

Optimizing the Process Parameters for Electrochemical Reduction of Carbon Dioxide

by

Santosh shekar Mudunur

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Graduate Supervisory Committee:

Arunachala Kannan, Chair  
Huei-Ping Huang  
Patrick Phelan

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## ABSTRACT

One the major problems of this modern industrialized world is its dependence on fossil fuels for its energy needs. Burning of fossils fuels generates green-house gases which have adverse effects on global climate contributing to global warming. According to Environmental Protection Agency (EPA), carbon dioxide makes up 80 percent of green-house gases emitted in USA. Electrochemical reduction of carbon dioxide is an approach which uses CO<sub>2</sub> emissions to produce other useful hydrocarbons which can be used in many ways.

In this study, primary focus was on optimizing the operating conditions, determining the better catalyst material, and analyzing the reaction products for the process of electrochemical reduction of carbon dioxide (ERC). Membrane electrode assemblies (MEA's) are developed by air bushing the metal particles with a spray gun on to Nafion-212 which is a solid polymer based electrolyte (SPE), to support the electrodes in the electrochemical reactor gas diffusion layers (GDL) are developed using porous carbon paper. Anode was always made using the same material which is platinum but cathode material was changed as it is the working electrode.

The membrane electrode assembly (MEA) is then placed into the electrochemical reactor along with gas diffusion layer (GDL) to assess the performance of the catalyst material by techniques like linear sweep voltammetry and chronoamperometry. Performance of MEA was analyzed at 4 different potentials, 2 different temperatures and for 2 different cathode catalyst materials. The reaction products of the process are analyzed using gas

chromatography (GC) which has thermal conductivity detector (TCD) used for detecting hydrogen ( $H_2$ ), carbon monoxide (CO) and flame ionization detector (FID) used for detecting hydrocarbons. The experiments performed at  $40^\circ C$  gave the better results when compared with the experiments performed at ambient temperature. Also results suggested that copper oxide cathode catalyst has better durability than platinum-carbon. Maximum faradaic efficiency for methane was 5.3% it was obtained at 2.25V using copper oxide catalyst. Furthermore, experiments must be carried out to make the electrochemical reactor more robust to withstand all the operating conditions like higher potentials and to make it a solar powered reactor.

## DEDICATION

This thesis is dedicated to my parents, Mudunur Saibaba and Mudunur Padmavathi who have provided me with moral support and guidance throughout my life. This is not possible without their constant love, affection, and belief in me. Also, I would like to thank my paternal grandparents late Soma Shekar, late Krishna Kumari, my maternal grandparents Krovvidi Subbarao, Krovvidi Umadevi, all my family members and friends whose moral support was very important in helping me accomplish this herculean task.

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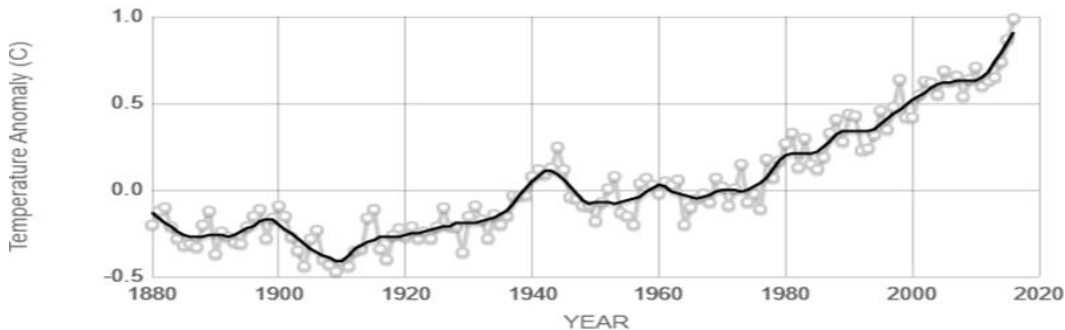
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## 1. INTRODUCTION

### 1.1 CO<sub>2</sub> Emissions- Sources and Effects

The rapid industrialization and increasing population in the past few decades have changed the face of the world dramatically. Forests have been destroyed for the sake of urbanization and to suffice the growing demand for wood. According to U.N. Food and Agricultural Organization, deforestation was at its highest rate in the 1990's, when the global net loss of the forest was 8.3 million hectares per year. This huge decrease in the forest area disturbed the delicate balance that existed in the nature thus causing the earth's temperature to soar high. NASA's Goddard Institute of Space Studies depicted that 16 of the 17 warmest years in 136-year record have occurred since 2001.



Source: [climate.nasa.gov](http://climate.nasa.gov)

Fig 1: Change in global surface temperatures relative to 1951-1980 average temperatures

Scientists have proven that increase in earth's temperature is directly related to green-house gas emissions. Worldwide, net emissions of green-house gases increased by 35 percent from 1991-2010. Carbon dioxide emission which make up about three fourth of green-house gas emissions increased by 42 percent during this period. Since, the industrial revolution the world has been largely dependent on fossil fuels to meet its energy

requirements. According to U.S. Energy Information Administration three fossil fuels- petroleum, coal and natural gas have provided more than 80 percent of total U.S. energy consumption for more than past 100 years. Burning of fossil fuels for producing energy emits green-house gases which have adverse effects on environment. Carbon dioxide is the major component in the green-house gases and carbon dioxide emissions are following an increasing trend for the past 200 years.

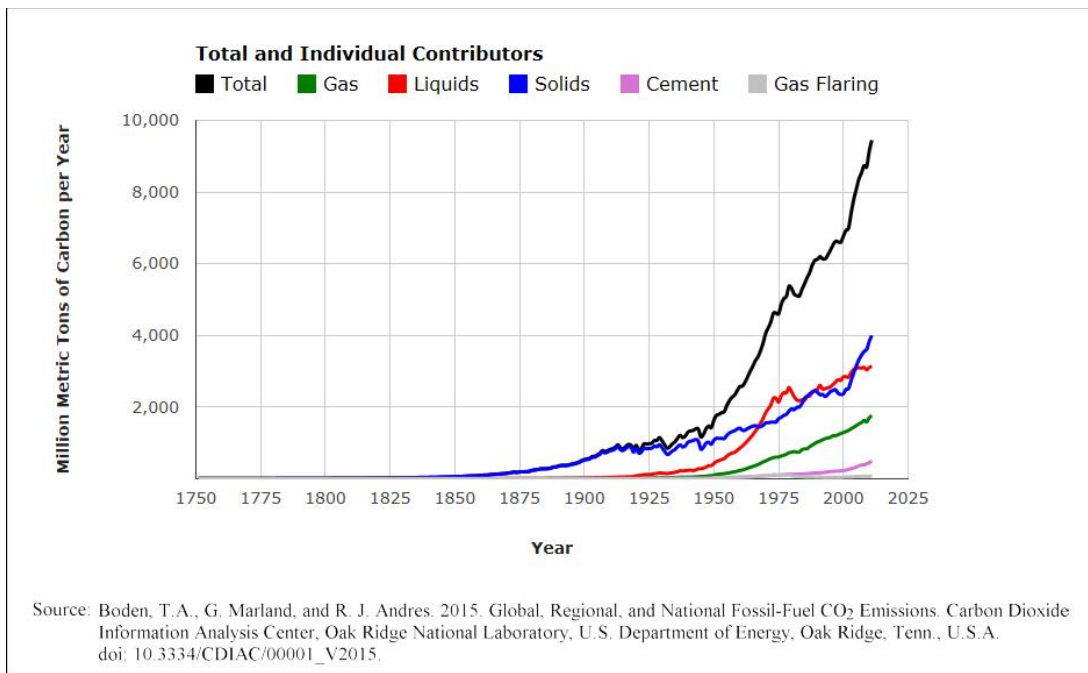
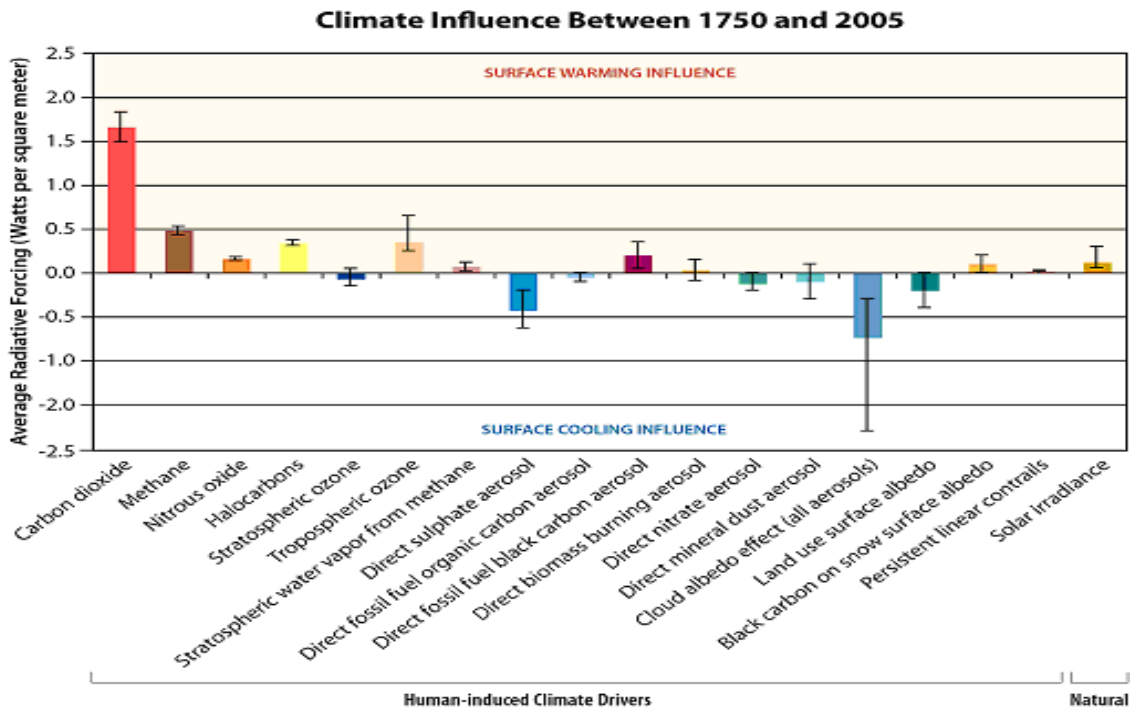


Fig 2: Carbon dioxide emissions per year for the past 200 years

All the green-house gases can trap the heat, but of all green-house gases carbon dioxide emissions put us at greatest risk for two reasons- Carbon dioxide stays longer in atmosphere than any other gas, carbon dioxide contributes most to the climate change. According to Intergovernmental Panel on Climate Change (IPCC), carbon dioxide has the highest positive radiative forcing.



Source: IPCC 2007 WGI Table 2.12; Figure: Union of Concerned Scientists

Fig 3: Radiative Forcing (RF) for different gases

Based on plausible emission scenarios, scientists predict that earth's temperature might rise from 2<sup>0</sup>C to 6<sup>0</sup>C by the end of 21<sup>st</sup> century. Today, greatest challenge for the humanity is to develop technologies that effectively meet the growing energy needs of the future generations and at the same time do not pose any threat to the nature thus making the world a better place to live.

### 1.2 Methods to capture and convert carbon dioxide

Carbon capture is the process of separating and capturing carbon dioxide from sources of CO<sub>2</sub> emissions for example flue gases from industry, this helps to prevent carbon dioxide from entering atmosphere thus reducing the global warming. Capturing carbon dioxide by natural or artificial processes and then storing it in the solid or liquid form is called carbon sequestration. One of the major issues faced by the carbon sequestration is large costs are

involved to store carbon dioxide and there is a high risk of stored carbon leaking into atmosphere. Carbon dioxide has very high retention rates of about 99 percent over 1000 years. International Panel on Climate Change believes that if 1 percent of carbon leaks, the next 100 years would see 63 percent of stored carbon evaporating into atmosphere.

This issues with carbon sequestration give rise to the question Why stop with carbon capture, storing? Think to convert carbon dioxide.

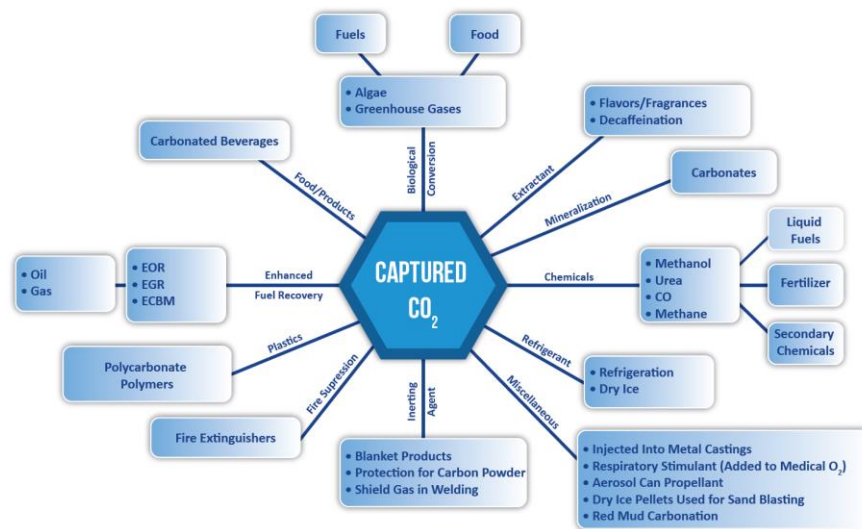


Fig 4: Various useful products that can be obtained by converting CO<sub>2</sub>

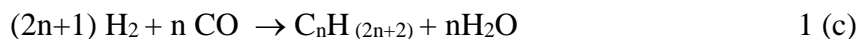
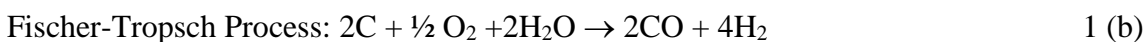
Fossil fuels are depleting fast and the world has already started looking towards renewable energy technologies to satisfy its ever-increasing energy needs. The major drawback of renewable energy sources is that they are intermittent for example, solar panels can produce power only during the day and wind turbines can produce power only when winds are blowing. To overcome this issue, we should be able to store the energy we produce. We can store the energy using batteries but energy densities obtained are lower compared to

the primary sources. Alternatively, this energy can be used to drive the electrochemical reactions to reduce carbon dioxide and form high energy density products.

Electrochemical reduction of carbon dioxide can be accomplished by two processes Sabatier process and Fischer-Tropsch process. French chemist Paul Sabatier discovered the Sabatier process by allowing carbon dioxide to react with hydrogen at high temperature and pressure in the presence of nickel catalyst forming methane and water. Equation 1(a) depicts the Sabatier process



Franz Fischer and Hans Tropsch discovered Fischer-Tropsch process. Unlike Sabatier process, this process involves a series of chemical reactions shown in equations 1(b) and 1(c)



n can range from 10-20, when n=1 methane is formed.

Apart from electrochemical reduction of carbon dioxide, many researchers are also concentrating on developing prototype models that reduce carbon dioxide by employing photochemical and biochemical techniques. However, these methods are less advantageous as they require either high temperature or high pressure or both, unlike electrochemical reduction which can reduce carbon dioxide at ambient conditions.



### 1.3 Objectives, Challenges, and Prospects of ERC

In the recent past, electrochemical reduction of carbon dioxide has gained significant prominence over other technologies because of the following advantages:

- a.) It is accomplished through reactants gaining or losing electrons at an electrode, and does not require an oxidizing or reducing agent. Although, it requires a small amount of catalyst. Therefore, this is a process that can be accomplished without producing trash.
- b.) It is a simpler process with fewer reactions.
- c.) Carbon dioxide is the cheapest resource of C1-materials and easily available.
- d.) It does not require either high temperature or high pressure thus significantly reducing energy consumption.
- e.) It provides great control over the products formed by allowing variations in metal electrodes, electrolytes, current and voltage.
- f.) It is easy to scale up the system to a larger size to meet the industry specific requirements.

Nonetheless, it also has challenges that need to be met to make it more efficient.

- a.) Catalyst poisoning is the major issue associated with electrochemical reduction of CO<sub>2</sub>.
- b.) Transporting the products from the catalyst layer without blocking the active reaction sites.
- c.) Collection and separation of the desired product from the mixture of several products obtained.
- d.) Identifying the new reaction pathways and catalysts.

Main objectives of this study are:

- i. Design and develop system that uses a solid polymer electrolyte to convert carbon dioxide to various useful products.
- ii. Optimize the operating parameters of the electrochemical reactor for efficient reduction of gaseous carbon dioxide.
- iii. Selecting the most appropriate catalyst for the process and quantify the reaction products for each catalyst.

Electrochemical reduction of carbon dioxide produces various products like methane, methanol, hydrogen, carbon monoxide and other hydrocarbons. The amount of each product formed depends on the selectivity of the catalyst used for reduction of carbon dioxide. For example, copper has more selectivity for methane whereas platinum produces hydrogen. If the electrochemical reactor is developed in such way that it has 100% selectivity for a specific product then theoretically the amount energy required for producing one mole of product from one mole of carbon dioxide is given in the table below.

Product	Amount of energy required to convert one mole of CO <sub>2</sub> (KJ)	Amount of energy required to convert one mole of CO <sub>2</sub> (KWh)
Methane	818	0.22
Methanol	700.59	0.19
Hydrogen	474.78	0.13
Ethanol	1146.42	0.31

#### 1.4 Thesis layout

Chapter 2 literature review of past studies on electrochemical reduction of carbon dioxide.

It includes different ways to reduce to carbon dioxide and the CO/CO<sub>2</sub> hydrogenation. A brief study on various electrolytes, electrode materials, operating conditions and the products formed. Discussions are made on the use of liquid electrolytes and the introduction of solid polymer based electrolyte and their effect on the performance. It is also mentioned how the change in electrolyte, electrode and operating conditions effect the products formed.

Chapter 3 gives a deeper insight into the reaction mechanism, experimental setup, including material properties, proportions, mixing procedures, fabrication of the electrodes and the membrane electrode assembly, gas diffusion layer and Nafion electrolyte and provides a brief explanation on electrochemical techniques used to assess the performance of the MEA.

Chapter 4 discusses the characterization techniques of the membranes as well as the performance of the membrane within the reactor. In- situ methods have been studied.

Chapter 5 provides a deeper understanding of the techniques used in product analysis and products formed by reducing carbon dioxide in electrochemical reactor using gas chromatography. Gas chromatography with TCD and FID detectors has been used.

Chapter 6 provides a detailed conclusion of the studies carried out on using different catalyst materials in the electrochemical reactor and future recommendations have also been made.

## 2. LITERATURE REVIEW

The following chapter contains broad literature survey with emphasis on the latest advancements in electrochemical reduction of carbon dioxide

### 2.1 CO<sub>2</sub> Reduction

Numerous methods have been kept forward by various researchers on the preparation of hydrocarbons and alcohols from carbon dioxide. Although the results of many experimental and start-up projects on hydrogenation of carbon dioxide had been positive, these are still inefficient because of involvement of extreme physical conditions like high temperature and high pressure along with the high amount of hydrogen being required, thus making it both economically and methodically easy to achieve them by reducing carbon dioxide in ambient conditions with the help of renewable energy. Hori has developed the conversion of carbon dioxide via aqueous electro catalytic reduction (Y. Hori, 2008).

### 2.2 CO/CO<sub>2</sub> Hydrogenation

There has been a tremendous amount of research over the past decades on hydrocarbon production from carbon dioxide. However, most of it was done in aqueous solutions. Moreover, in many situations, ERC was performed at high pressures to obtain high performance. One such process was discussed earlier, the Fischer-Tropsch process invented by Hans Tropsch and Franz Fisher in 1920 (“Fisher-Tropsch Process” 2016). This process involves a two-step procedure. The first step involves the conversion of natural gas by partial oxidation into CO<sub>2</sub> and Hydrogen gas, which is later converted into formic acid, methanol, ethanol et cetera. Methanol is generally produced from Syngas or synthesis gas which is a combination of carbon monoxide, hydrogen, and traces of carbon dioxide. The combination of Syngas explained by a stoichiometric number S is given below.

$$S = \frac{\text{molH}_2 - \text{molCO}_2}{\text{molCO} + \text{molCO}_2} \quad (2.1)$$

The value of S is slightly below 2 for the formation of CH<sub>3</sub>OH. From the above equation, we can clearly see that value of S is lower if carbon dioxide is present and higher if hydrogen is present and for a higher productivity the value of S must be lower. The studies have shown that a mixture of CO and CO<sub>2</sub> in proper concentrations increases the methanol concentration at the same time decreasing reaction's activation energy (Klier et al., 1982; King and Nix, 1996; J. S. Lee et al., 1993). Although many different catalyst combinations have been studied over past few years, copper – zinc oxides along with various promoters, for example, ZrO<sub>2</sub>, SiO<sub>2</sub> and Ga<sub>2</sub>O<sub>3</sub> are few important among various other promoters (Yee, Zhang and Ladewig 2013). The process of achieving CH<sub>3</sub>OH with the help of copper based catalysts is a surface sensitive reaction and the selectivity and the activity of the final product will be decided by the stability and surface structure of the catalyst in use. Several researches mention CH<sub>3</sub>OH is one of the largely formed product among many other products from a Cu based catalyst. (Jingfa et al. 1996; Pan et al. 1988; Rasmussen et al. 1994). There are different opinions on the how the catalyst. For example, (Chinchen, Waugh and Whan 1986) say that the formation of product is independent of the copper surface area while Herman (Herman et al. 1979) claims that the Cu<sup>+</sup> ions are responsible for the formation of the product. (Szanyi and Goodman 1991) says that oxidization of copper particles will lead to higher chances of formation of the products.

Soon, renewable sources like solar energy and hydro energy are expected to replace their non-renewable counterparts such as fossil fuels and petroleum. Various emissions present in the atmosphere would ensure an abundance in the quantity of CO<sub>2</sub> available for methanol

production. By reversing the emissions, i.e. taking in the carbon dioxide from the atmosphere, the supply of required CO<sub>2</sub> for hydrogenation will be ensured. But, there are a few limitations to this process as it requires a great amount of energy to generate hydrogen which is a great deal than capturing CO<sub>2</sub>. Electrolysis of water is another method for production of hydrogen which involves electric current being applied to the electrodes when immersed in water but the disadvantage here is that this requires more hydrogen than products, i.e. hydrocarbons and alcohol can consume. To avoid these circumstances, we can opt for other methods such as electrochemical reduction of carbon dioxide. This process enables us to obtain H<sub>2</sub>, CO, CH<sub>4</sub>, CH<sub>3</sub>OH, and HCOOH with high selectivity at ambient temperatures.

### 2.3 Electrochemical reduction of CO<sub>2</sub>

Electrochemistry deals with the study of reactions that occur at the interface of the electrolyte and the electrode. They generally involve a transfer of electrons from the electrode to the electrolyte, i.e. one being oxidized and the other being reduced at the same time. Hence, they are called redox reactions.

Several studies have innovative ways of producing useful products from CO<sub>2</sub>. Experiments have been performed at various physical conditions such as temperature and pressure in addition to the usage of solar energy in different ways to perform the above-discussed redox reaction. As discussed earlier, H<sub>2</sub>, CO, CH<sub>4</sub>, CH<sub>3</sub>OH and HCOOH are formed more commonly due to the electrochemical reduction of CO<sub>2</sub> on metal electrodes. Even this process doesn't have high efficiency and probability of formation. Many studies have used a liquid electrolyte for CO<sub>2</sub> reduction, but the use of a solid polymer electrolyte can reduce

material handling problems, simplify the process, and can be modified to our needs.

However, the polymer under use must meet certain requirements. They are

1. High ionic conductivity
2. Electrochemically and thermally stable
3. Possess good tensile strength
4. Good mechanical properties
5. Economical and Easy to manufacture
6. It should be made practically possible and easy to scale up
7. It should be reliable and lasting.

Table 1: Studies on Various Parameters for Electrochemical Reduction of CO<sub>2</sub>

Electrode	Electrolyte	Operating Conditions	Main Products (Faradaic Efficiency %)	References
Indium	NaHCO <sub>3</sub>	pH=8,40 mA.cm <sup>-2</sup>	Formate(45)	Narayanan et al. 2012
Cu <sub>2</sub> O/Zn	KOH/methanol	243K, pH=7.5	CH <sub>4</sub> (7.5) ; C <sub>2</sub> H <sub>4</sub> (28)	J. Yano and Yamasaki 2008
Cu mesh	0.1 MKHCO <sub>3</sub>	14.78 cm <sup>3</sup> min <sup>-1</sup>	C <sub>2</sub> H <sub>4</sub> (10.7); C <sub>2</sub> H <sub>6</sub> (3.7)	Goncalves et. al. 2010
Lead	NaOH	2.5 mA.cm <sup>-2</sup> ,pH=8.5	Formate(70)	Innocent et al. 2008
CuBr	3M KBr	46.1 mA.cm <sup>-2</sup> , pH=3	C <sub>2</sub> H <sub>4</sub> (80) ; H <sub>2</sub> (9)	H. Yano et al. 2004
Cu foil	0.5 M KHCO <sub>3</sub>	(-)1.85 V	CH <sub>4</sub> (31); C <sub>2</sub> H <sub>4</sub> (10); CO (3)	Kyriacou and Anagnostopoulos 1993

Cu	0.45M KHCO <sub>3</sub>	22 mA.cm <sup>-2</sup> , 298K	Formate (86)	Y. Hori et al. 2005
Cu <sub>2</sub> O-ZnO	0.5 M KHCO <sub>3</sub>	-1.8V vs. Ag/AgCl	CH <sub>3</sub> OH (25.2)	Albo et al. 2015
Cu foil	0.1 M KHCO <sub>3</sub>	10 mA.cm <sup>-2</sup>	CH <sub>3</sub> OH (0.1)	Kuhl et al. 2012
Cu foil	0.5 M KHCO <sub>3</sub>	30–35mAcm <sup>-2</sup> at –2.00V	CH <sub>4</sub> -C <sub>2</sub> H <sub>4</sub> (64)	Dewulf and Bard 1988

The above table (Aeshala et.al.,) descriptively summarizes the findings from various studies. These include key factors such as products obtained along with their efficiencies, pH, Voltage applied, catalyst, effects of electrolytes, the conductivity of the electrolyte and other experimental parameters.

The electrochemical reduction of carbon dioxide, mainly depending upon the catalyst materials, operating conditions and the reaction medium produce many useful products. We can conclude after clearly observing the table that the output of the reaction can be altered by changing the electrolyte and the electrode composition. It is also clear that many studies have used metal catalysts such as platinum, lead, tin, copper and combination of Cu and Zn etc. along with liquid electrolyte like aqueous bicarbonate. The products formed were also affected by the operating temperatures. It is also observed that the common byproduct of the reaction was generally the simplest carboxyl acid that is HCOOH and occurred naturally. The application of formic acid is mainly in livestock feed as a preservative. However, the formation of hydrocarbons from carbon dioxide is relatively a challenging task. The past few decades have seen studies discussing various catalysts, the



combination of them and different procedures which generally considered along with few other promoters, the main catalysts to be Cu and Cu-Zn oxides (Liu et al. 2003). These catalysts help in the electrochemical reduction of carbon dioxide as discussed earlier into many useful products. Since these catalysts are highly surface sensitive, the activity and selectivity strongly depend on the catalyst's surface structure and stability. It is also said that as the area of the catalyst increases, the catalyst activity also increases (Askgaard et al. 1995; Pan et al. 1988; Rasmussen et al. 1994).

Generally,  $\text{KHCO}_3$  solution is used as an electrolyte with the help of Cu electrodes for reducing carbon dioxide electrochemically (Kyriacou and Anagnostopoulos 1993; Y. Hori et al. 2005; Yoshio Hori et al. 1986; Kaneco et al. 2003). The occurrence of ethylene after the reduction of carbon dioxide over Cu electrodes was a flatterer as there was a decrease in the bicarbonate concentration along with an increase in the pH at the surface of the electrode which in turn caused the reduction in the methane-ethylene ratio (Murata and Hori 1991). But, there was no considerable effect on the methane ethylene ratio when potassium chloride electrolyte solution was used along with Cu electrodes because of the high pH value at the surface of the electrode in comparison with Potassium carbonate ion. After a series of tests by Lee in 1999 using Cu/PTFE GDE along with various concentrations of  $\text{KHCO}_3$  electrolyte (K. R Lee et al. 1999), showed that there is a reduction in the methane-ethylene ratio with an increase in  $\text{HCO}_3^-$  and in turn an increase in the pH at the surface of electrode. It was also observed that there was a reduction in the evolution of methane in the order of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ . Ethylene evolution was seen

to be higher than methanol when promoters like potassium hydroxide were used whereas with the addition of sodium and lithium perchlorate the evolution of methane was high in methanol. A decrease in the hydrogen evolution was observed with a decrease in the cationic size in the aqueous solutions.

The interconnection between attributes of copper as an electrode and the evolution of hydrocarbons was the main idea for many treatments on Cu (Terunuma, Saitoh, and Momose 1997). Copper metal surfaced can be easily poisoned by organic compounds due to its strong affinity for adsorbed oxygen. Copper oxide has the higher activity for reduction of protons. Ikeda used a Cu coated gas diffusion electrode in 1995 (Ikeda et al. 1996) which resulted in the formation of Methane, Ethane, Ethanol, carbon monoxide and Formate ion as the products. Comparatively low faradic efficiencies were observed than those with Copper I oxide electrodes. Goncalves reported the formation of ethylene in the reduction process when cathode was found with deposits of Cu (Goncalves et al. 2010). The observations were essential in stating that there was an increase in the ethylene evolution with the increase of the surface area from 18.7 percent to 33 percent of Cu deposits on the cathode. Experiments conducted by placing Pt near Carbon dioxide showed the formation of CH<sub>4</sub> with 38.8 percent faradic efficiency. Centi et al., could convert gas phase carbon dioxide to liquid carbon chain at room temperature and pressure using the Nafion membrane as electrolyte and platinum nanoparticles as catalyst. It was also reported that there was an increase in the methane evolution with respect to the increase in the pressure with a peak limit of 20atm.

Methanol was identified to be the main product as the result of the electrochemical reduction of carbon dioxide when  $\text{Cu}_2\text{O}$  is used as catalyst (Chang et al. 2009 a). It is also stated that the stability of the intermediate products improved with cuprous oxide, which plays a dominant role in  $\text{CH}_3\text{OH}$  formation (Lee et al. 2011).

There is a phenomenal response showed by copper towards ERC when the oxidation state and the stability of electrode were not accounted. But there was a need for a more stable catalyst for high selectivity because simultaneous reactions would corrode copper oxide thus making the experiments with the same electrode non-repetitive. As we have seen a positive result for studies working with copper oxide, stabilization of the copper oxide surface would make better sense.

Various studies have been done on different types of copper materials such as meshes, foils and other derived electrodes which show that the hydrocarbon formation faradaic efficiency is very low and there is a larger scope of development in this area. So, to reduce the disadvantages of aqueous solutions and improve the performance, a solid polymer electrolyte or SPE has been proposed for ERC. Despite all this research, the improvement in this area is limited and a lot of work is to be done to incorporate the use of solid polymer electrolyte in ERC on large scale basis.

### 3. EXPERIMENTAL SETUP

In this chapter, reaction mechanisms and setup that is adopted for the process of electrochemical reduction of carbon dioxide using renewable energy is explained in detail. The two main components of this setup are electrochemical reactor and membrane electrode assembly (MEA) which sits right in the middle of the electrochemical reactor.

#### 3.1 Reaction Mechanism

The process of electrochemical reduction of carbon dioxide (ERC) uses an electrochemical reactor where the reactions takes place and the end products are released. Solar power drives the reactions that occur in this process, therefore it is also called as artificial photosynthesis as solar energy is being used to reduce carbon dioxide to other carbon-based fuels.

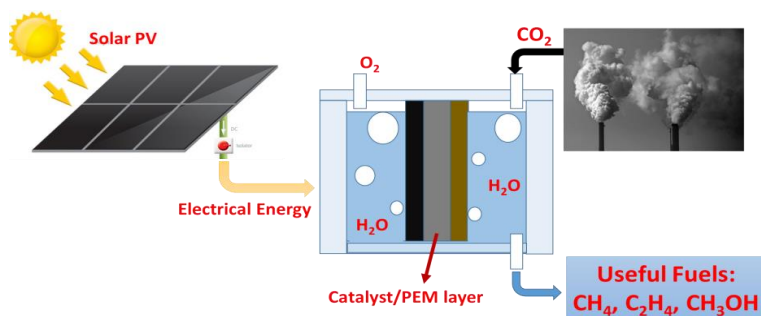


Fig 5 a: Illustration of Solar Powered Electrochemical Reduction of CO<sub>2</sub>

In general, there are two types of electrochemical cells galvanic and electrolytic. Chemical energy of fuel is directly converted into electrical energy by induced spontaneous reactions in galvanic cell, whereas in electrolytic cell electrical energy is to be supplied by external means to drive the non-spontaneous reactions. Electrochemical reactor that we used for our process is an electrolytic cell that uses solar power to reduce carbon dioxide at cathode and

to oxidize water at anode. Equation 3.1 shows the oxidation of water at anode which produces electrons, protons, and oxygen. Electrons produced at the anode are transported to the cathode via external circuit and reduction of carbon dioxide takes place at cathode according to the equation 3.2. The overall reaction is shown in equation 3.3.

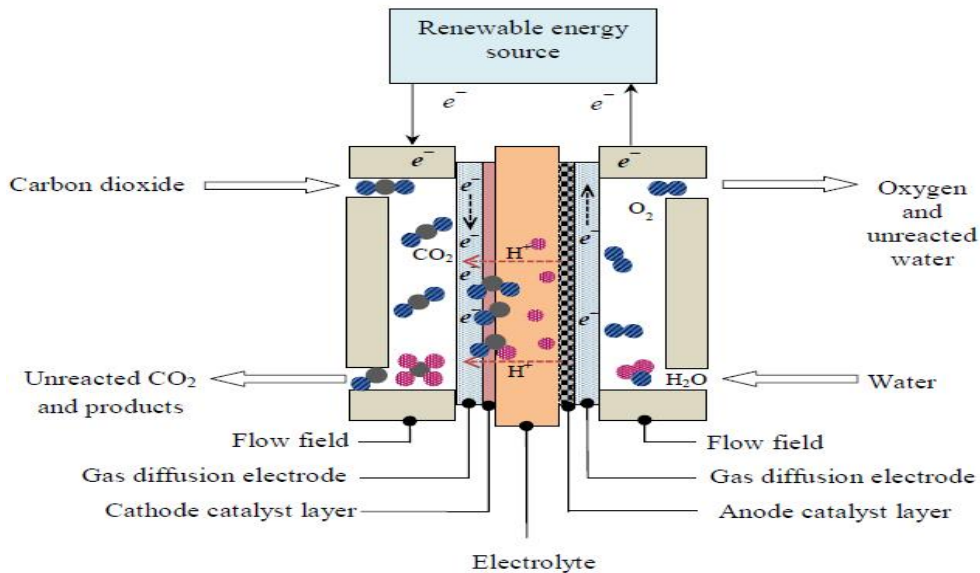
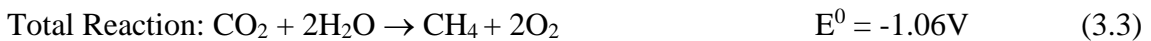
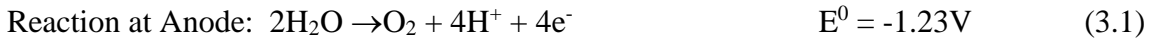


Fig 5b: Pictorial description of oxidation and reduction reactions

### 3.2 Electrochemical Reactor

Electrochemical reactor used in the process of electrochemical reduction of CO<sub>2</sub> consists of two graphite plates which have flow channels engraved on them which facilitate the flow of reactants from input channels to the catalyst and the flow of products from active reaction sites to the output channels. The reactor also consists of monopolar plates also

called as endplates which have two outputs, two input channels and it is these plates which help in holding the cell together. Input channel on the cathode side is connected to the source of carbon dioxide which in our case is a carbon dioxide cylinder and the input channel on the anode side is connected to a water reservoir via peristaltic pump which pumps the water from reservoir to the electrochemical reactor at a very slow flow rate of 1 ml/min. Fig 5 depicts the assembly of the electrochemical reactor. The potential is applied to the gold-plated terminals using EZ-Stat Pro Potentiostat. The electrons formed on the anode side are compiled by the end plate on anode side, flow through the terminals and are transported to the end plate on the cathode side by the external circuit. Rubber sleeves are used to prevent the reactor from short circuit. Membrane Electrode Assembly (MEA) is placed in between the graphite plates and the reactor is sealed using the tie rods.

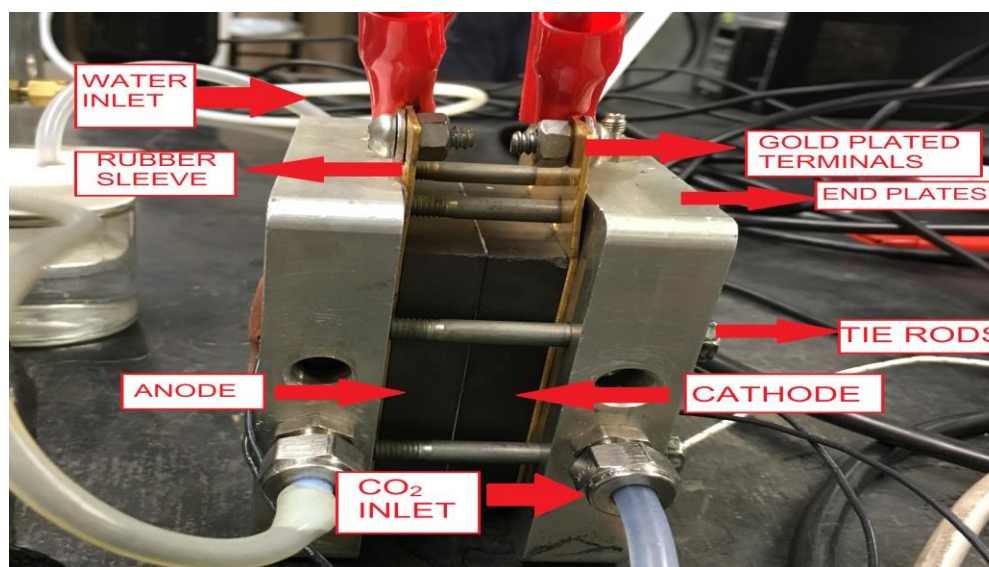


Fig 6: Electrochemical reactor

### 3.3 Fabrication of Membrane Electrode Assembly (MEA) and Gas Diffusion Layer (GDL)

Gas Diffusion Layers (GDL's) are fabricated using porous carbon paper. Hollingsworth & Vose Company's carbon paper has been used from Massachusetts, USA. The main purpose of using gas diffusion layer is to provide support for the anode and cathode catalyst materials in the electrochemical reactor. An ink is coated on the porous carbon paper to increase the conductivity as it provides the electrical contact between catalyst material and current collector. The ink is made by thoroughly mixing pure black (PB) and vapor grown carbon fiber (VGCF) in the ratio of 3:1. A very little amount of Sodium Dodecyl Sulfate (SDS) is then added to this mixture along with distilled water and sonicated for 30 min followed by stirring for 60 min. Polytetrafluoroethylene (PTFE) is then added and stirring is continued for 10 more minutes.

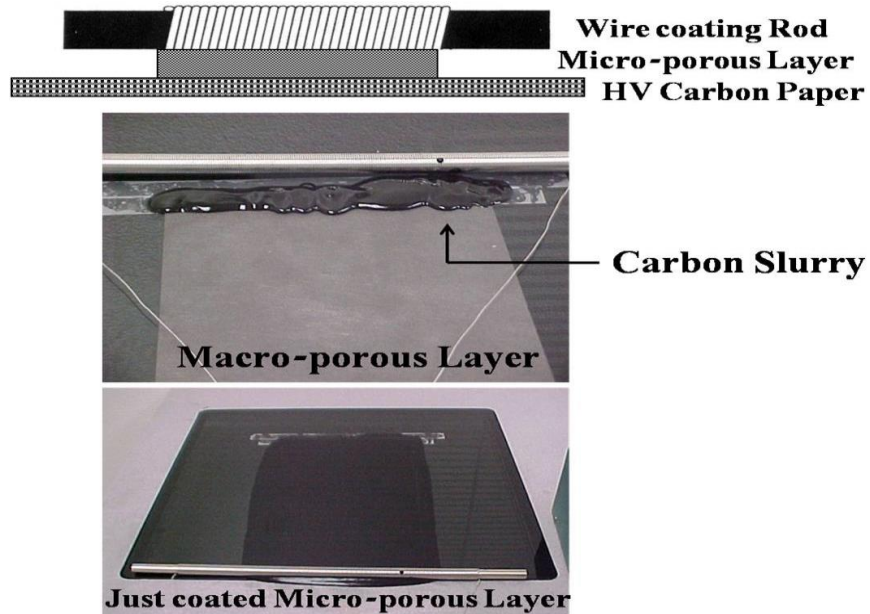


Fig 7: Illustration of coating ink on porous carbon paper

This ink is then coated on porous carbon paper using wire rod coating machine and the sample is left over night to dry at room temperature. Next day the sample is sintered at a high temperature for 30 min and washed with distilled water and allowed to dry completely before use.

The electrodes are fabricated by air depositing the catalyst ink on to the solid polymer electrolyte membrane (Nafion-212) with the help of a spray gun. Anode for both Pt and Cu<sub>2</sub>O MEA's is fabricated using platinum-carbon catalyst ink which is prepared by mixing 40 wt% pt/c catalyst powder, IPA (Iso- Propyl Alcohol) and 5 wt% Nafion dispersion and sonicating this mixture for approximately 30 minutes followed by stirring for 30 min. The composition of ink by weight is 70 percent platinum and 30 percent Nafion. Catalyst loading on the anode side is always kept constant at 0.3 ml which is approximately 0.4 mg/cm<sup>2</sup>. Cathode for the Pt-MEA is developed by coating the same platinum catalyst ink, but the catalyst loading on cathode side is increased to 0.6 ml which is approximately 0.8 mg/cm<sup>2</sup>. Cathode for copper oxide (Cu<sub>2</sub>O)- MEA is developed by coating copper oxide catalyst onto SPE ink with spray gun, Cu<sub>2</sub>O catalyst ink is prepared by mixing 99.98% pure Cu<sub>2</sub>O nanoparticles of size 18nm with ethanol to make 1.5% (w/v) solution and then adding 5wt% nafion to this solution to act as binder. Catalyst loading on the cathode side for the Cu<sub>2</sub>O-MEA is approximately 3 mg/cm<sup>2</sup>.



Membrane Electrode Assembly (MEA)	Cathode, Loading (mg/cm <sup>2</sup> )	Anode, Loading (mg/cm <sup>2</sup> )
Platinum-carbon	Platinum-carbon, 0.8 mg/cm <sup>2</sup>	Platinum-carbon, 0.4 mg/cm <sup>2</sup>
Copper oxide (Cu <sub>2</sub> O)	Copper oxide, 3 mg/cm <sup>2</sup>	Platinum-carbon, 0.4 mg/cm <sup>2</sup>

Table 2: Two different catalysts, loading on cathode and anode sides

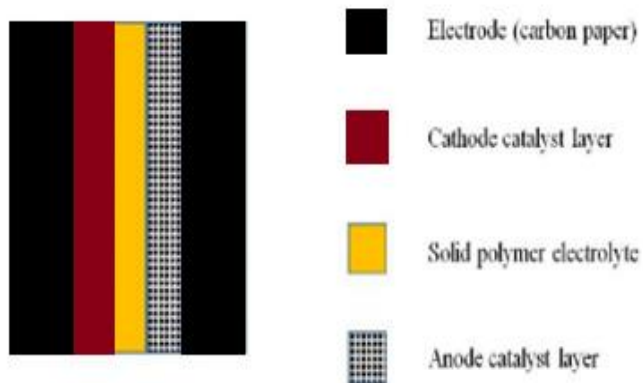


Fig 8a. Illustration of MEA with GDL

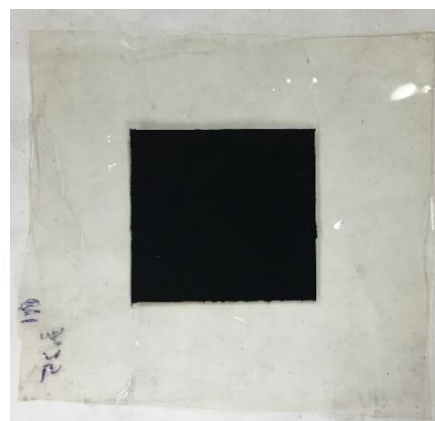


Fig 8b. Snap shot of MEA

#### 4 CHARACTERISATION OF CATHODE CATALYSTS USING LSV

After the fabrication of Membrane Electrode Assembly (MEA), it is sandwiched between graphite plates of electrochemical reactor for characterizing the cathode catalysts. 99.995% pure carbon dioxide from the pressurized cylinder is fed into inlet on the cathode side at a flow rate of 20 ml/min. Flow rate of carbon dioxide is monitored by rotameter. Deionized water from the reservoir is fed into the inlet on the anode side at a flow rate of 1 ml/min with the help of a peristaltic pump. Excess water is collected from the outlet on the anode side and is fed back to the reservoir. The outlet of cathode is where the reactions products are collected for further analysis using GC. Temperature of the electrochemical reactor is varied using a heater that is controlled by a PID controller.

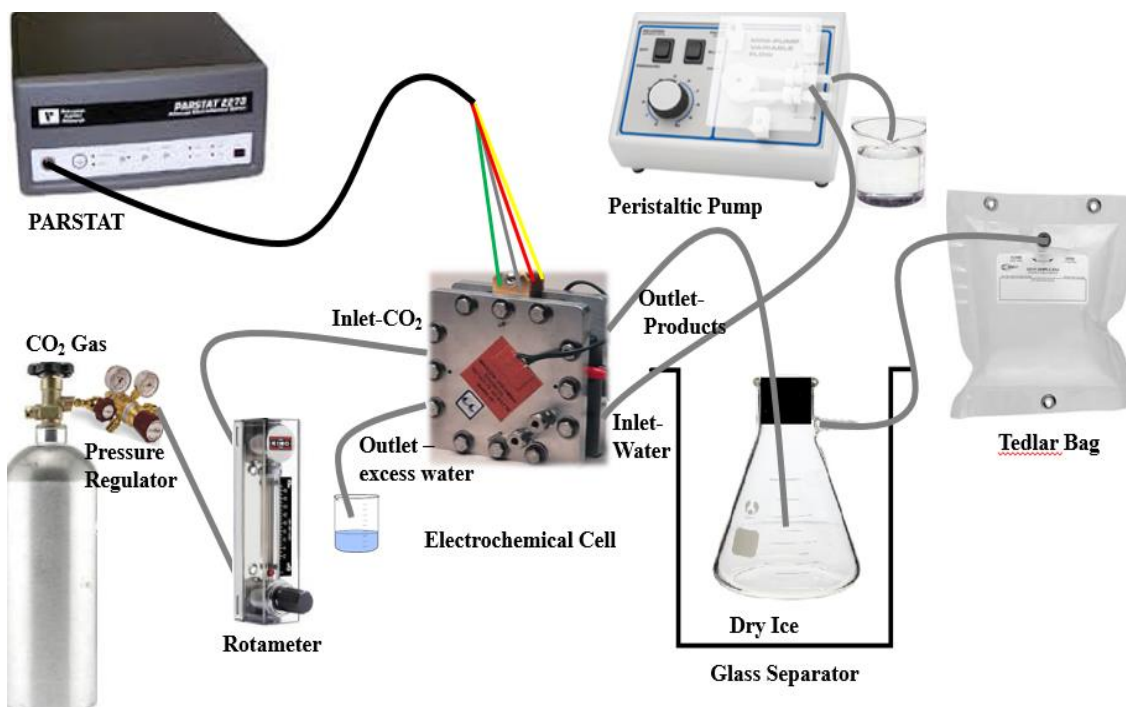


Fig 9: Pictorial representation of electrochemical reduction of carbon dioxide.

Potential applied to the electrochemical reactor during the process of electrochemical reduction of carbon dioxide is controlled by using EZ-STAT Pro potentiostat. The two techniques that are employed during the experiments to assess the performance of the membrane are chronoamperometry and linear sweep voltammetry.

#### 4.1 Chronoamperometry

Chronoamperometry is used to study the kinetics of reaction, diffusion processes and adsorption. It is the technique of measuring current as a function of time by keeping the voltage constant. The potential vs time profile on the left side in figure 8 is the input given to the system where  $E_i$  is the initial voltage and  $E_1$  is the final voltage. At time  $t=0$ , voltage spontaneously rises from  $E_i$  to the final value. The current vs time profile on the right side is obtained as an output for the given input. For reactions that are under diffusion control current decay follows Cottrell equation. Faradaic efficiencies and total mole products can be obtained by integrating the current response which gives us the total system charge.

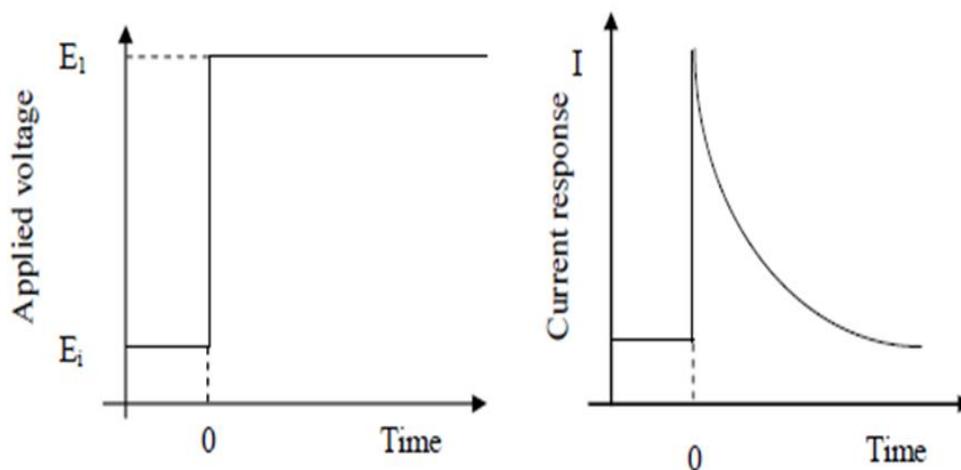


Fig 10a: Voltage and Current profiles using Chronoamperometry technique

#### 4.2 Linear Sweep Voltammetry (LSV)

Linear sweep voltammetry is an electrochemical technique where the current at a working electrode is measured while the potential between the working electrode and a reference electrode is swept linearly in time. In linear sweep voltammetry, a specified voltage range is applied and is scanned from lower limit to upper limit. By changing the scan rate, we can alter the time taken to sweep the range. The characteristics of linear sweep voltammogram recorded can be influenced by number of factors which include chemical reactivity of electroactive species, rate of electron transfer reactions and voltage scan rate.

Picture on the left side of figure 9 shows the potential-time profile which is generated by giving the initial ( $V_1$ ), final ( $V_2$ ) values for the potential and the voltage scan rate. Picture on the right side shows the output current profile that is obtained as voltage changes from  $V_1$  to  $V_2$ . The scan begins from left hand side of voltage/current plot, as the voltage begins to increase from left to right the current also increases and reaches a peak and then drops. In reactions where electron transfer rate is faster relative to the voltage sweep rate an equilibrium is established at the electrode surface and for the reactions where electron transfer process is slow relative to the voltage scan rate they are called as irreversible electron transfer reactions. This happens when the kinetics of the reaction are slow and current takes more time to react to the applied voltage, equilibria cannot be established rapidly. In this situation, the shape of voltammogram recorded would be to the one in figure 9 but the position of peak current shifts depending on reduction rate constant.

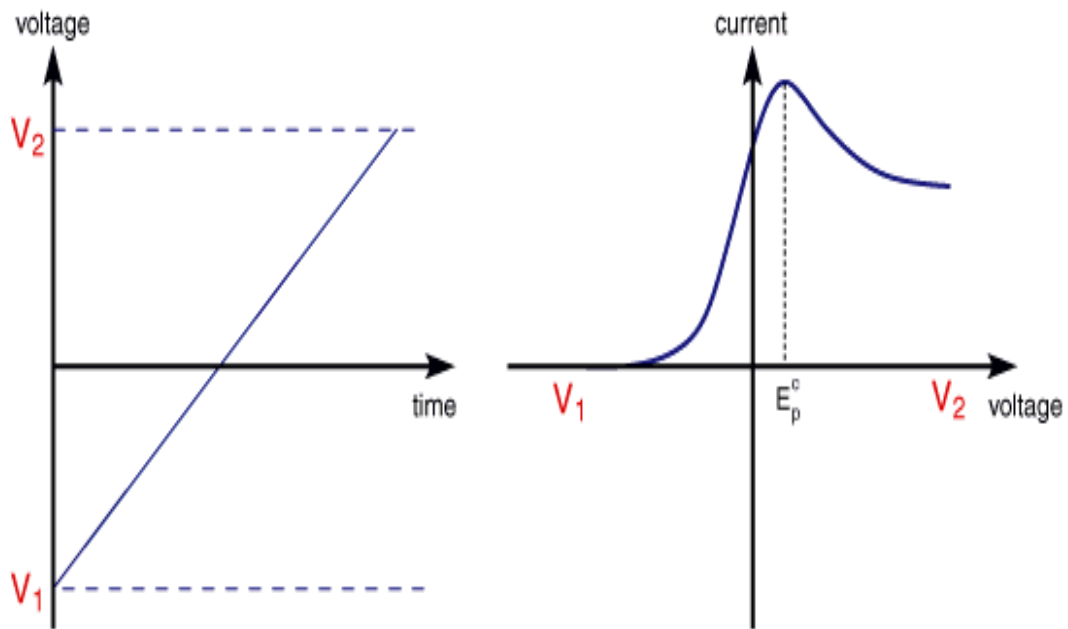


Fig 10b: Measurement using linear sweep voltammetry (<http://www.ceb.cam.ac.uk>)

## 5. PRODUCT ANALYSIS

### 5.1 Gas Chromatography

Gas chromatography was discovered by Mikhail Semenovich Tsvett, in early 1900s, it is a technique used in analytical chemistry for separating and analyzing compounds that can be vaporized without decomposition. Generally, it is used to determine the purity of a substance, separate the components of a mixture, and can determine relative amounts of each component in the mixture. Gas chromatography is performed by using instrument called 'gas chromatograph' and is used by several researchers and in industries.

A gas chromatograph usually consists of a column, injection port, gas flow control equipment, heaters which are used for maintaining temperatures of the injection port and the column, ovens, an integrator chart recorder and a detector. The sample dissolved in a solvent is vaporized to separate the analytes by distributing it between two phases mobile phase and stationary phase. Usually, inert gases like Argon or Helium is used as a mobile phase which acts as a carrier for analyte through the heated column. The Stationary phase is either a liquid on an inert support (Gas Liquid Chromatography) or a solid adsorbent (Gas Solid Chromatography).

Gas Liquid Chromatography is the most commonly used method, in this method liquid stationary phase is adsorbed on to solid inert packing or immobilized on the capillary tubing walls. There are two types of columns that are used in gas chromatography open tubular columns and packed columns. Column is considered as packed column if the glass or metal column tubing is packed with small spherical inert supports. Open tubular columns are then subdivided into wall-coated open tubular columns (WCOT) and support coated open tubular columns (SCOT). Fused silica wall coated columns are a special type

of WCOT columns with diameters as small as 0.1 mm and lengths 100 m. Packed columns are manufactured using the glass or a metal tubing which is closely packed with a solid support. Packing the tubing uniformly is difficult, so these have a larger diameter when compared with open tubular columns. Packed columns can only achieve about half of the efficiency when compared with WCOT column.

	Type of Column			
	FSWC	WCOT	SCOT	Packed
Length	10 to 1000 m	10 to 1000 m	10 to 100 m	1 to 6 m
Inner Diameter	0.1 to 0.3 mm	0.25 to 0.75 mm	0.5 mm	2 to 4 mm
Efficiency (plates/m)	2000 to 4000	1000 to 4000	600 to 1200	500 to 1000
Sample Size	10 to 75 ng	10 to 1000 ng	10 to 1000 ng	10 to 10 <sup>6</sup> ng
Pressure	Low	Low	Low	High
Speed	Fast	Fast	Fast	Slow
Inertness	Best	Good	Fair	Poor

Table 3: Properties of gas chromatography columns.

Source:

[https://chem.libretexts.org/Core/Analytical\\_Chemistry/Instrumental\\_Analysis/Chromatography/Gas\\_Chromatography](https://chem.libretexts.org/Core/Analytical_Chemistry/Instrumental_Analysis/Chromatography/Gas_Chromatography)

The Sample port is used to inject the sample into the head of the column. Modern techniques like heated sample ports facilitate the injection and vaporization of the sample in near simultaneous fashion. Vaporization chamber is generally heated 500C above the lowest boiling point of the sample and is subsequently mixed with carrier gas for transportation into the column.

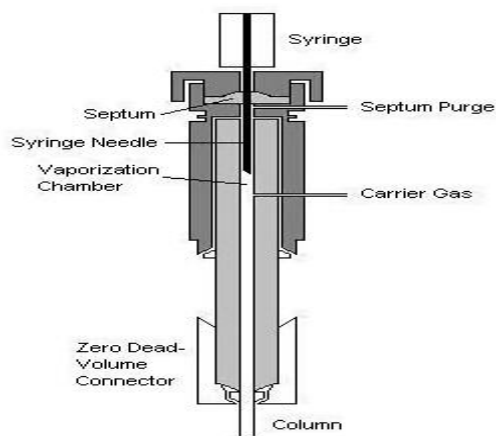


Fig 11: Cross sectional view of microflash vaporizer direct injector

When the sample passes through the column, the products interact with the stationary phase in the column. Stronger the interaction between stationary phase and product larger is the retention time and vice-versa. Several factors influence the separation of compounds in the column and retention time. Source: <https://www.chromatographytoday.com>

### ***Boiling point***

Different compounds have different boiling points. Compound spends more time in gas phase if its boiling point is low when compared to compound with the higher boiling point. Thus, it will have a lower retention time when compared to a compound with a higher boiling point.

### ***Column length***

Longer the column longer the retention time and gives better separation but, if a component must travel more time in the column, it may result in diffusive effect.



### ***Carrier gas flow-rate***

A high carrier gas flow rate results in poor separation.

### ***Column temperature***

High column temperature will often result in shorter retention times thus resulting in inadequate separation. To have good separation, the compounds should interact with the stationary phase.

### ***Polarity of the component and stationary phase***

Choosing the polarity of stationary phase is one of the key factors while setting up the GC method. The similar polarity of the target compound and stationary phase leads to greater interaction between the two. Thus, the retention time will be longer for polar compounds on polar stationary phases and shorter on non-polar stationary phases.

### ***Amount of material injected***

Chromatogram displays peaks in symmetric shape also called as Gaussian curve. If the excess sample is injected a significant tailing is depicted in the peaks which lead to poor separation. Detectors are relatively sensitive and under standard operating conditions only 1-2% of the compound injected goes through the column. To avoid excess loading of the sample most of the gas chromatographs use split-mode, alternatively split-less mode can be used if the expected concentration is extremely low.

After passing through the entire length of the column, the sample interacts with the detector. At this point of interaction an electronic signal is generated and a chromatogram

is plotted between the magnitude of the signal and time taken from the point of injection. The area under peaks in chromatogram can be directly related to the concentration of compound in the sample. Detector has two parts which when used together convert the detected property changes into an electrical signal which will be recorded as a chromatogram. The first part of the detector is the sensor which is placed as close to the column exit as possible for optimized detection. The second is the equipment used to convert the analog signal to digital signal so that a computer can analyze the acquired chromatogram. Depending upon their sensitivity to different functional groups and compounds detectors are classified into different types.

**Mass Spectroscopy Detectors:** Mass spectrometer detectors are the powerful of all detectors. In this detector, sample is bombarded by energetic electrons which ionize the molecule, furthermore bombardment causes the ion fragmentation. The ions are then passed into mass analyzer, where they are sorted according to their  $m/z$  value.

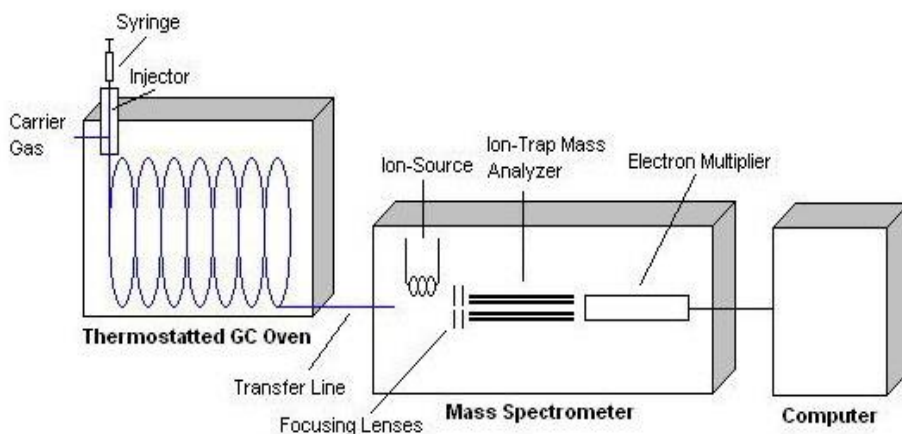


Fig 12: Schematic representation of GC-MS

**Thermal Conductivity Detectors:** TCD's as they are usually known are one of the earliest detectors developed for use in gas chromatography. It is simpler in design and consists of an electrically heated source maintained at constant power. The temperature of the source varies depending upon the thermal conductivities of the gases in the surrounding. They typically have two detectors one is used as the reference for the carrier gas and the other which monitors the thermal conductivity of the carrier gas and sample. The greatest drawback of this detectors is low sensitivity when compared to other detection methods.

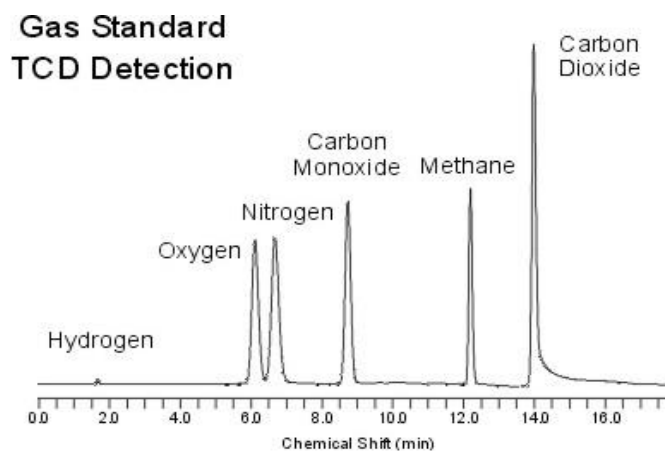


Fig 13: Standard Chromatogram for a mixture of gases.

**Flame Ionization Detectors:** These are the most widely used detectors. The sample after exiting the column, is directed to a high temperature air-hydrogen flame where the sample undergoes pyrolysis. Upon undergoing pyrolysis, compounds in sample release ions and electrons that carry current which is measured by high impedance picoammeter to monitor sample's elution. This detector is known for its high sensitivity; however, the sample gets destroyed in detector.

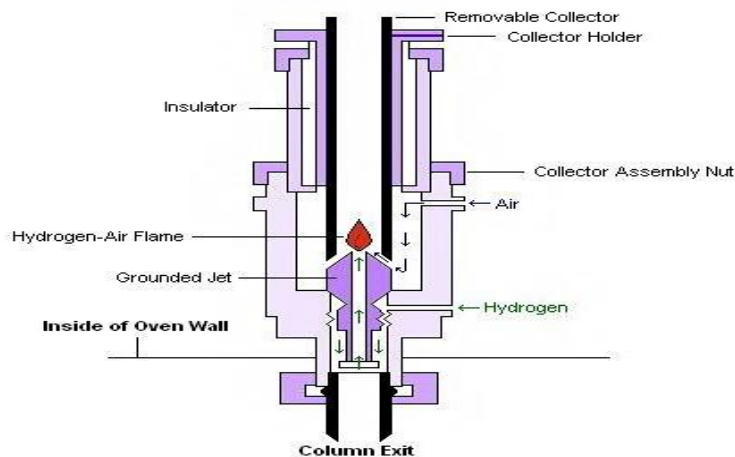


Fig 14: Flame Ionization Detector (FID)

**Electron Capture Detector:** These are highly selective detectors. It is used for detecting organic compounds and to detect some of the organic species which have electronegative functional groups. Utmost care must be taken when using this as it is dangerous owing to its radioactivity.

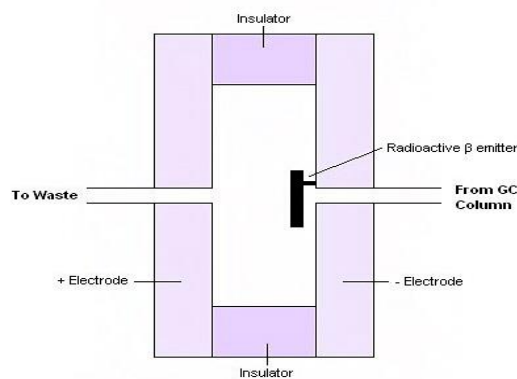


Fig15: Electron Capture Detector (ECD)

Source:

[https://chem.libretexts.org/Core/Analytical\\_Chemistry/Instrumental\\_Analysis/Chromatography/Gas\\_Chromatography](https://chem.libretexts.org/Core/Analytical_Chemistry/Instrumental_Analysis/Chromatography/Gas_Chromatography)

Table 4: Different Detectors and their detection limits

Detector Type	Samples Accepted	Detection Limit
Mass Spectrometer	Any sample	0.25 to 100 pg.
Flame Ionization	Hydrocarbons	1 pg./s
Thermal Conductivity	Any sample	500 pg./ml
Electron Capture	Halogenated Hydrocarbons	5 fg/s
Photoionization	Vapor and gaseous compounds	0.002 to 0.02 µg/L

## 6. RESULTS AND DISCUSSIONS

### 6.1 Results obtained using LSV and Chronoamperometry

Electrochemical behavior of several cathode catalysts materials was evaluated in the previous year's research and following results were obtained. The following graph and table depict the linear sweep voltammetry results obtained by using different catalyst materials and different loadings at 40°C.

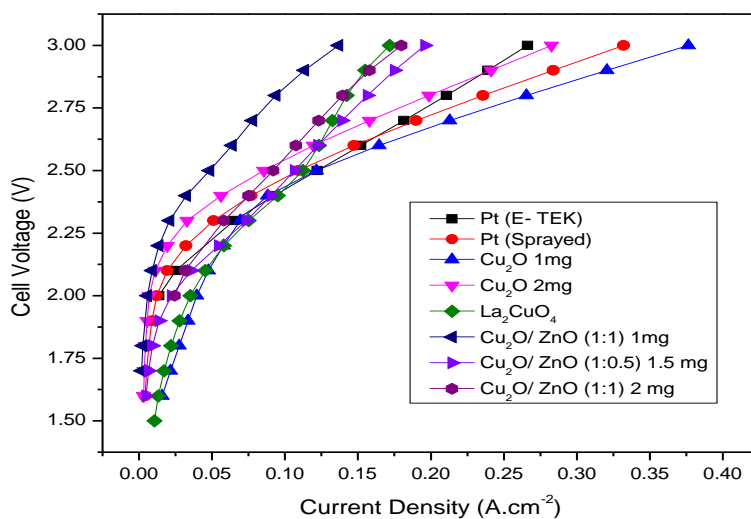


Fig 16: Linear Polarization curves for different catalysts

Electrode	Cu <sub>2</sub> O: ZnO weight ratio	Catalytic Loading (mg.cm <sup>2</sup> )	Current Density (A.cm <sup>-2</sup> )
Cu <sub>2</sub> O	1:0	1	0.376
Platinum	-	1	0.331
E-Tek	-	1	0.266
Cu <sub>2</sub> O	1:0	2	0.282

Cu <sub>2</sub> O-ZnO	1:0.5	1.5	0.195
Cu <sub>2</sub> O-ZnO	1:1	2	0.179
La <sub>2</sub> CuO <sub>4</sub>	-	2	0.171
Cu <sub>2</sub> O-ZnO	1:1	1	0.136

Table 5: Current Density values for different catalysts

From the results obtained, it is clearly evident that Cu<sub>2</sub>O and Platinum are better cathode catalysts for the reduction process of carbon dioxide. This year primary focus was laid on optimizing the process parameters using these two materials as cathode catalysts. The results depicted above were obtained in a dynamic state, so in this work more emphasis was laid on assessing the performance of cathode catalysts in a stable state. Also, the potentiostat was changed from PARSTAT 2273 to Ez-stat Pro, so we had to limit the applied potential to 2.5 V in cases where cell current was exceeding 1 A to avoid any damage to the instrument. Initially, similar results were obtained using the same operating conditions that were used in previous year's research to ensure everything is up & running.

Temperature (°C)	Current Density (mA.cm <sup>-2</sup> )
25	239
30	273
35	294
40	312

Table 6: Current densities for Pt/c

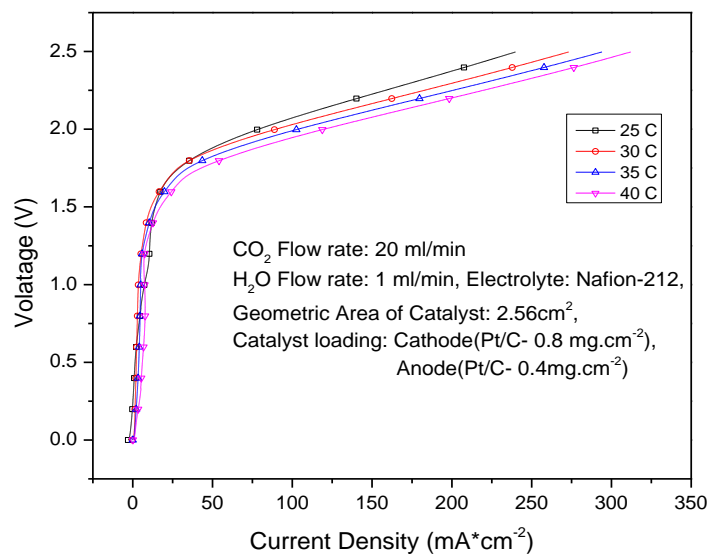


Fig 17: LSV at different temperatures for Pt/C catalyst

To determine the durability of platinum-carbon cathode catalyst, 4 trials of linear sweep voltammetry (LSV) were carried out at each temperature with a time gap of approximately 10 minutes between each trial. Experiments were performed on single MEA, to include the effects of degradation. Interestingly, current density values followed a decreasing trend as the time progressed even when the temperature was increased.



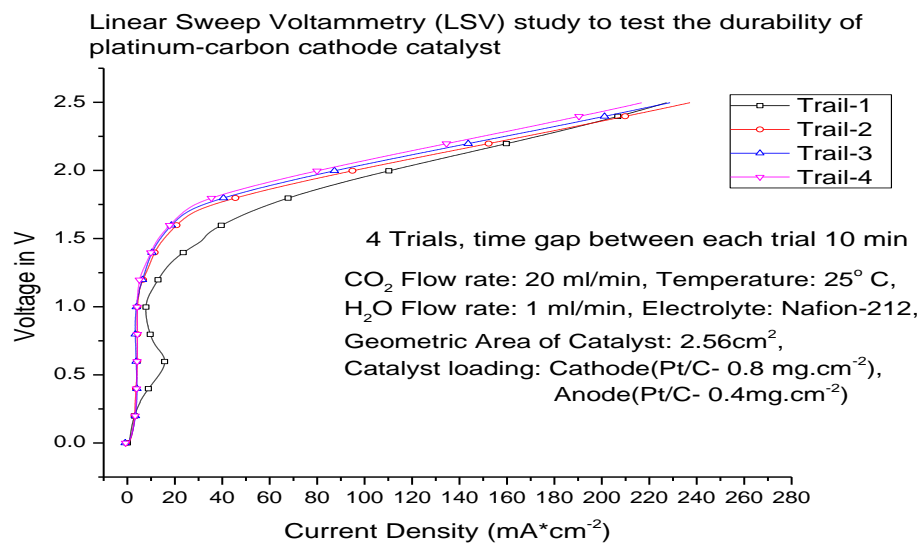


Fig 18: 4 LSV Trials at 25°C

Trial	Current Density (mA.cm <sup>-2</sup> )
1	227
2	237
3	228
4	216

Table 7: Current Densities at 25°C

When experiment was carried out at 25°C, current density value dropped from 227 mA/cm<sup>2</sup> to 216 mA/cm<sup>2</sup> in a period of 40 minutes. Similar trend was followed when experiments were performed at 30°C but the rate of decrease in current density values was higher.

Linear Sweep Voltammetry (LSV) study to test the durability of platinum-carbon cathode catalyst

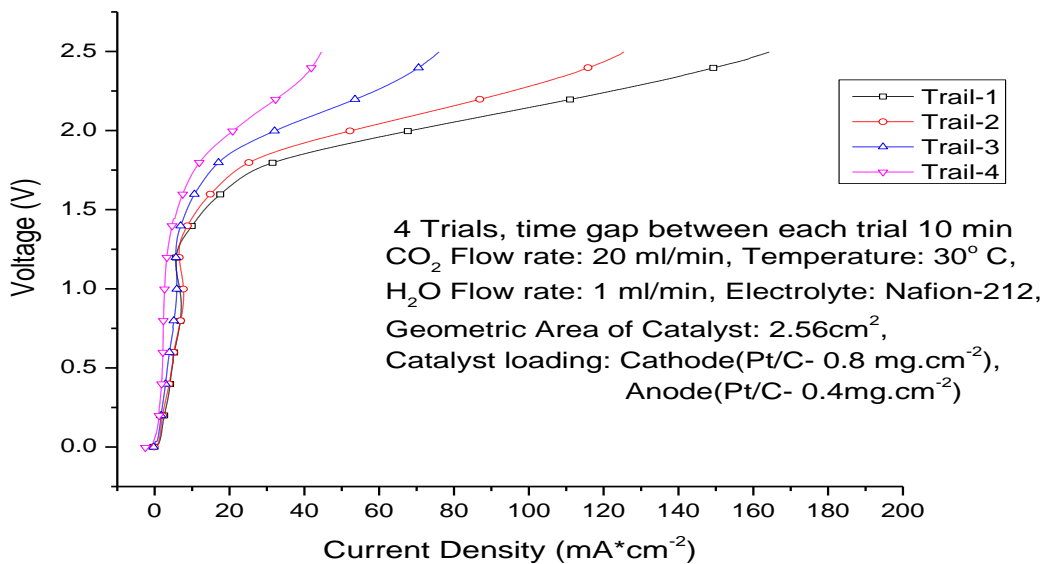


Fig 19: 4 LSV Trials at 30<sup>0</sup>C

Trial	Current Density (mA.cm <sup>-2</sup> )
1	165
2	125
3	75
4	44

Table 8: Current Densities at 30<sup>0</sup>C

At 35<sup>0</sup>C and 40<sup>0</sup>C two trials of linear sweep voltammetry were recorded with a time gap of 40 min between each trial.

Linear Sweep Voltammetry (LSV) study to test the durability of platinum-carbon cathode catalyst

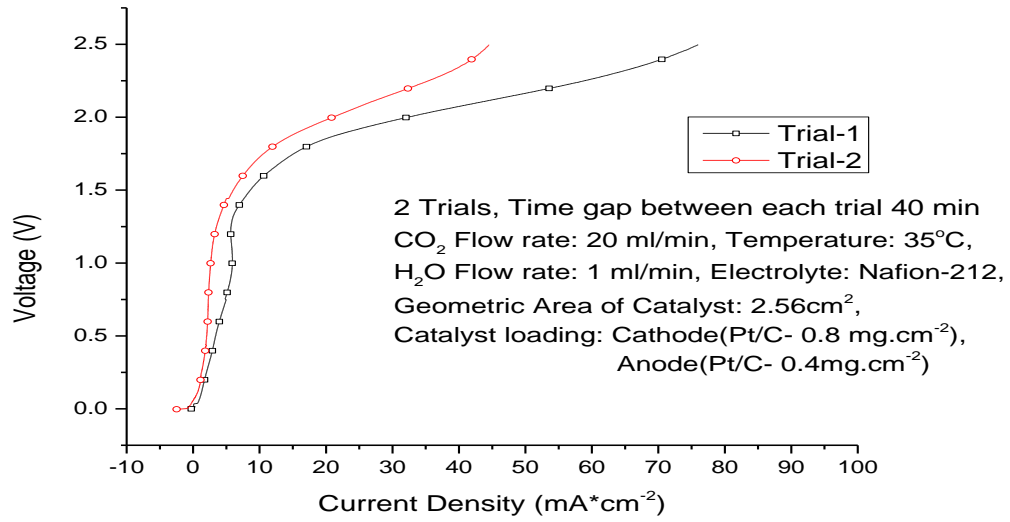


Fig 20: 2 LSV Trials at 35<sup>0</sup>C

Trial	Current Density (mA.cm <sup>-2</sup> )
1	75
2	44

Table 9: Current Densities at 35°C

Trial	Current Density (mA.cm <sup>-2</sup> )
1	31
2	28

Table 10: Current Densities at 40°C

Linear Sweep Voltammetry (LSV) study to test the durability of platinum-carbon cathode catalyst

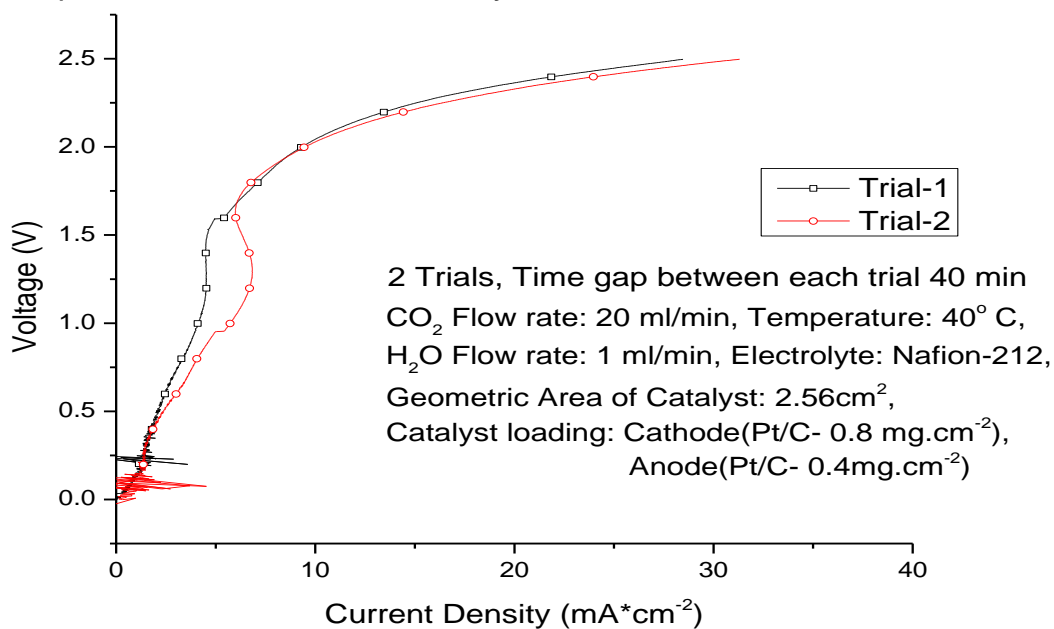


Fig 21: 2 LSV Trials at 40<sup>0</sup>C

Similar experiments were carried out using copper-oxide as cathode catalyst material. The results recorded using copper-oxide cathode catalyst exhibited greater stability when compared with platinum-carbon cathode catalyst. However, the initial current density values obtained using copper-oxide cathode catalyst are small.

Temperature (°C)	Current Density (mA.cm <sup>-2</sup> )
25	30.9
30	31.8
35	32
40	35

Table 11: Current Densities for Cu<sub>2</sub>O

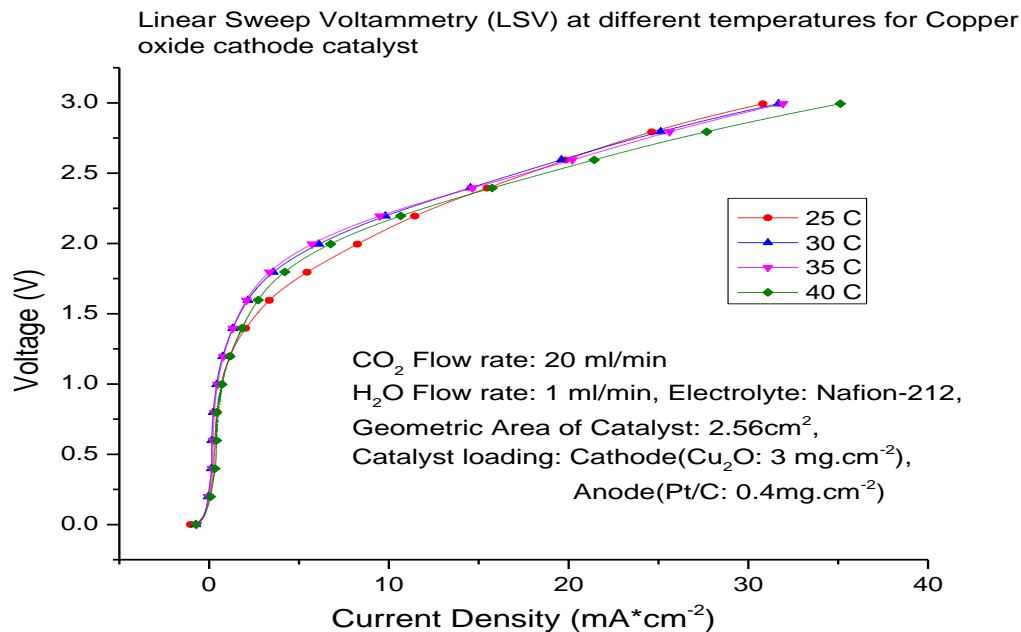


Fig 22: LSV at different temperatures

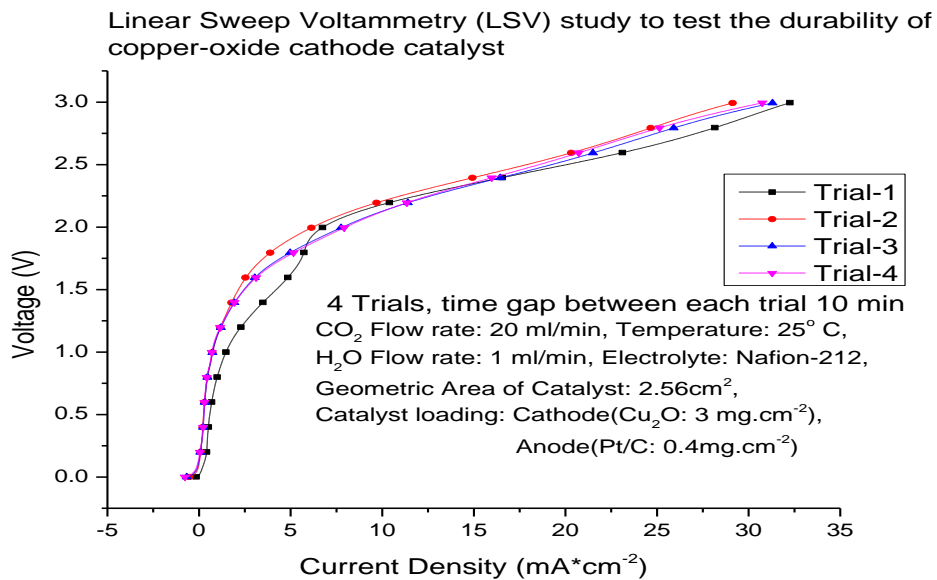


Fig 23: 4 LSV Trials at 25<sup>0</sup>C

Trial	Current Density (mA.cm <sup>-2</sup> )
1	32.3
2	29.2
3	31.4
4	30.8

Table 12: Current Densities for Cu<sub>2</sub>O at 25°C

Flow rate of carbon dioxide and deionized water were constantly monitored to ensure uniformity. The following curves depict the linear sweep voltammetry results obtained at different temperatures using copper-oxide cathode catalyst. It is observed that, though there is slight fluctuation in the values of current density at each trial the difference among them is minimal. Similar results were obtained even at higher temperatures, same MEA was used for all temperatures to include the effects of degradation.

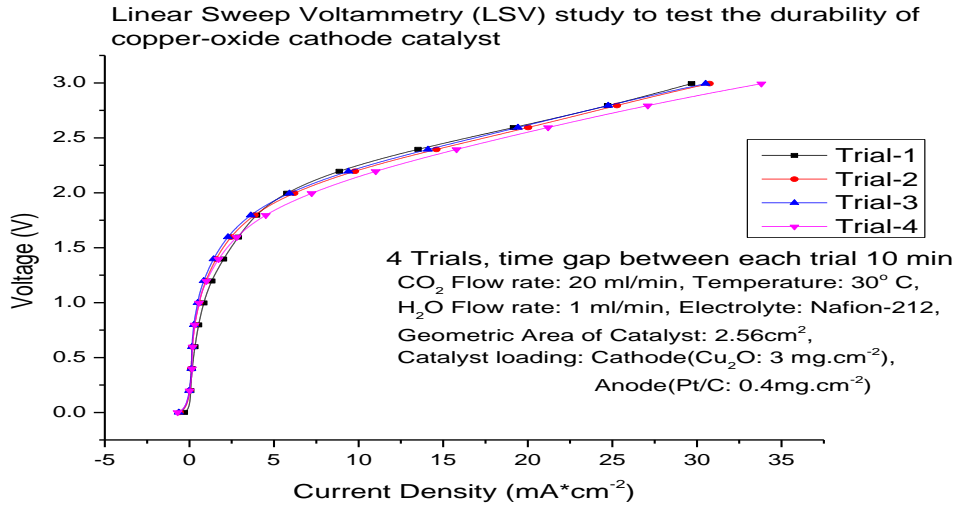


Fig 24: 4 LSV Trials at 30°C

Trial	Current Density (mA.cm <sup>-2</sup> )
1	29.7
2	30.8
3	30.5
4	33.9

Table 13: Current Densities for Cu<sub>2</sub>O at 30°C

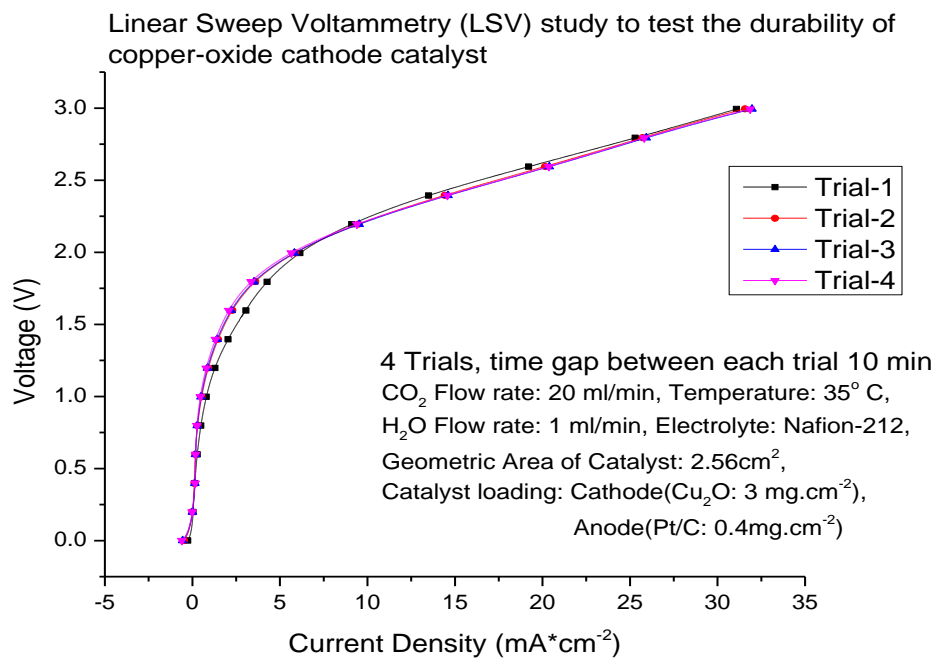


Fig 25: 4 LSV Trials at 35<sup>0</sup>C

Trial	Current Density (mA.cm <sup>-2</sup> )
1	31.6
2	31.2
3	32
4	32.03

Table 14: Current Densities at 35°C

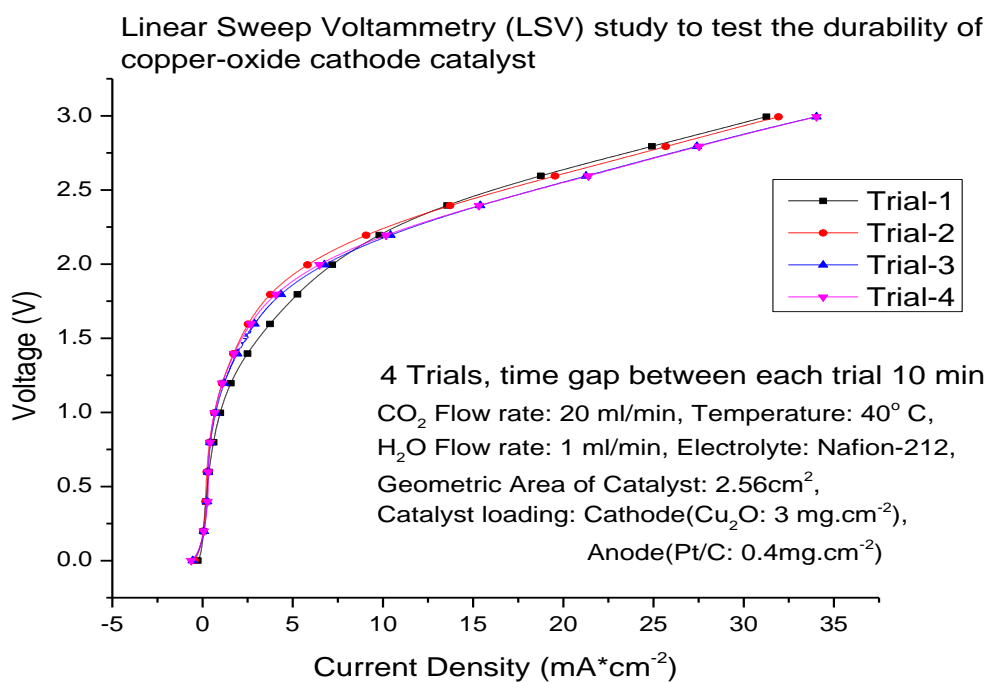


Fig 26: 4 LSV Trials at 40°C



Trial	Current Density (mA.cm <sup>-2</sup> )
1	31.3
2	32
3	34
4	34

Table 15: Current Densities at 40°C

It is observed that at all the temperatures, current density values obtained copper-oxide cathode catalyst depicted greater stability and showed less deviation with the progress of time. The results are encouraging as they suggest a higher durability for copper-oxide cathode catalyst when compared with platinum-carbon cathode catalyst. Moreover, the values of current densities obtained by using these two cathode catalysts at the end of all these trials runs are close.

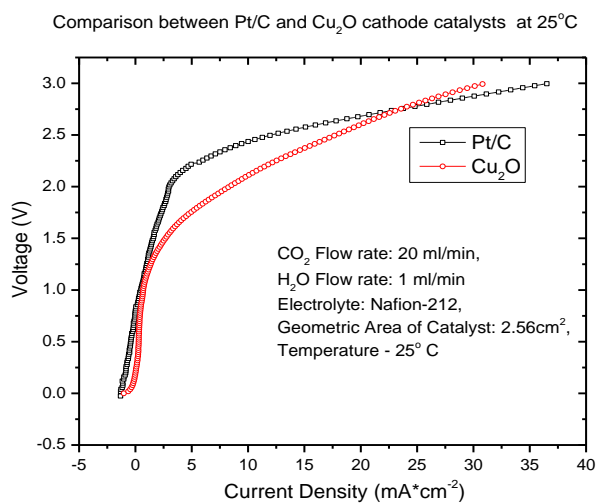


Fig 27: LSV for Cu<sub>2</sub>O and Pt/C at 25°C

Comparison between Pt/C and Cu<sub>2</sub>O cathode catalysts at 40°C

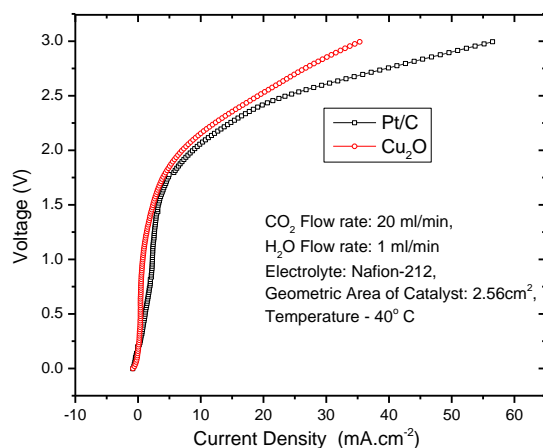


Fig 28: LSV for Cu<sub>2</sub>O and Pt/C at 40°C

From the above comparison, it is evident that both the cathode catalysts have similar performance until approximately 2.75 V only after this mark platinum-carbon curve shows an increase in the value of current density.

Furthermore, chronoamperometric studies were performed on both the cathode catalysts to assess their performance when electrochemical reactor was run for longer periods. The following curves depict the results obtained using chronoamperometric technique. Chronoamperometric studies provided a much deeper insight onto how the current density values drop much quicker when platinum-carbon cathode catalyst is used.

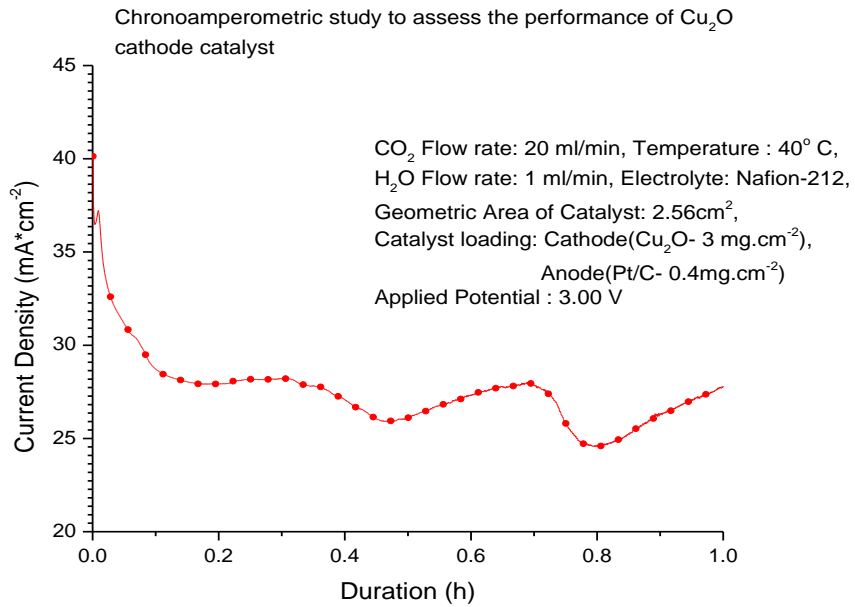


Fig 29: Chronoamperometric Study on  $\text{Cu}_2\text{O}$  for 1 hour

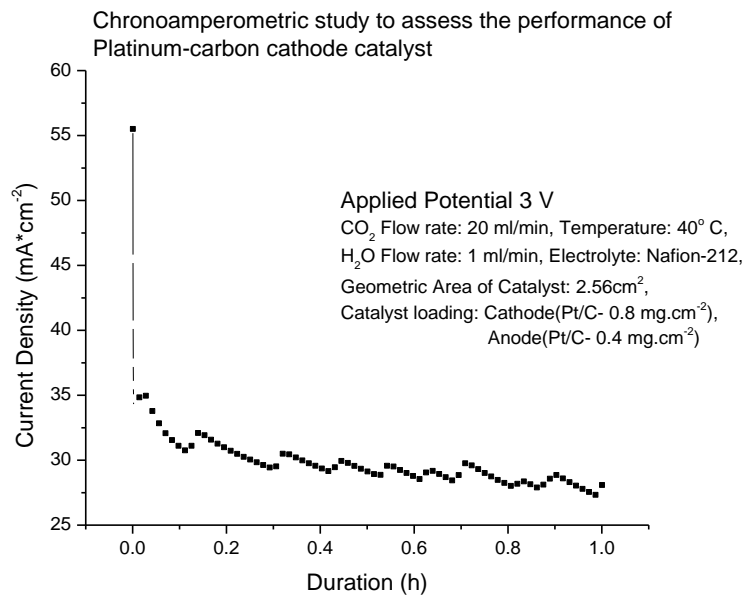


Fig 30: Chronoamperometric Study on Pt/C for 1 hour

Chronoamperometric studies provided a much deeper insight onto how the current density values drop much quicker when platinum-carbon cathode catalyst is used.

Chronoamperometric studies were also performed at different potentials ranging from 2 V to 2.75 V at two different temperatures to have deeper understanding on the performance of cathode catalysts. The following curves depict the performance of platinum-carbon cathode catalyst when chronoamperometric study was performed at different voltages for two different temperatures.

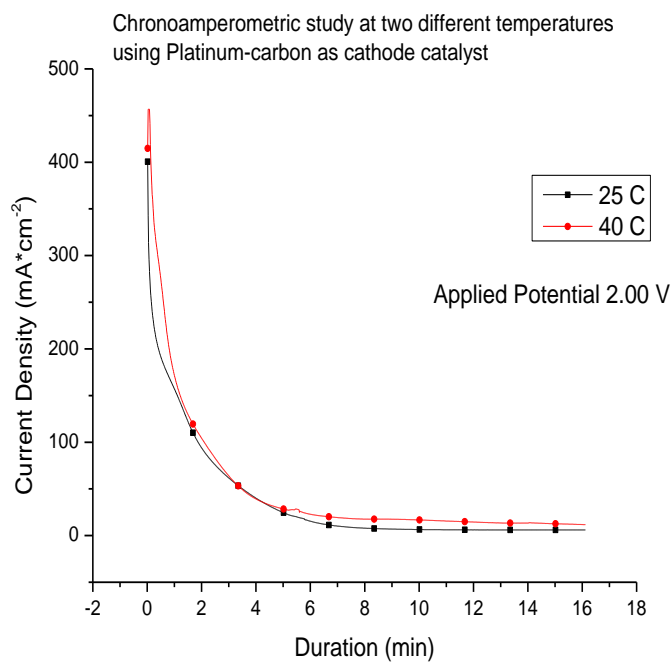


Fig 31a: Comparison of Chronoamperometric curves of Pt/C at 2V

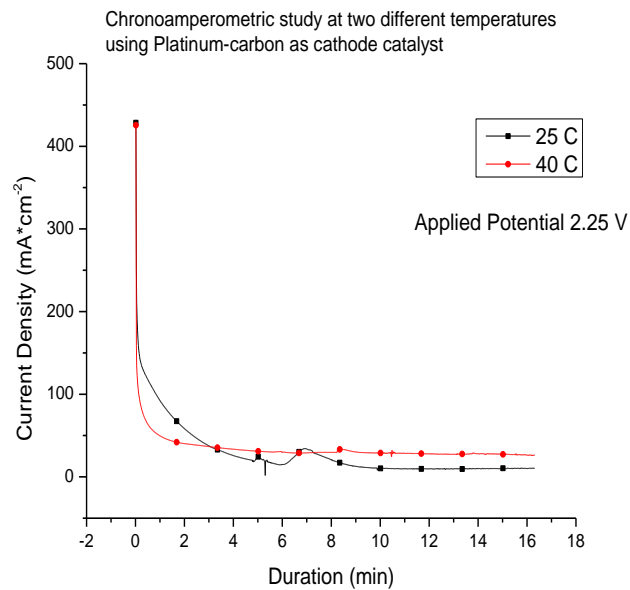


Fig 31b: Comparison of Chronoamperometric curves of Pt/C at 2.25V

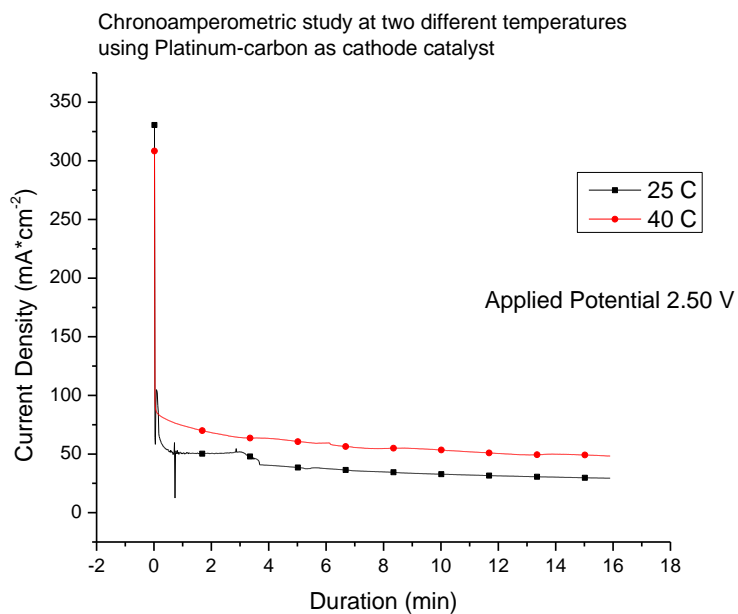


Fig 31c: Comparison of Chronoamperometric curves of Pt/C at 2.5V

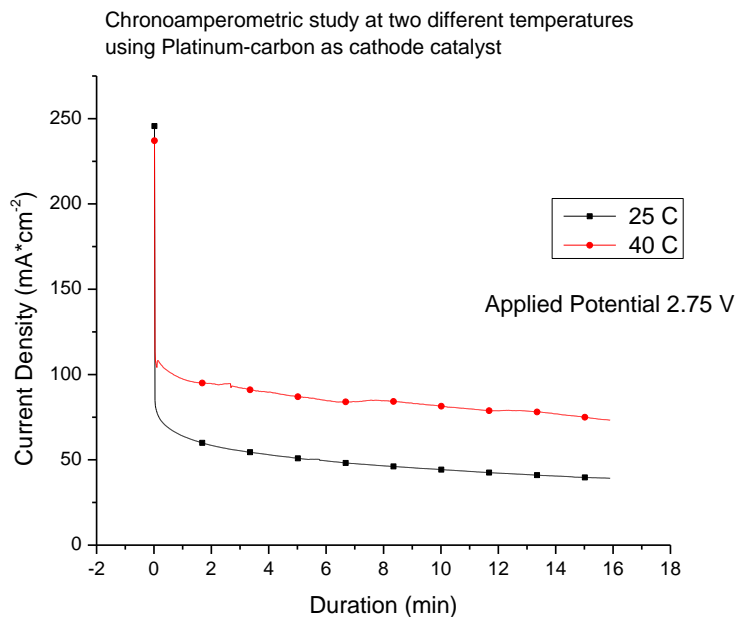


Fig 31d: Comparison of Chronoamperometric curves of Pt/C at 2.75V

Applied Potential	Current density for Pt/C at 25°C (mA*cm <sup>-2</sup> )	Current density for Pt/C at 40°C (mA*cm <sup>-2</sup> )
2.00	6.06	11.3
2.25	10.3	26
2.50	29.37	50
2.75	39.15	71.8

Table depicting the values of current density for figures 31 (a-d)

Chronoamperometric study was performed for 15 min at each potential at 25°C and 40°C. From the results it can be inferred that at 2 V and 2.25 V platinum carbon cathode catalyst performance is approximately same without having any effect of change in temperature.

But, as the potential is increased to 2.5 V and 2.75 V we can see a clear difference in performance curves at 25°C and 40°C.

Similar set of experiments were performed using copper-oxide cathode catalyst and the results are shown below.

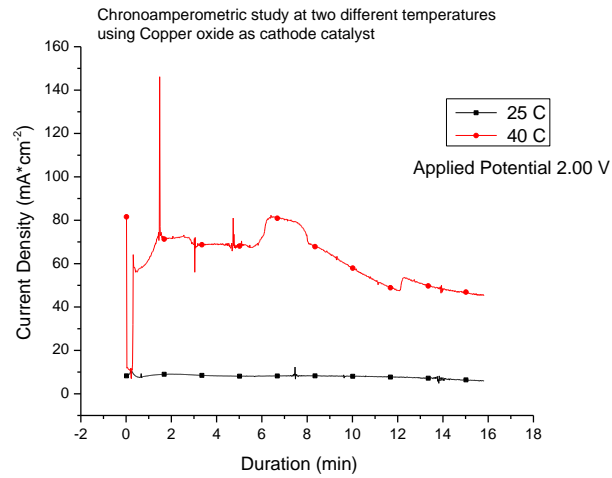


Fig 32a: Comparison of Chronoamperometric curves of Cu<sub>2</sub>O at 2V

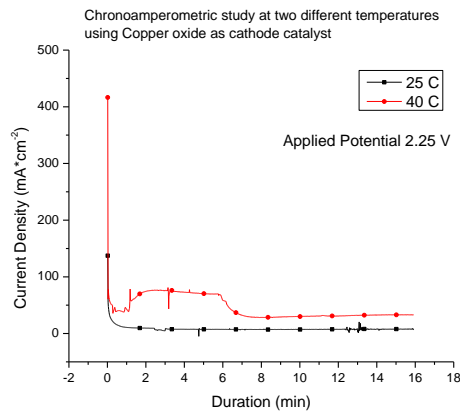


Fig 32b: Comparison of Chronoamperometric curves of Cu<sub>2</sub>O at 2.25V

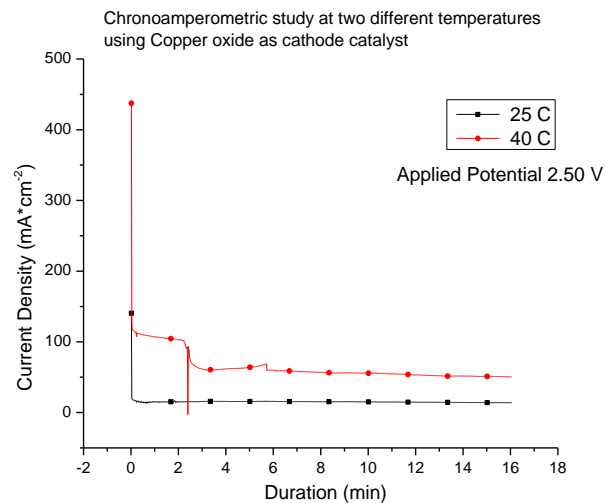


Fig 32c: Comparison of Chronoamperometric curves of Cu<sub>2</sub>O at 2.5V

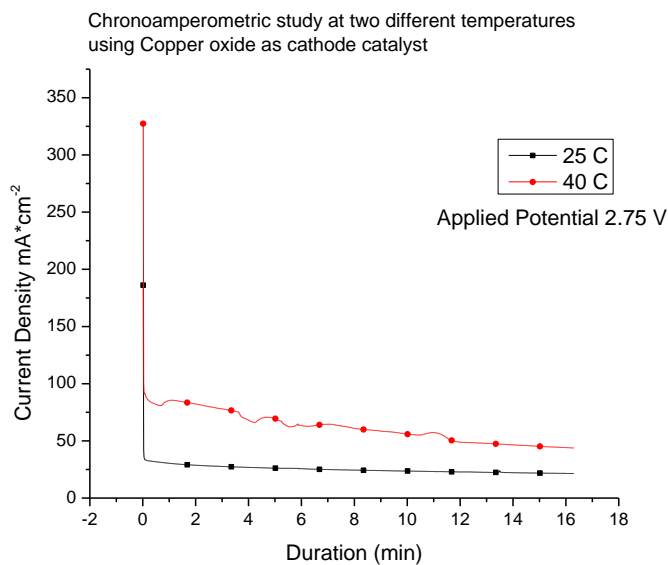


Fig 32d: Comparison of Chronoamperometric curves of Cu<sub>2</sub>O at 2.75V



Applied Potential	Current density for Cu <sub>2</sub> O at 25°C (mA*cm <sup>-2</sup> )	Current density for Cu <sub>2</sub> O at 40°C (mA*cm <sup>-2</sup> )
2.00	8.08	45
2.25	9.91	46.7
2.50	13.9	48
2.75	21.4	49.3

Table depicting the values of current density for figures 32 (a-d)

From the results obtained, it is evident that performance of copper oxide cathode catalyst at 40°C is better at all applied potentials, unlike, platinum-carbon which does not show a great change in performance with change in temperature at lower applied potential. To have a better understanding, platinum-carbon and copper-oxide cathode catalysts performance curves are plotted at 40°C for each of the potentials discussed above.

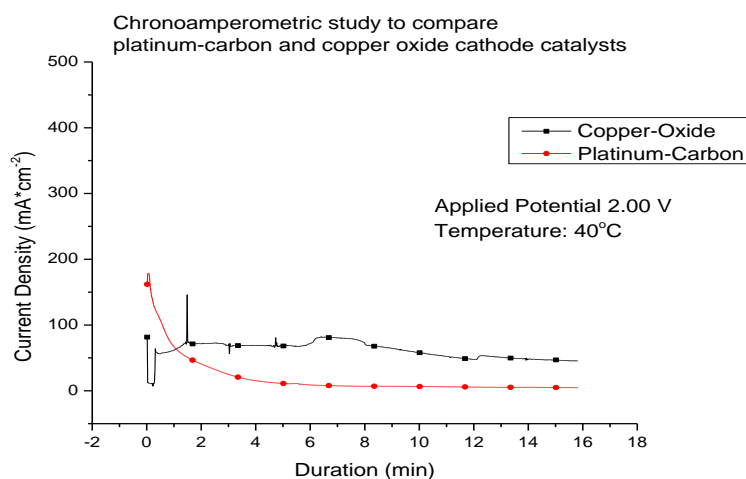


Fig 33a: Comparison of Pt/C and Cu<sub>2</sub>O at 2V, 40°C

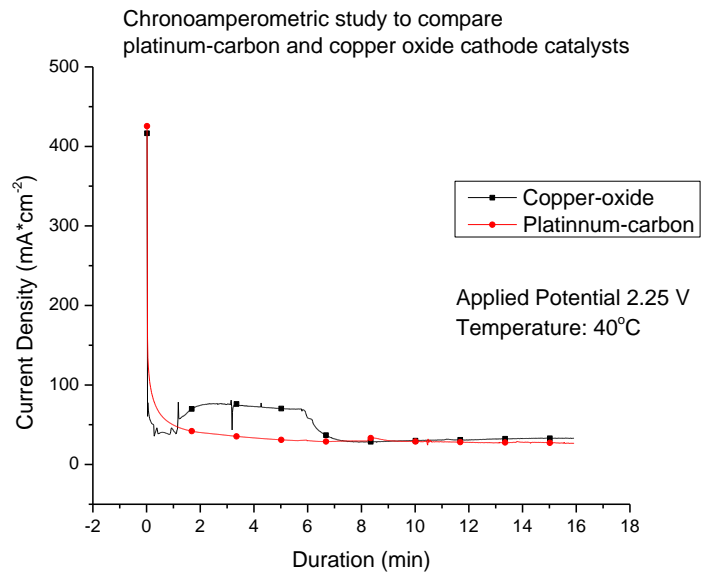


Fig 33b: Comparison of Pt/C and Cu<sub>2</sub>O at 2.25V, 40°C

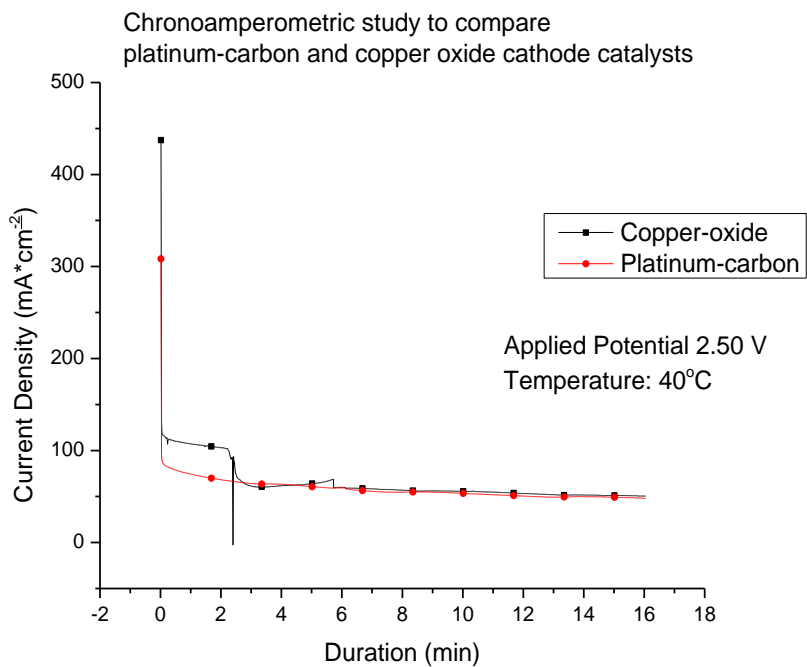


Fig 33c: Comparison of Pt/C and Cu<sub>2</sub>O at 2.5V, 40°C

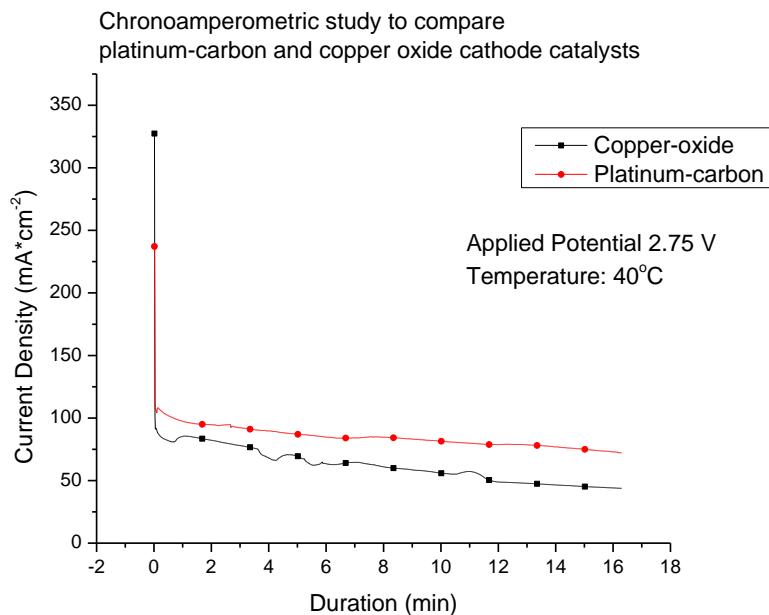


Fig 33d: Comparison of Pt/C and Cu<sub>2</sub>O at 2.75V, 40oC

Table depicting the values of current density for figures 33 (a-d)

Applied Potential	Current density for Pt/C (mA*cm <sup>-2</sup> )	Current density for Cu <sub>2</sub> O (mA*cm <sup>-2</sup> )
2.00	11.3	45
2.25	26	46.7
2.50	50	48
2.75	71.8	49.3

From this comparative study we observe that, performance of copper-oxide catalyst is better than platinum-carbon at lower applied potentials 2 V and 2.25 V. At 2.5V, the performance both the catalyst materials are same and as we increase the voltage further to

2.75 V current density obtained using platinum is higher. This result reaffirms the linear sweep polarization curves.

## 6.2 Product analysis using GC

Electrolysis was performed at 25°C and 40°C for 15 minutes at each of the different potentials 2V, 2.25V, 2.5V and 2.75V. Products are collected after 5 minutes and are analyzed using Gas Chromatography TCD and FID detectors. We can see from the linear sweep polarization curves and chronoamperometric studies that as the applied potential increases current density also increases which implies that the rate of reactions is also directly proportional to the applied voltage. Increase in rate of charge means that there is increase in charge absorbed by the chemical reactions at the electrode surface. Interestingly for the same amount of sample collected, platinum-carbon catalyst produces more hydrogen than copper-oxide. From this we can imply that most the energy supplied is being utilized for hydrogen production. Thus, hydrogen evolution reaction is dominating carbon dioxide reduction when platinum-carbon cathode catalyst is used. Furthermore, when platinum-carbon was used no carbon monoxide was detected in the products this can attributed high binding energy of platinum for CO. This can also be the reason for rapid degradation in the current density values as carbon monoxide is known for its poisoning effect on the platinum catalyst.

Amount of hydrogen formed increases with the increase in applied potential and faradaic efficiency for formation of hydrogen is close to 90%. Highest faradaic efficiency for methane using platinum-carbon catalyst was 2.4% at 40°C, 2.25V

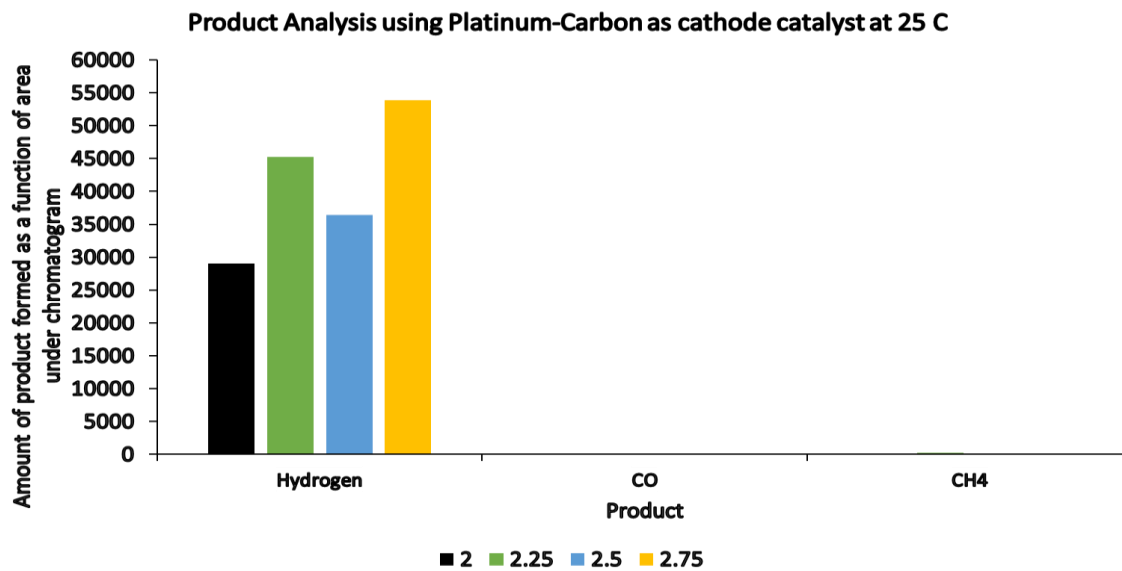


Fig 34a: Product analysis using Pt/C at 25°C

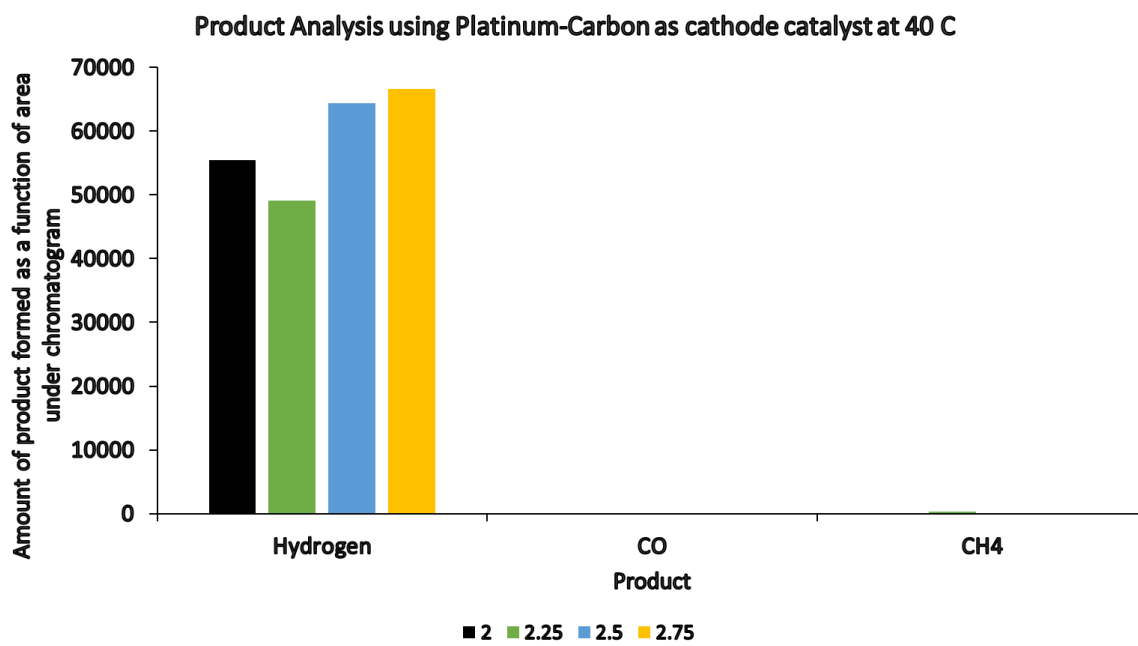


Fig 34b: Product analysis using Pt/C at 40°C

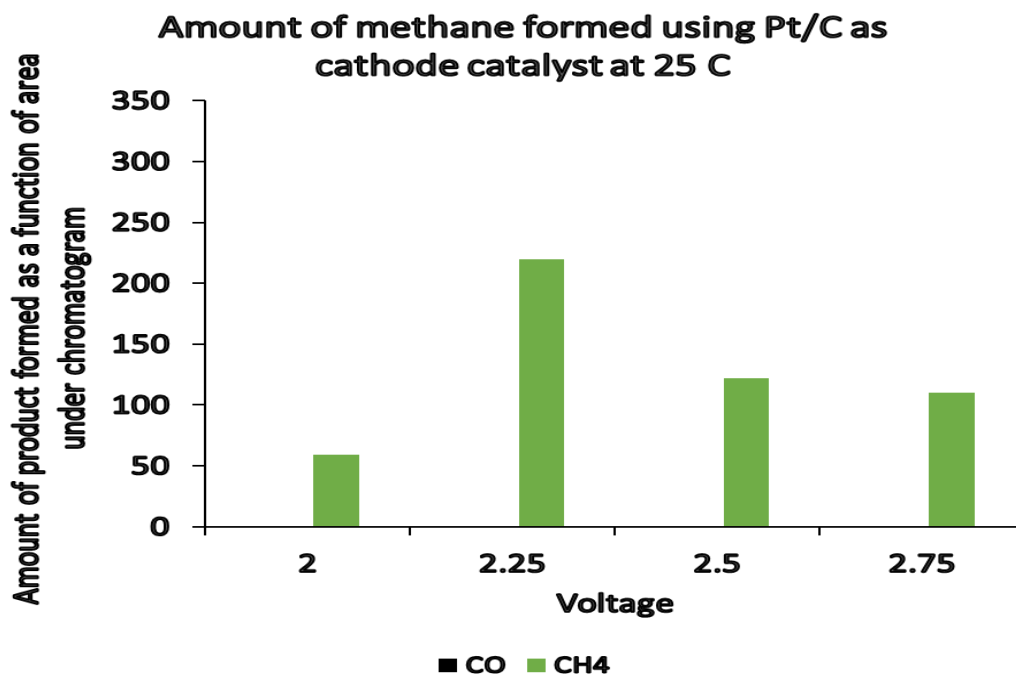


Fig 34c: Amount of methane produced using Pt/C at 25°C

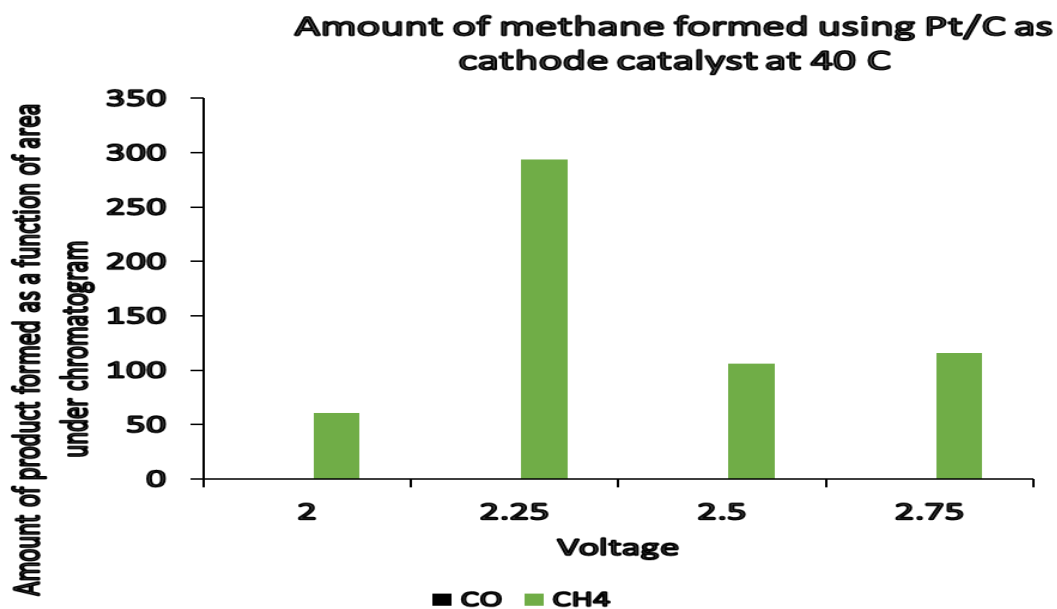


Fig 34d: Amount of methane produced using Pt/C at 40°C

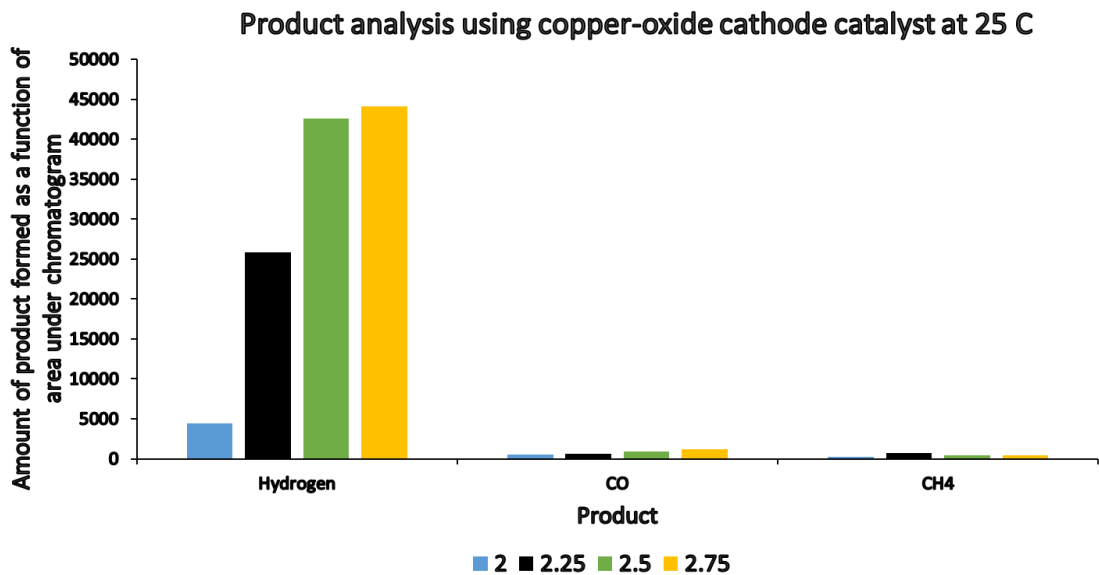


Fig 35a: Product analysis using  $\text{Cu}_2\text{O}$  at  $25^\circ\text{C}$

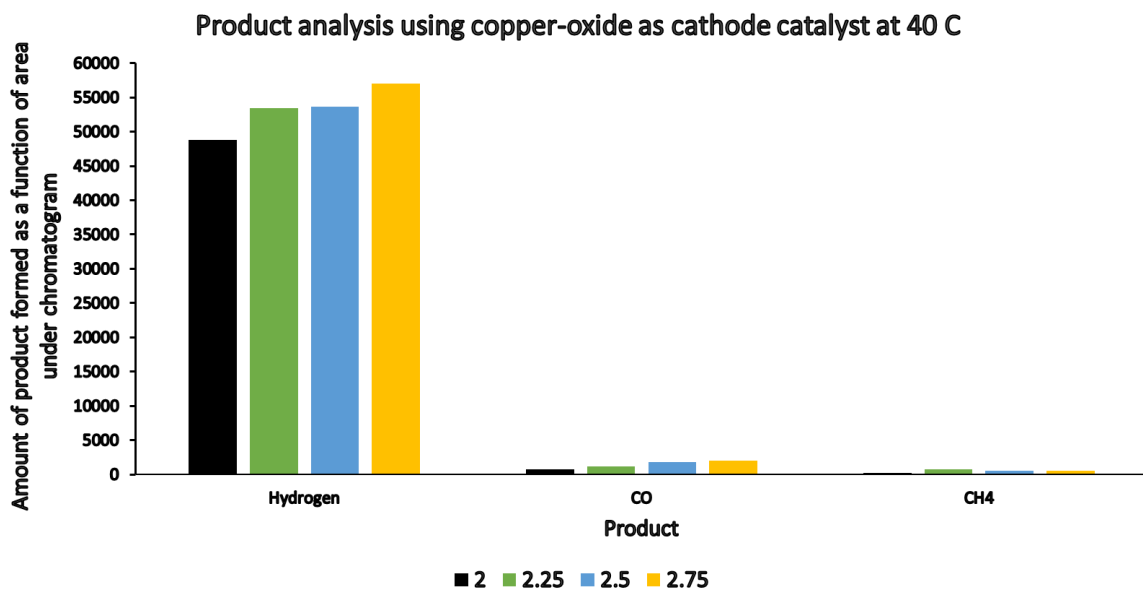


Fig 35b: Product analysis using  $\text{Cu}_2\text{O}$  at  $40^\circ\text{C}$

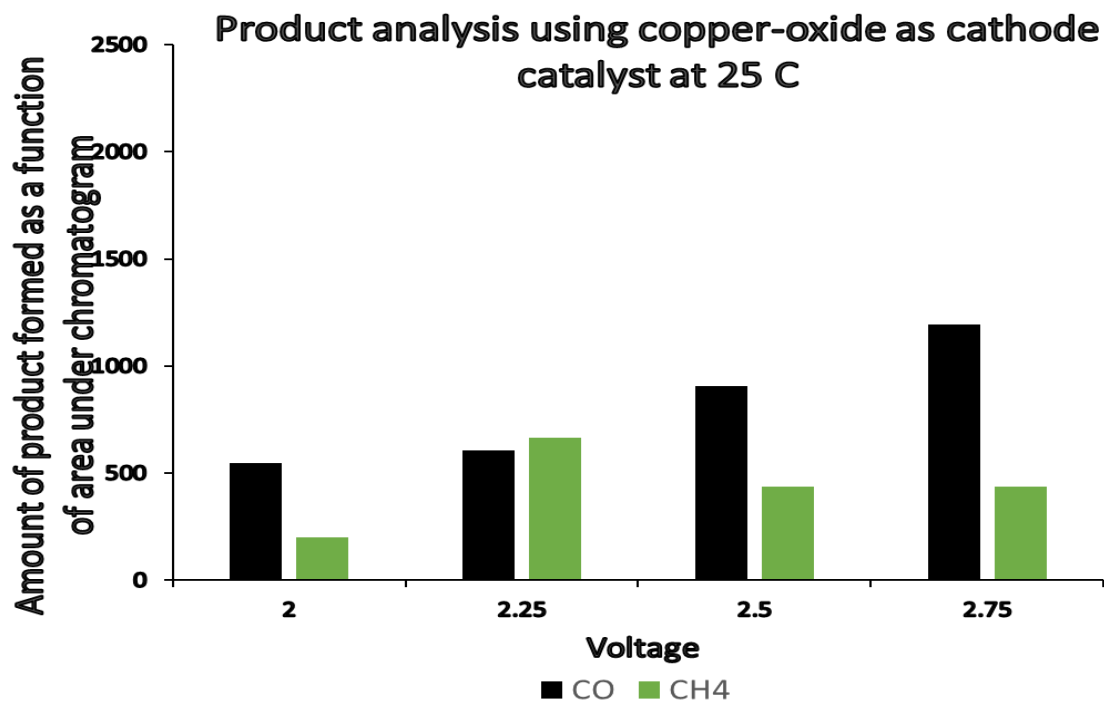


Fig 35c: Amount of CO and Methane formed using  $\text{Cu}_2\text{O}$  at 25°C

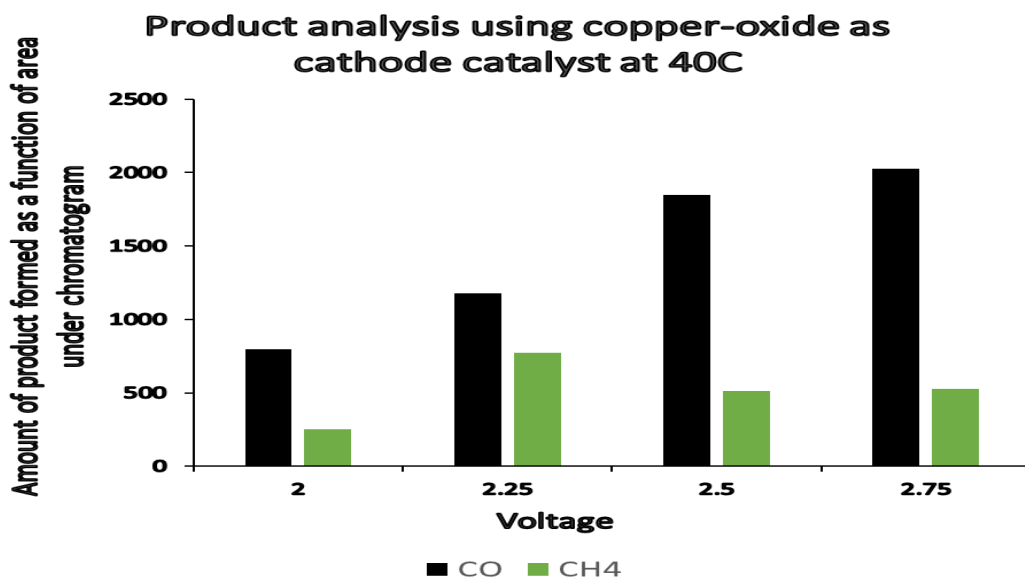


Fig 35d: Amount of CO and Methane formed using  $\text{Cu}_2\text{O}$  at 40°C



Voltage	Hydrogen (Faradaic Efficiency)	Methane (Faradaic Efficiency)
2 V	84.3	1.25
2.25 V	85.6	2.4
2.5 V	87.9	1.18
2.75 V	90.4	1.36

Faradaic Efficiencies using Pt/C at 40°C

Voltage	Hydrogen (Faradaic Efficiency)	Carbon monoxide (Faradaic Efficiency)	Methane (Faradaic Efficiency)
2 V	78.7	8.93	1.6
2.25 V	81	9.1	5.3
2.5 V	82.3	10.8	2.2
2.75 V	83.2	11.4	2.36

Faradaic Efficiencies using Cu<sub>2</sub>O at 40°C

When copper-oxide was used as cathode catalyst, carbon monoxide was detected in products and its concentration increased with increase in applied voltage. Also, the amount of hydrogen produced using copper oxide was less compared with the amount produced using platinum carbon. For copper oxide catalyst, maximum faradaic efficiency for methane was 5.3% at 2.25V and 40°C. Hydrogen evolution reaction was less predominant using copper oxide catalyst.

## 7. CONCLUSION

### 7.1 Overview

In this study MEA's were fabricated using two different cathode catalyst materials platinum carbon and copper oxide. Their performance was evaluated using electrochemical techniques like linear sweep voltammetry and chronoamperometry. Primary focus was to optimize the operating parameters for the process of electrochemical reduction of carbon dioxide. To assess the performance of catalyst chronoamperometric studies were performed at 4 different potentials and two different temperatures. It was observed catalysts performed well at higher temperatures and the optimum voltage for the process is 2.25V as the faradaic efficiencies for the formation of methane are higher at this potential. Also, it was noted that copper-oxide cathode catalyst had greater durability in long run when compared to platinum-carbon cathode catalyst which depicted a degradation with progress in time.

Copper oxide and Platinum carbon exhibited similar performance until 2.5V, only after this potential platinum carbon gave a better performance than copper oxide. From the results of product analysis, we inferred that hydrogen evolution reaction was more predominant when platinum-carbon catalyst was used implying that most energy supplied to reactor was used primarily used for producing hydrogen. Hydrogen evolution is considerably less when copper-oxide is used as cathode catalyst which make it a good fit for the process and high faradaic efficiency of 5.3% for formation of methane was obtained using this catalyst at 2.25V, 40°C.

## 7.2 Future Scope

More experiments must be done to determine various other factors that help in suppressing hydrogen evolution and increasing the carbon dioxide reduction. Replacing platinum catalyst with copper oxide can reduce this to some extent, but to make the electrochemical reduction of carbon dioxide more efficient research has to be done on other catalyst materials like silver. Also, for experiments in this study 99.995% pure carbon dioxide was used but in real world situation would be different where carbon dioxide has impurities. So, furthermore experiments must be performed using impure carbon dioxide and observe how the results vary from the present scenario. To convert large amounts of carbon dioxide into hydrocarbons this setup must be scaled up to a higher capacity which requires a research on the physical characteristics of the electrochemical reactor. Also, the electrochemical reactor must be coupled with a renewable energy source which can supply energy for the reactions. This technology of reducing carbon dioxide to a useful product using solid polymer electrolyte coupled with renewable energy source will undoubtedly become practical and economically feasible soon.

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