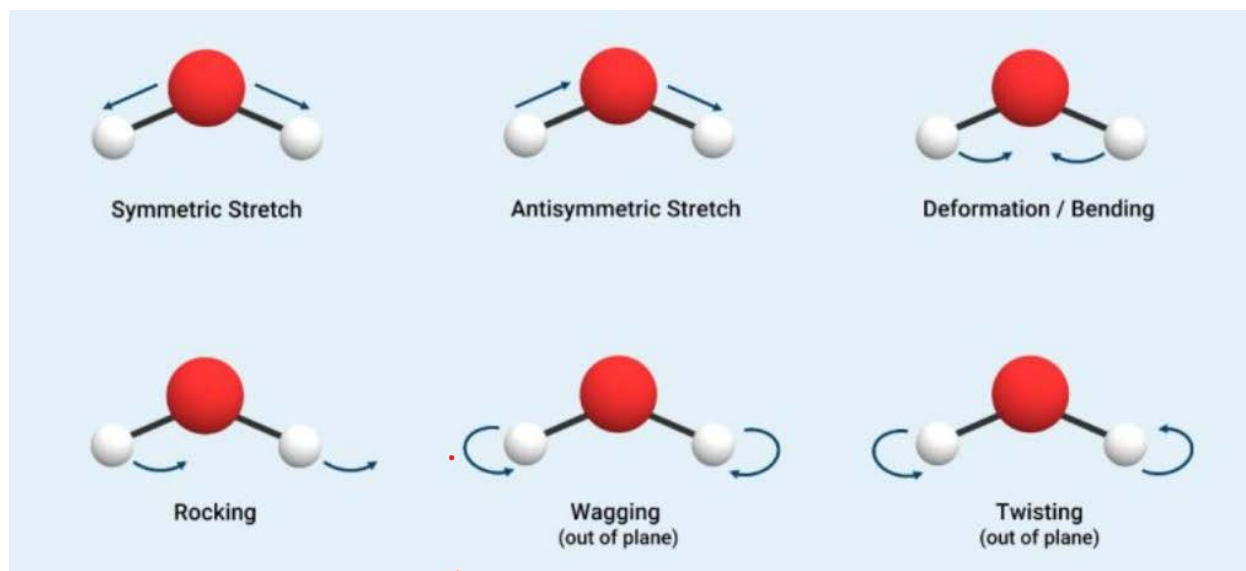


Figure 4: The various vibrational modes of IR sensitive molecules based on their bond angles and bond length to mid-infrared light

FTIR spectroscopy can provide real-time tracking and monitoring of reaction progress to help develop ideas in how reactions work and how to improve on their activity. Chemical reactions are too complex and therefore understanding how they work is a major challenge and an opportunity for researchers. Knowing how reactions work and the ideal conditions to develop, scale-up and

operate processes are very important towards achieving our research objective, final products and their purity.

Functional groups library (figure 5) is used as a standard from which peaks detected from sample analysis are read and assigned a name or character. It is divided into two regions. The region from 1500 – 4000 cm^{-1} wavenumber is referred to as the structural or functional group region, and this region can be analyzed distinctly without challenges due to the clear nature of its peaks. The region to the right, fingerprint region, is from 1500 – 500 cm^{-1} wavenumbers. This region cannot be interpreted easily because it contains many complicated series of absorption mainly due to several bending vibrations within the molecule

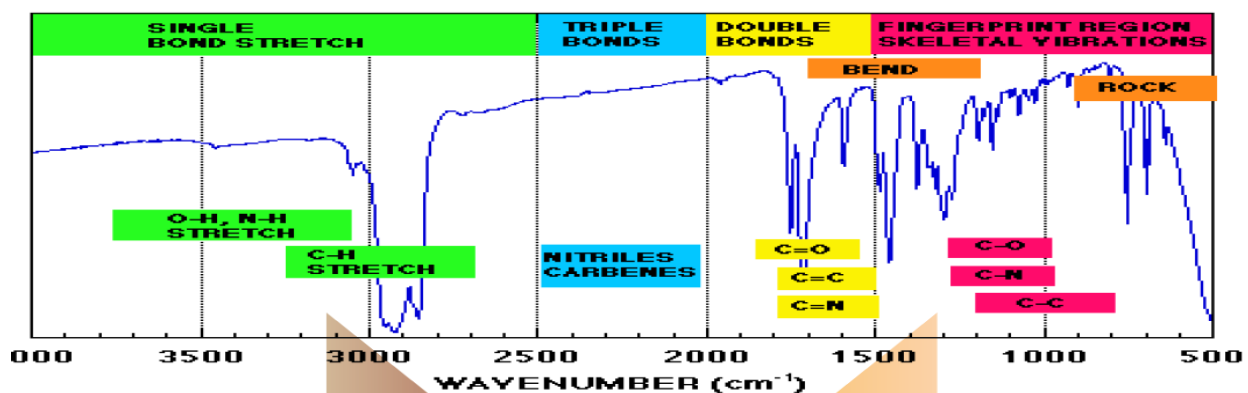


Figure 5: Functional groups library for FTIR spectroscopy

(Source: <https://www.chm.bris.ac.uk/webprojects1997/RogerEC/welcome.htm>)

3.1. The FTIR chamber

The FTIR chamber is a column where the IR light passes from the source, through the sample to the detector. It operates both in a ventilated and evacuated mode. A ventilated chamber is one kept under atmospheric pressure with inert gas (eg, Neon) circulating within the chamber. This condition helps to maintain liquid samples in place.

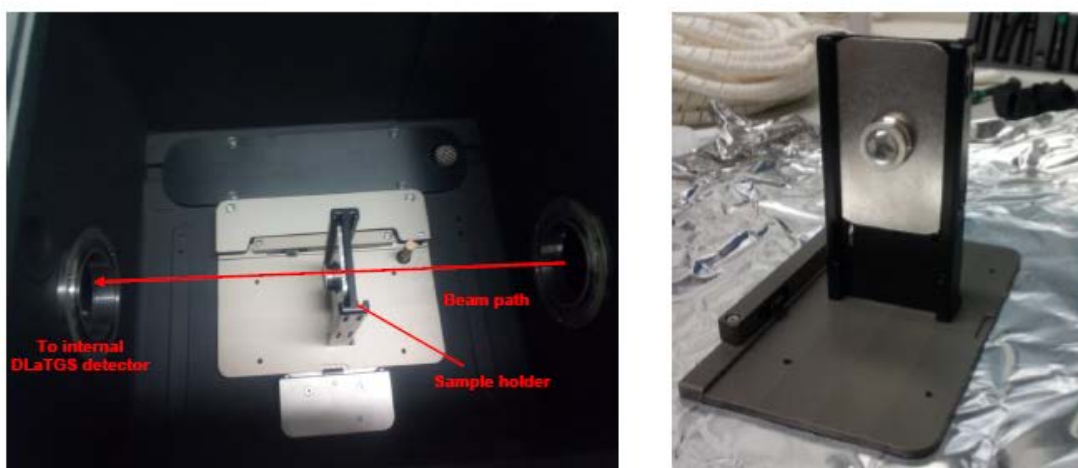
Evacuated chamber is one under a low pressure. As air is drawn out of the chamber, liquid samples become frozen. This may render the molecules of the sample insensitive to IR light and will not allow transmission.

In this work both chambers (evacuated and ventilated) were used in order to investigate the effect of pressure on the samples that were analyzed. Results in the evacuated (low pressure) chamber

showed results that had almost 100% absorption. This meant zero transmittance. It was suspected that the samples got frozen and absorb all the IR light. The vent chamber analysis with the same samples showed clear peaks of transmittance. The vent chamber created a high pressure on the samples, like thermodynamic work done into the system, that created changes in the bond angles and lengths of the samples causing them to vibrate and emit absorbed IR light to the detector for analysis.

Sample compartment

Interior



Mitglied der Helmholtz-Gemeinschaft



Figure 6: The FTIR Transmission chamber

3.2. The Sample Holder and its components

The figure 6 shows SPECAC omni-cell liquid and solid sample holder for FTIR transmission technique. This device holds liquid samples that can be analyzed by IR light through transmission spectroscopy. It has window materials that are pH selective, path length and spacers suitable for FTIR sample analysis.

It is important to note that the chemical properties of the sample to be analyzed and its IR light wavelength range of absorption, is what determine the choice of window materials, the path length and window configuration for its sample analysis. Some of the window materials available for the omni-cell liquid sample holder include sodium chloride, potassium bromide, calcium fluoride, Barium fluoride, Zinc selenide, Silica(IR), Silver bromide, Silicon and Polythene.

This thesis used the quantitative methodology for sample analysis and therefore works with a measured pathlength of 0.5 mm and calcium Fluoride window material. The reason for the choice of the short pathlength is that the shorter the path length, the sharper the image of the spectra. Calcium Fluoride window material was quite suitable because it is insoluble in an aqueous solution of a slight alkaline character. Also, it was used because of its availability even though it has a high refractive index of 2.4, and this may affect image brightness of a spectra (Rigaut et al 1990, Shaw and Rawlins 1991, Carlsson 1991). The choice for Omni-cell liquid sample holder is because it is compatible with all FTIR spectrometers and can easily be configured with demountable liquid cells, permanently sealed liquid cells or mull cells.

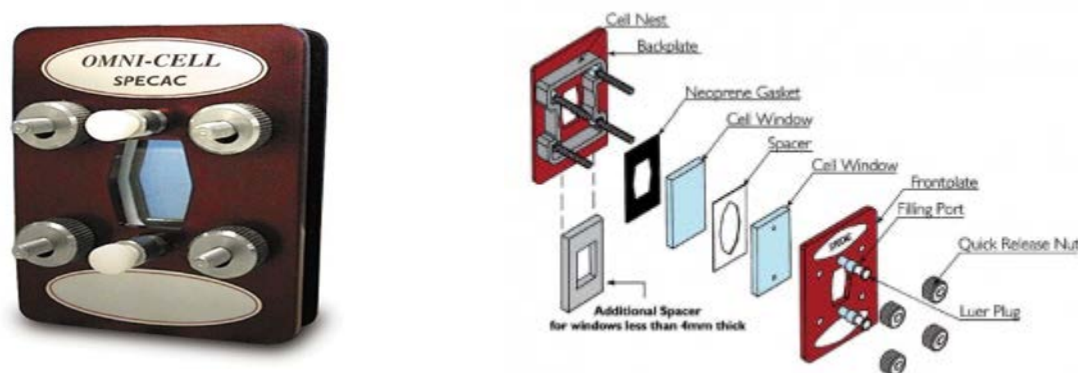


Figure 7: Liquid and solid samples holder for FTIR Transmittance spectroscopy

(Source: <https://www.sigmaldrich.com/DE/de/product/sial/z804428>)

3.3. Preparation of liquid samples

If a liquid sample is concentrated, it will be diluted first with a solvent that is insensitive to mid-infrared light. Tetrachloromethane is the commonly used solvent for this purpose. Highly concentrated liquid samples absorb more IR light and allow very little or none to pass through which in most cases give distorted spectrograms which cannot be analyzed. The aqueous electrolyte (KHCO_3) that contained the samples was in a diluted state and does not require further

dilution. A tiny volume of the liquid sample was collected and injected into the CaF_2 windows for the transmittance technique using a needle and syringe, and a similar procedure was followed for the ATR-IR technique where the sample was injected on the surface of the diamond crystal fitted on a stage with little exposure on the surface. Great care was taken to avoid contact between the syringe needle and the diamond crystal in order to prevent any scratch on the diamond surface. The sample was now ready to be analyzed.

This thesis deals with liquid sample obtained from carbon dioxide reduction reaction only.

3.4. Different FTIR Spectroscopy Techniques

There are three (3) main IR techniques:

- i. Transmission
- ii. Attenuated Total Reflection
- iii. Reflection

3.4.1. Transmission IR Spectroscopy

In this technique, IR light is made to pass through a sample (see Figure 7). The sample absorbs the IR light which causes a change in its dipole moment and makes it to vibrate and transmit some of the absorbed radiation to a detector which convert them into a spectrum that can be used to analyze the molecules contained in the sample.

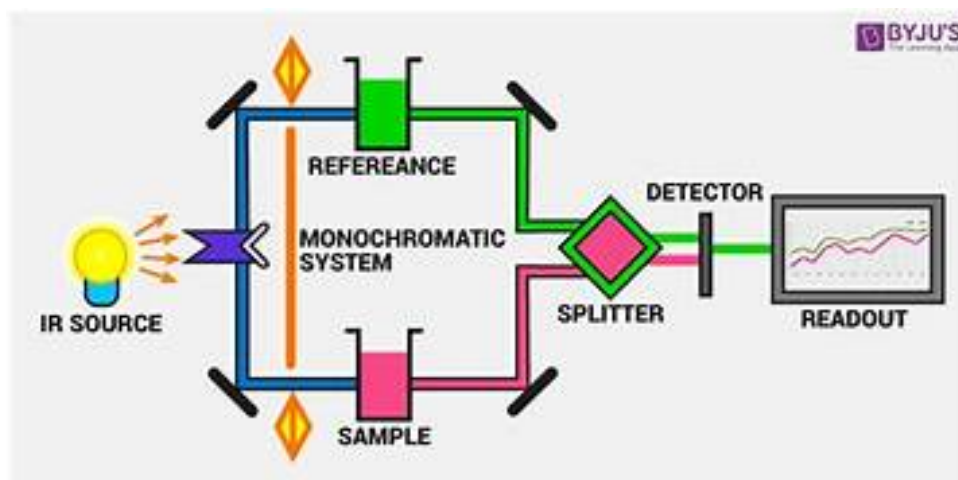


Figure 8: Transmission IR spectroscopy

(Source:

https://tse1.mm.bing.net/th?id=OIP.f_jR_aOut5d0FFJyJIaYDwHaDt&pid=Api&P=0&h=180)

However, care must be taken when preparing the sample. Solid and liquid samples should not be too thick otherwise, the sample will absorb most of the IR and this will produce noisy peak quality that will make it difficult or impossible to analyze the sample correctly.

In the preparation of solid samples for transmission spectroscopy, the solid sample must be grounded together with alkali cation salts (eg, KBr), which does is not IR sensitive to MIR range so as to pose as a background and facilitates the grinding process of the solid sample. It is preferable to apply thin film solid power samples or dilute liquid samples (making sure the solvent is not MIR active, eg, CCl₄ or D₂O). Always apply a very little amount of the sample to be analyzed on the sample holder.

This technique of FTIR is particularly useful in the field of forensics, biological analysis of tissue samples and in investigating microplastics in environmental sciences.

3.4.2. Attenuated Total Reflectance Technique

This technique involves the partial absorption of IR light by the sample which reflects part of the absorbed IR to a detector for analysis. In this technique, a small amount of the sample is placed on top of a crystal usually made up of germanium, zinc selenide or diamond. As IR light is passed through the crystal, some of the light is absorbed by the sample creating a change in its dipole moment which cause its molecules to vibrate and bounces the IR light back to the crystal from where it is reflected to a detector for analysis.

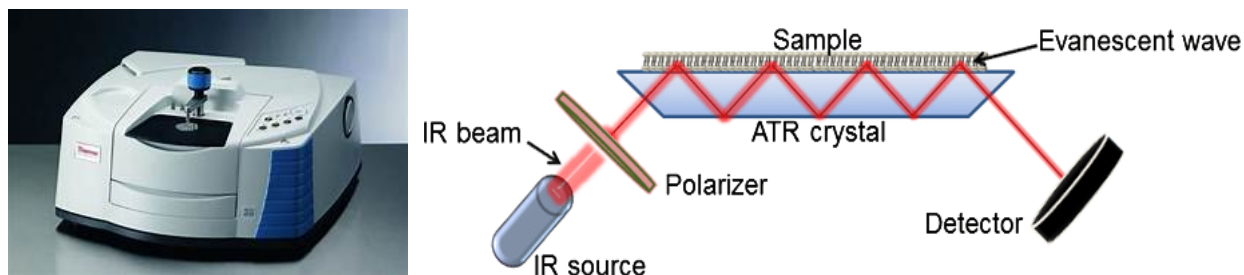


Figure 9: ATR-IR spectroscopy technique

(Source: https://www.zkg.de/imgs/101523522_3ee27ae695.jpg, DOI: [10.3233/BSI-150104](https://doi.org/10.3233/BSI-150104))

It is worth noting that in this technique, IR light only penetrate the sample partially by a few microns and as such does not require detail sample preparation. Little or no sample preparation is required. This makes the technique very simple and produces high quality spectra.

3.4.3. Reflection IR Spectroscopy Technique

In this technique, the reflected IR light from the sample's surface is the one that is analyzed by the detector, not the one from the internal reflection. This is one of the reasons what makes this method so important because it can be used to analyze solid samples that may not be transparent to light. However, this technique has the challenge of not being able to give reliable analysis of the entire sample since it is only dealing with surface molecules, unless when the sample molecules are homogenous.

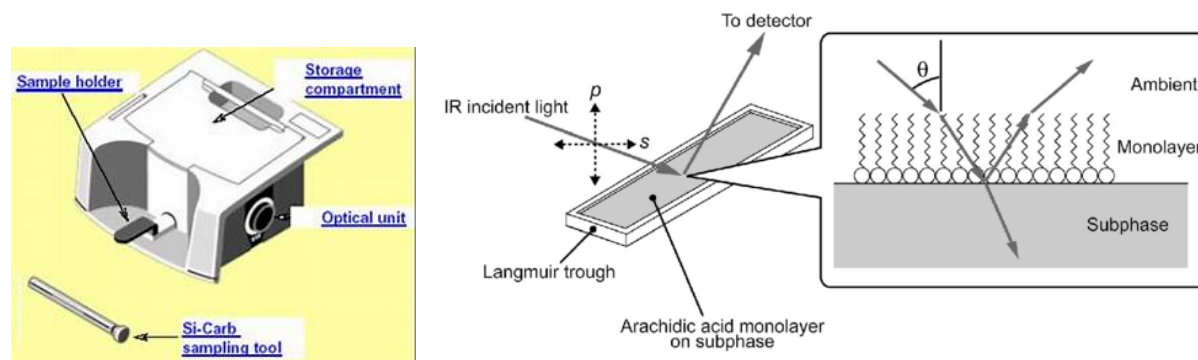


Figure 10: FTIR reflectance technique (DOI: [10.2109/jcersj.115.124](https://doi.org/10.2109/jcersj.115.124))

3.5. Data collection

Software called OMNIC for FTIR spectroscopy techniques was used to analyze all the samples in this project. First, a background sample of the air in the chamber consisting a mixture of gases such as, water vapor and carbon dioxide molecules is collected and subtracted out to avoid its interference on the sample. Then the sample contained in a sample holder is place properly along the path of the IR light and the chamber lid is closed.

The software will scan the sample within a period of two minutes and display the spectrogram of the sample on the monitor assembled with the device. Peak heights, width and areas are assigned on the peaks for further analysis. The data can be printed or saved in a library as a resource material for further research.

With the ATR-IR technique, the prepared sample (liquid) was carefully placed on a crystal ball fitted on a stage with the help of a needle and syringe, as earlier on mentioned. The Omnic software is also used in this technique to analyze the sample. Again, the same pattern of operation is carried out with the software as in the case of the transmittance technique.

The data collected through the transmittance technique was done in the Plasma Physic Laboratory, while the data collected from the ATR-IR technique were measured at the IEK-14 laboratory.

3.6. Set up for electrochemical reduction of Carbon dioxide.

The anode and cathode components of the micro flow electrochemical cell are 8.8cm^2 each in area and oxidation occurs at the anode while reduction occurs at the cathode. Ion transfer occurs through the nafion membrane which separates the two electrode components. Electrons from a renewable source of energy (in our case solar module based on silicon heterojunction solar cells) is pass through the cathode to the electrolyte for the reduction of carbon dioxide.

The ethylene propylene diene monomer rubber (EPDM) made from polytetrafluorethylene(PTFE), serves to keep the other components adhere firmly together and prevent any leakage of electrolyte or gas outside the electrolytic cell. The EPDM contain holes at its corners meant for the passage of the electrolyte to reach the gas diffusion layer(GDL). The nafion membrane is the main component that divides the electrochemical cell (EC) into two but allows the exchange of protons from the anode to the cathode. A copper plate, referred to as a current collector, serves as the passage of electric current from a renewable source (e.g., solar module) into the electrocatalyst. A copper metal support with an aperture, for the attachment of the electrocatalyst.

For this work, silver (Ag) electrocatalyst of about 55 nm width was used. The silver was deposited on a mesoporous gas diffusion layer (GDL) made up of carbon fibers that serve as a support on which the silver catalyst used for this work was deposited. The fact that the carbon fiber on which the silver was deposited is also conductive, made the combined components an electrode, being referred to as the gas diffusion electrode (GDE).

CO₂ reduction setup – editable version

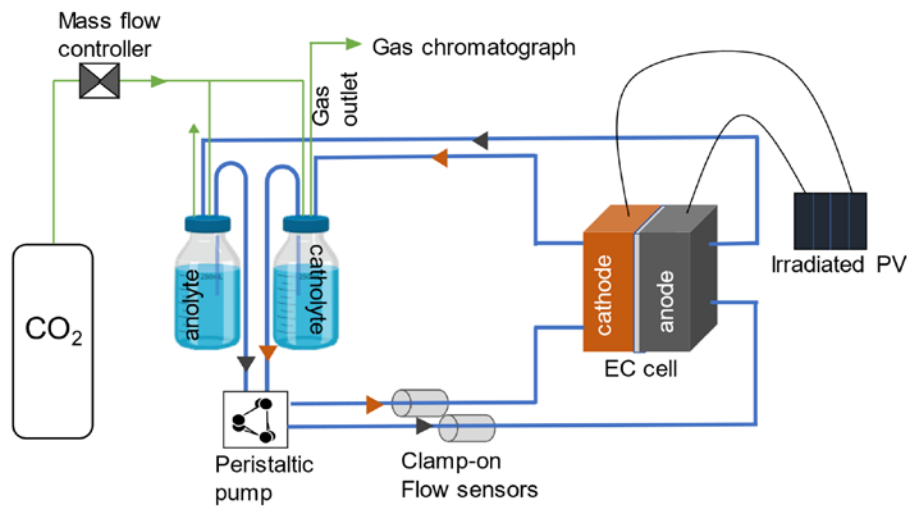


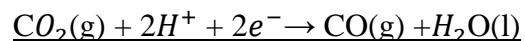
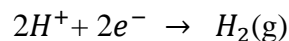
Figure 11: The setup of a common Electrolytic cell

Aqueous potassium hydrogen carbonate was chosen as electrolyte to dissolve carbon dioxide and got it ready for electrochemical reduction. The parameters used in the preparation of the electrolyte included 0.1 M and pH 8.6 with varied electrode potential from 2.6 to 3.2 V to obtain the five samples analyzed. There is an inlet for carbon dioxide gas to diffuse into the gas chamber of the cathode, where it will further dissolve into the catholyte and increase its concentration. Carbon dioxide was bubbled into the electrolyte at a rate of 80 sccm.

The electrochemical reduction process was done in two compartment cells, separated by a proton exchange membrane (nafion). Oxidation occurred at the anode while reduction occurred at the cathode. The half-cell reactions at the anode and cathode are shown as follows:



Cathode (reduction is in two stages):



The products formed in the net equation are in agreement with Shu, D., et al (2021). Hydrogen, carbon monoxide and oxygen are products of carbon dioxide reduction reaction under the operation of the silver catalyst used in this work. The products (CO and H₂) from the CO₂ reduction were analyzed by gas chromatography as a reference experiment followed by FTIR measurements.

Figure shows the important intermediates of the electrochemical reduction of carbon dioxide as seen by SEIRAS in situ technique. The figure shows all the possible species formed and the reaction mechanism that leads to the final products of the reaction.

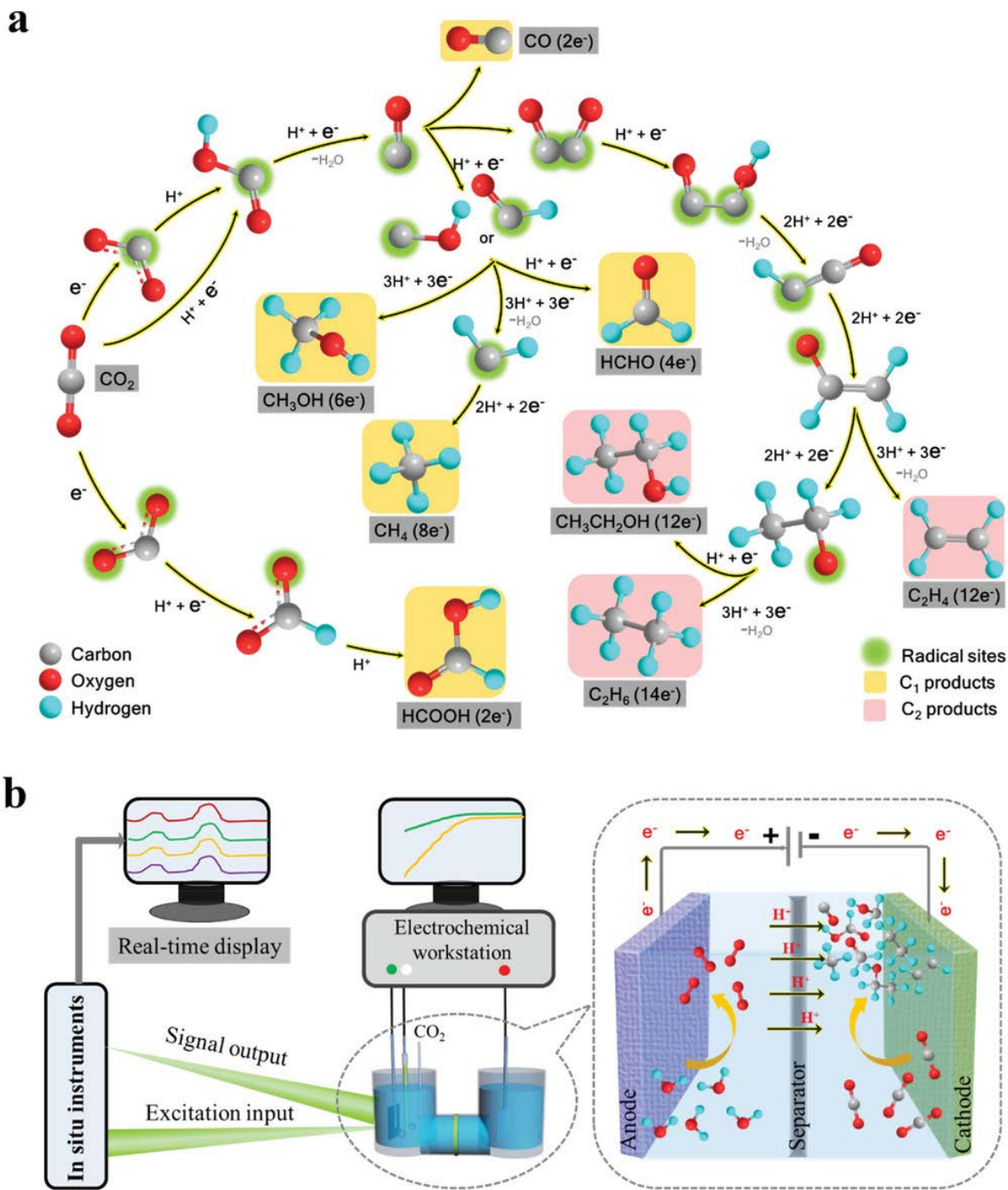


Figure 12: (a) Shows carbon dioxide reduction into different intermediate species and products (b) describes how the in situ arrangement can be quite useful in revealing the reacting species as the reduction reaction proceeds

(Source: <https://onlinelibrary.wiley.com/cms/asset/e11d6d0a-537e-43d7-89f6-710b2af4ae85/smt202100700-fig-0001-m.jpg>)

3.7. Gas chromatography

This is another analytical method used widely to analyze vaporized liquid or gaseous samples that do not undergo decomposition. In this technique, the vaporized sample is injected in an inlet tube, and then carried by a carrier gas (mobile phase) through a column that is fitted with a stationary phase, to a detector.

Each component of the mixture interacts with the stationary phase in a specific way that will determine their time of exit from the column to the detector. This time is called retention time. Some molecules of substances have a strong affinity for the stationary phase than the mobile phase, and have a longer retention time than others which are carried by the mobile phase to the detector. The retention time of each molecule is unique to that molecule. A library is used to assign each molecule a name based on their retention time. This is the basis on which the gas chromatography works.

Gas chromatography is widely used to conduct quantitative and qualitative analysis of gas mixtures and purity, among others. GC is also applicable in industries to monitor gas flows to prevent them from being contaminated. GC technique is also used in the analysis of air to determine the level of pollution, alcohol in blood and the purity of food products.

The reason for conducting analysis using this device on carbon dioxide reduction reaction is to help identify gas and vaporized liquid products that might not be detected by FTIR techniques, and to use the results obtain as a reference measurement to the FTIR technique.

Correct column installation in injector

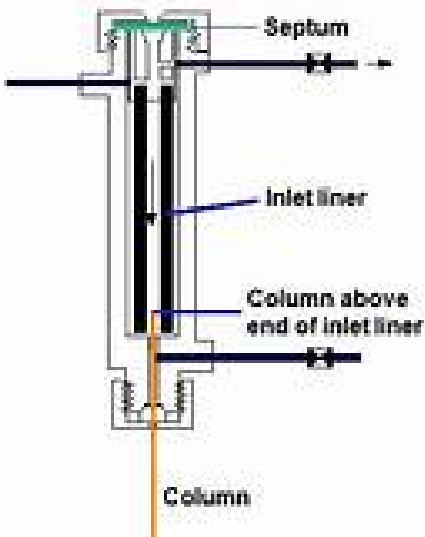


Figure 13: The Gas Chromatography Column

(Source: <https://image.made-in-china.com/2f0j00CsVauercbJzp/Biobase-Bk-GC7820-Gas-Chromatography-Gas-Chromatograph.jpg>)

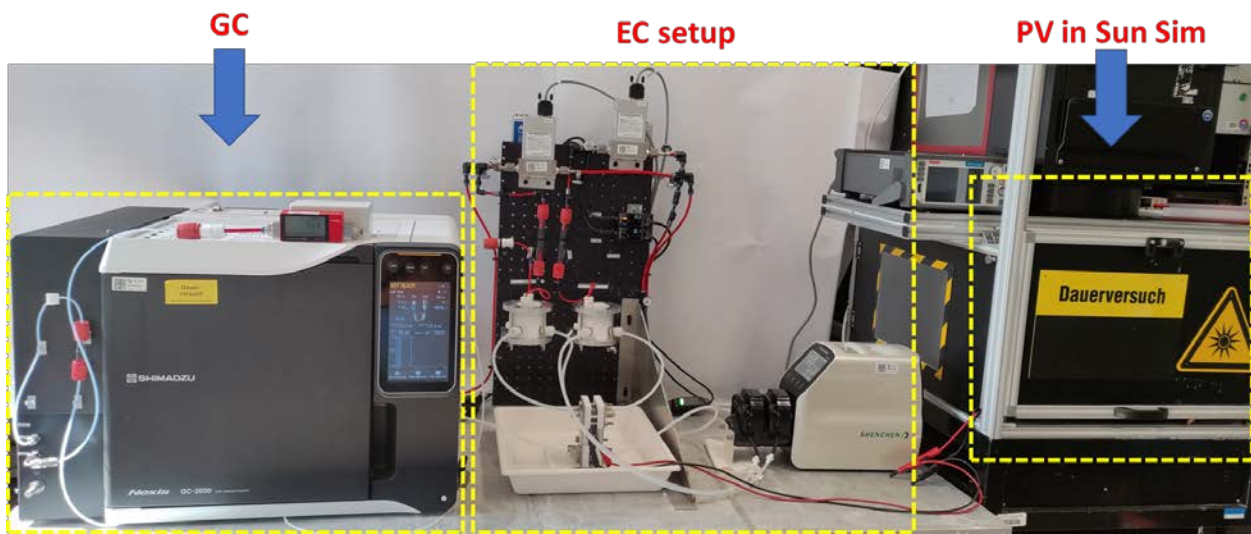


Figure 14: Picture of CO₂ reduction measurement set up including gas chromatograph (GC), electrochemical (EC) and Sun simulator

Chapter IV

Results and Discussions

4.1 FTIR transmittance results from CO₂ reduction

Three type of samples, namely reduced KHCO₃ sample, samples prepared by purging KHCO₃ with three different concentrations of folic acid (FA), and sample fabricated by purging KHCO₃ with carbon dioxide were analyzed with the FTIR transmittance technique. It was observed that the transmittance spectra of all five samples displayed the functional groups they contain and their concentrations. All the samples displayed sharp transmittance peaks of the hydroxyl (OH⁻) functional group of carboxylic acid at a wavenumber of 3300 cm⁻¹.

A second peak of carbon monoxide was also shown at around 1700 cm⁻¹ and a third peak of a CH group was also displayed at around 1450 cm⁻¹. These spectra have revealed that all the samples contain carboxylic acid. In addition, the spectra have also displayed the variation of the concentrations of carboxylic acid that is contained in each sample. What these results have shown is that FTIR techniques are quite applicable in revealing what happens inside the electrochemical reduction of carbon dioxide reaction.

4.2 Gas chromatography results from CO₂ reduction

The Chromatogram on Figure 17 shows the composition of the products from electrochemical reduction of carbon dioxide identified and analyzed by the Gas chromatography . The products shown are hydrogen, carbon monoxide and carbon dioxide respectively. The electrode potential used was varied from 2.6 V to 3.2 V.

The color codes indicate the variation of the electrode potentials. The black color show carbon dioxide reduction at 2.6 V, 100 sccm; purple color indicates carbon dioxide reduction at 2.8 V, 100 sccm; blue color show carbon dioxide reduction at 3.2 V, 100 sccm, and the green color indicates carbon dioxide reduction at 3.4 V, 100 sccm.

Table 1 shows the parameters under which the electrolytic cell was operated. It also shows that there is a direct proportional increase in the concentration of both the hydrogen and carbon monoxide gases produced as the electrode potential was increased gradually even though the gas flow rate of the carbon dioxide remained constant at 100 sccm.

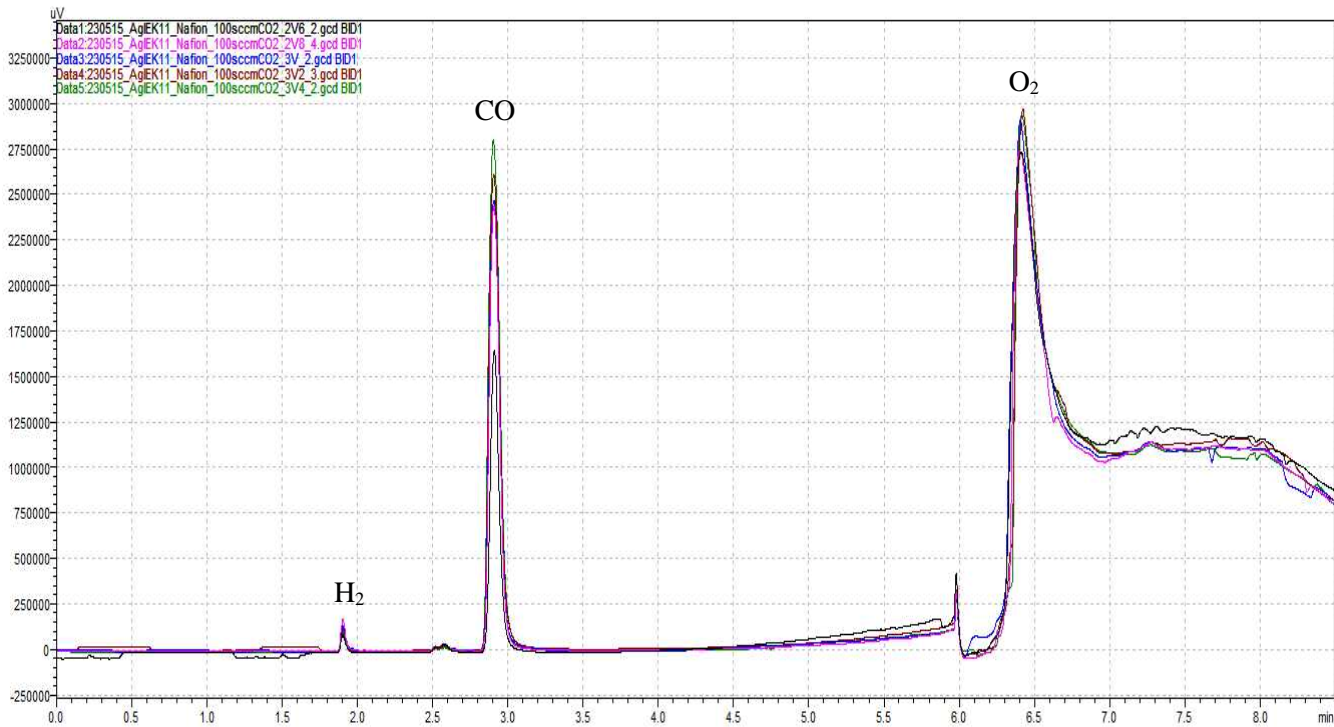


Figure 15: Gas chromatogram of carbon dioxide reduction reaction of five samples

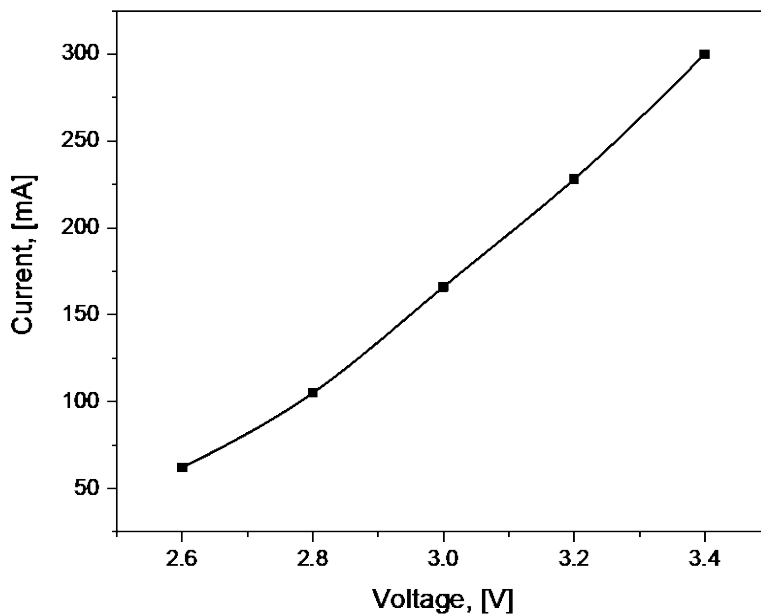


Figure 16: Steady state polarization curve of Ag catalyst

Figure 18 shows the polarization curve of Ag catholyte catalyst used in the reduction reaction of carbon dioxide for all the five samples used in the analysis. Again, the two parameters of voltage

and current show the expected direct proportionality relationship between them. As the current increases, the voltage increases as well. This shows a steady progress towards products formation as the current and voltage increase steadily. FTIR in situ-SEIRAS technique show that increase in the voltage of the electrode promotes the release of more intermediate species, and this subsequently increased products formation.

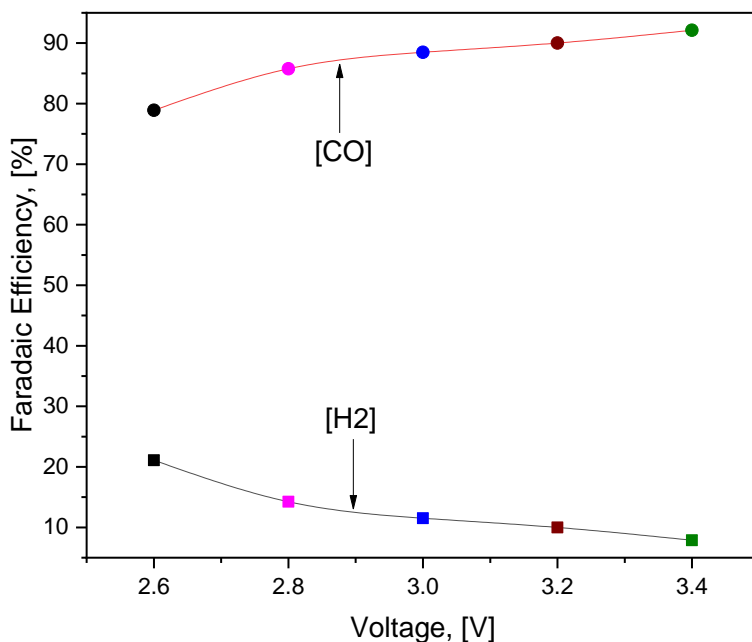


Figure 17: Faradaic efficiencies of hydrogen and carbon monoxide

Table 1: Shows the various parameters involved in the electrochemical reduction of carbon dioxide in an electrolytic cell with silver as the reducing electrode(cathode), the products formed, their concentrations and faradaic efficiency

| | Voltage [V] | Current [mA] | [H ₂] ppm | [CO] ppm | Syngas [H ₂ +CO] | FE _[H₂] % | FE _[CO] % | FE total measured | Ratio CO:H ₂ |
|--|-------------|--------------|-----------------------|----------|-----------------------------|---------------------------------|----------------------|-------------------|-------------------------|
| Ag_2.6V | 2.6 | 62 | 1821.7 | 6819.1 | 8640.8 | 21.1 | 78.9 | 100.5 | 3.7 |
| Ag_2.8V | 2.8 | 105 | 2085.9 | 12547.7 | 14633.6 | 14.3 | 85.7 | 74.2 | 6.0 |
| Ag_3.0V | 3.0 | 166 | 2663.8 | 20471.2 | 23135.0 | 11.5 | 88.5 | 76.3 | 7.7 |
| Ag_3.2V | 3.2 | 228 | 3177.6 | 28598.2 | 31775.8 | 10.0 | 90.0 | 68.5 | 9.0 |
| Ag_3.4V | 3.4 | 300 | 3291.0 | 38519.3 | 41810.3 | 7.9 | 92.1 | 80.2 | 11.7 |
| The catalyst has a geometrical area of 8.8 cm² | | | | | | | | | |

Figure 20 is a chromatogram showing different graduation of the concentrations of the products of the samples that were analyzed by gas chromatography technique. The main products analyzed on the samples were carbon monoxide and hydrogen. It was seen that carbon monoxide was selected the most compared to hydrogen, and their concentrations increase with increase in voltage.

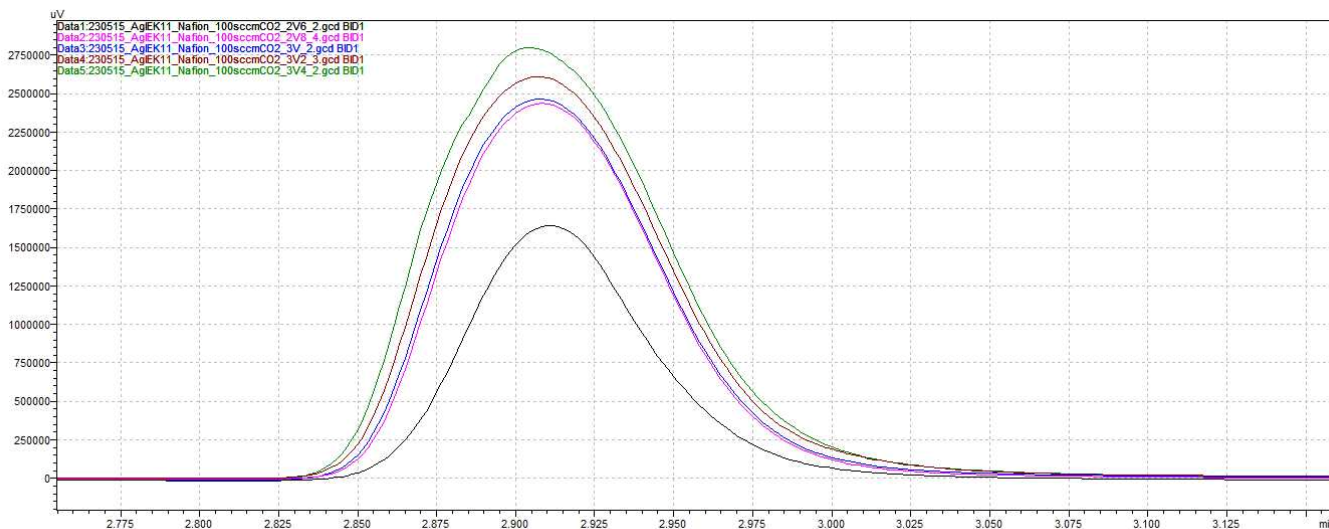


Figure 18: Shows the Gas spectrogram of electrochemically reduced carbon dioxide at varied voltages

4.3 Attenuated total reflection analysis result

The attenuated total reflection technique showed mirror results to those seen in the transmittance technique. The hydroxyl (OH^-) functional group of carboxyl acid is shown at 3300 cm^{-1} wave number, and the carbon monoxide and carbon-hydrogen (C-H) stretch were also seen at 1700 and 1450 cm^{-1} wave numbers respectively.

Attenuated infrared analysis (figure 21) is shown below, and it has similar results to those obtained from transmittance FTIR technique. Here, only the reduced KHCO_3 sample was analyzed.

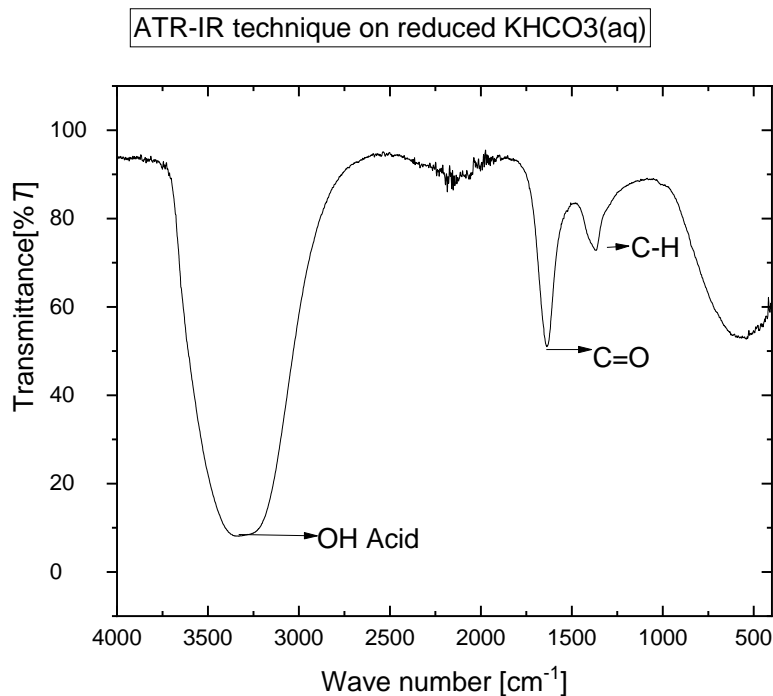


Figure 19: FTIR (ATR-IR) spectrogram

Figure 22 is obtained from the attenuated total reflectance analysis of both fresh and reduced samples of KHCO_3 . It is worth noting that the two samples were not analyzed on the same day. The reduced KHCO_3 sample was analyzed three days after analyzing the fresh sample.

The reduced sample lost some of its content species because it spent some time in the shelf. HCOO^- and OCH_3 ions are volatile and they escape the container where it was placed. These are very important in forming carboxylic acid, and the more they are in the electrolyte, the more they constitute a higher concentration of the acid and other products formed.

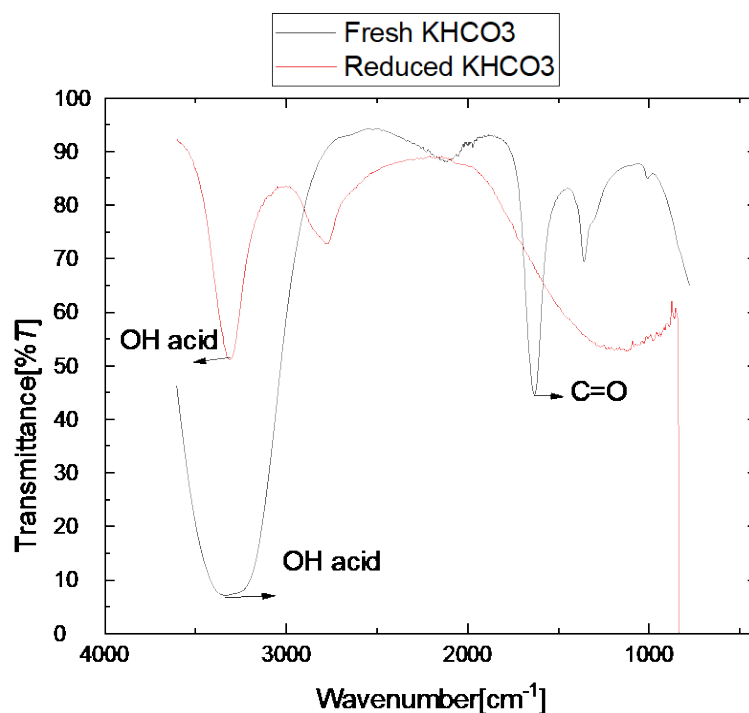


Figure 20: Spectral diagram of fresh KHCO_3 against reduced KHCO_3 under

4.4 Discussions

FTIR techniques (transmittance and attenuated total reflectance) have been used in this work to analyze and identify products formed from carbon dioxide reduction. In this work FTIR techniques have shown that carbon dioxide reduction can produce solar fuels and other important chemicals (methane, ethane, ethene, hydrogen and carboxylic acids.) based on the spectrogram results analyzed from the samples in both the gas chromatography and FTIR techniques. The various functional groups of the broad peaks of hydroxyl ions shown at around 3300cm^{-1} wavenumber indicates the presence of an acid, while the scissors peak seen at around 1700cm^{-1} indicates the presence of a carbonyl functional group. A combination of these peaks can be analyzed and identified as the presence of a carboxylic acid molecule in the sample as supported by Chen, S., & Chen, A. (2019). Several important intermediates are produced along formic acid that have the potential to produce more low carbon /hydrogen products but the silver catalyst and aqueous potassium hydrogen carbonate electrolyte used in this work cannot provide the active sites and the activation energy required that could have resulted in the formation of more products as supported by the results of. Osawa, M., (1997). A silver catalyst can only convert carbon dioxide to carbon

monoxide intermediates. If the silver catalyst used was coupled with copper in a specific ratio, then hydrocarbon products could have been formed. The reason for this to happen is that copper is quite capable of converting carbon monoxide intermediates to methane, ethane and ethene.

It is quite important to also emphasize that the best way to observe carbon dioxide reduction with FTIR techniques is through in situ operando method. This helps to observe important intermediate species and those that are enhanced on catalyst surfaces in real time. The species seen during the reaction process will help to predict the products formed. This thesis uses the ex-situ method and as such not much activity was seen during analysis of the sample. The disadvantages of the ex-situ method on the sample are that it is extremely likely to lose some of the products formed during the process of transferring samples from the electrochemical cell to test tubes that will hold the sample and it is also prone to sample contamination. This happens because some of the products are quite volatile and intermediate species have a high affinity for protons.

The challenges that are slowing down the development of this technology are on the stability of the catalyst used, the electrodes, the electrolyte and the lack of sufficient knowledge on the reaction mechanism of the reduction reaction of carbon dioxide.

FTIR techniques can be relied upon to analyze and identify the products of carbon dioxide reduction and having these techniques coupled with gas chromatography technique will reveal more products of carbon dioxide reduction reactions.

Chapter V: Conclusion and perspectives

This work is meant to prove that FTIR techniques are quite applicable in revealing the products of carbon dioxide reduction, and have confirm the possibility of doing so by displaying spectral images of functional groups of molecules that are consistent with those present in known compounds.

The results obtained from the ATR technique which show the presence hydroxyl ion (OH⁻) and carbon monoxide functional groups were also seen in the results of the transmittance technique. This consistency in the analysis of results from the same samples is a clear indication that the techniques are convincing and can be depended upon. Consistency is a sign of reliability. A net balanced chemical equation from the half-cell reactions in both electrodes agree with the results obtain in both the FTIR techniques and the gas chromatography.

FTIR techniques have shown their applicability in the analysis of the products of electrochemical reduction of carbon dioxide in KHCO₃ (aq), and as well as in adulterated samples of KHCO₃ with various concentrations of folic acid and carbon dioxide with remarkable results that can be compared with those obtained in a gas chromatography device. The products seen from the FTIR analysis where folic acid, carbon monoxide and C-H functional group.

One way to see more intermediate species as the reduction process of carbon dioxide proceeds is to use non-aqueous electrolytes such as, tetrachloromethane, carbon disulphide, chloroform, acetone or acetonitrile, for the reduction of carbon dioxide. These types of electrolytes do not contain water and have the advantage of preventing fresh water interference in the spectrum that may appear from aqueous electrolytes.

Also, heavy water (D₂O) can be used as a solvent or electrolyte instead of fresh water (H₂O) in some liquid sample analysis in FTIR spectroscopy. This application can be done in liquid protein samples of amines and enzymes. As a solvent, D₂O water band forms around 1600 cm⁻¹ wave number, while amine band forms around 3400 cm⁻¹ wave number. If fresh water is used in such analysis, then there will be peak interference that will negatively affect the result of the FTIR spectroscopy analysis because the O-H band from fresh water also forms around 3400cm⁻¹ wave number.

Another reason why fresh water should be avoided in sample preparation for FTIR analysis is that it dissolves window materials made of salt, such as sodium chloride and potassium bromide. Salt

window materials have a very low refractive index which is required to produce sharp spectral images.

In the future, it is important to combine in situ ATR-SEIRAS, isotopic labelling and mass spectroscopy techniques to be able to have a detailed identification and analysis of reaction intermediates and pathways of the reaction mechanism. In situ operando with SEIRAS have also revealed that the majority of the carbon dioxide utilized for the electrochemical reduction of carbon dioxide does not come from the one diffused into the catholyte, but rather from the one that maintains the steady state of equilibrium between the electrolyte and the bicarbonate ions in the solution. In the future, there is no need for diffusing carbon dioxide into the catholyte with the aim of improving the reduction process.

Signal intensities can be improved upon so that the reaction intermediates can be captured. This could be done by combining FTIR and Raman through SEIRAS technique. This can be done in a contactless and non-destructive manner with the catalyst, and intense signals can be captured.

There is need also to have a direct observation of active sites and reaction intermediates in real time. This will give an insight on the reaction mechanism, important intermediates and products.

Even though a lot of effort have been made to develop in situ and operando characterization techniques, more effort will be needed to further develop this technique to give more insight into carbon dioxide reduction reaction.

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