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# Ways To Mitigate Greenhouse Carbon Dioxide Through Electro-Catalytic Pathways

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## ABSTRACT

The global issue of Carbon dioxide emission has become a headache for the whole world, and therefore techniques like Carbon Capture Utilization and Sequestration (CCUS), Carbon Capture Utilization (CCU), and Carbon Capture Sequestration (CCS) are getting high attention. This paper deals with the Utilization of $CO_2$ to produce methanol in electro-catalytic ways due to the high availability of methanol in the field of chemicals & fuels. A process flow sheet regarding the process of converting Carbon dioxide to methanol has been mentioned. Today, methanol is predominantly produced from natural gas by reforming the gas with steam and then converting and distilling the resulting synthesized gas mixture to create pure methanol instead if we produce methanol from $CO_2$ this process is economically feasible and detailed economics regarding the production of methanol from $CO_2$ has been mentioned.

## INTRODUCTION

The consequences of climate change are felt by all of us in our life ranging from sea level rise, weather condition and many more. The recent estimates suggest that due to global warming we could see a rise in earth temperature by $1.5^0$ C in near future. To avoid this situation, we must start using lower carbon emission technology.[4] According to research conducted in Indonesia, the number of vehicles in Indonesia have reached 11,42,09,266. These flashing number of vehicles with high energy demands leads to the production of carbon dioxide. Further rise in the emission of carbon dioxide is triggered by the growth of industries, the use of fossil fuels, which accounts for the increase of carbon dioxide by three quarters in air. [1]

In May 2019, the concentration of $CO_2$ in the atmosphere exceeded the value of 415 ppm, which is nearly about 48% higher than that before the industrial revolution. Research also shows that global warming results to some of the quiet volcanoes becoming restless due to increase in rainfall. As per the reports 230 Mt of Carbon dioxide is used annually. However, the utilization of $CO_2$ is less than 1% that of the total carbon dioxide produced. Agriculture sector is the largest consumer of the carbon dioxide produced which accounts for more than half of the $CO_2$ produced which is about 130 Mt of carbon dioxide used for the manufacturing of urea.

In the upcoming future we will switch to sustainable energy like hydroelectricity, wind, photovoltaic energy. Due to variations in the nature, these energies must be stored at the times of surplus production to use it during the times of low production. One way is to convert it into chemical energy and produce methanol, this method is often regarded as one of the most promising methods. Methanol has high potential because of its availability in the field of chemicals and fuels.[2]

$CO_2$ utilization means using of $CO_2$, at concentration above atmospheric level. The Technology to capture, utilize and store carbon oxides mainly, carbon dioxide and carbon monoxide has been in operation for many decades. Carbon utilization is used to depict different pathways in which captured carbon dioxide and in few instances carbon monoxide are used to produce some valuable products. The reports suggest that Enhanced Oil Recovery uses most of the captured carbon dioxide. America uses around nineteen million tons of $CO_2$ for EOR. [4]

The advantages of $CO_2$ utilization include - improvement of catalysts for manufacturing of syngas through dry reforming of methane with $CO_2$, development of effective photo/electrocatalysts to liberate hydrogen from water, enhancement of photo/electrocatalysts for breakdown of $CO_2$, development of reversibly reducible metal oxides for generation of syngas with the use of rich sunlight, make new building materials, involving wood.This technique has the potential to reduce the industry's carbon dioxide level up to 20% of the total carbon dioxide release.His method retains $CO_2$ that can fulfill up to 40% of global energy requirements in industries and refineries.

## LITERATURE REVIEW


[14][15][16]

The $CO2$ is the most dominant gas release from any industry and manufacturing plant, so receiving this $CO2$ for the utilization purpose can be made. This can reduce the effect of $CO2$ on the environment. This can be conducted by CCS and CCU techniques.

Carbon capture sequestration (CCS)

- This technique as a **carbon capture sequestration** is majorly performed in three main steps **capture, transport, and sequestration.** The capture of $CO2$ is a key step of CCS technology which is done by post-combustion, pre-combustion, and oxy-fuel combustion (zero-emission cycle). While the Sequestration(storage) is conducted by various methods like **Geological storage, Algae/bacteria Mineral storage, Enhanced oil recovery. [15]**

**ADVANTAGE**

This technique has the potential to reduce the industry's CO2 level by up to 20% of total CO2 release.

The pure and high concentrated $CO2$ can be obtained by the oxy-fuel method in CCUS which work on a zero-emission cycle.

OXY-FUEL method of CCS also decreases pollutants like $NO2$, NO, and $SO2$ by 50% by implementing this method overall.

The overall cost of carbon can also reduce if we capture the carbon dioxide.[9]

**DISADVANTAGE**

IF we implement the CCS technology in current plants and industries the operation cost of equipment increases up to **50-80%** by electricity consumption.

The capture $CO2$ by the CCS method is a low-grade **carbon** in most industries, so sometimes cost recovery is more than the actual carbon price.

In the enhanced oil recovery method, we recover a cardon and inject it into the oil tank and when we utilize it will again release the carbon, so most methods have this problem in CCS.

While the storage of $CO2$ we are taking care of more safety issues.[9]

**Carbon capture utilization (CCU)**

- This CCU method is carried out by capture of carbon from **industries** and **manufacturing plants** and then utilizing them to make carbon product that contributes to the economy and add a social valve to the people. The CCU can be carried out by various methods like electrochemical conversion, thermochemical conversion, biological conversion, and photochemical conversion. Through these various methods, many products are from **methanol, ethanol, methane, Syngas, carbon monoxide, and formic acid. [13]**

**Advantage**

This technology's focus is to utilize the capture $CO_2$ from any plant and industry.

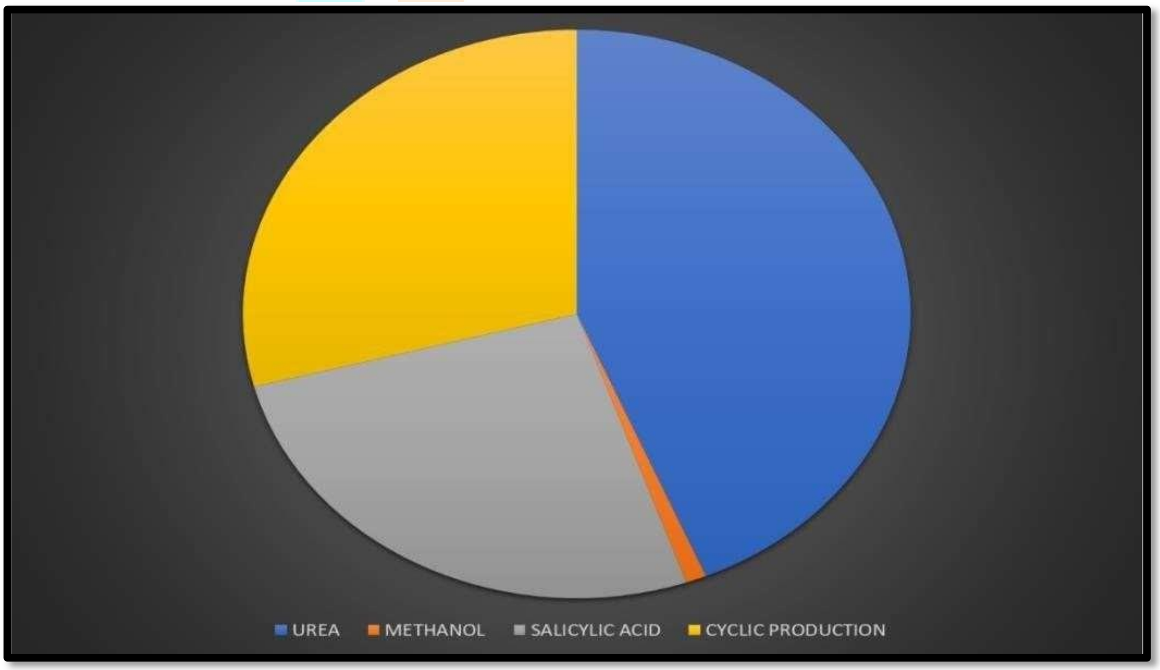
CCU technology capture $CO_2$ is used to make valuable products like fuel, hydrocarbon, various gas, innovative carbon-based product.

In this process, the storage problem is no more in the picture of carbon utilization.

This is closely related to the sustainable development of carbon product and help in the industry's cycle.

**Disadvantage**

This process requires huge costs for implementation in any continuously running company and industry.




[13]

**CCUS**

**Advantage**

This technique can fulfil the global requirement of $CO_2$ in a sustainable manner that does not affect nature and save the environment.

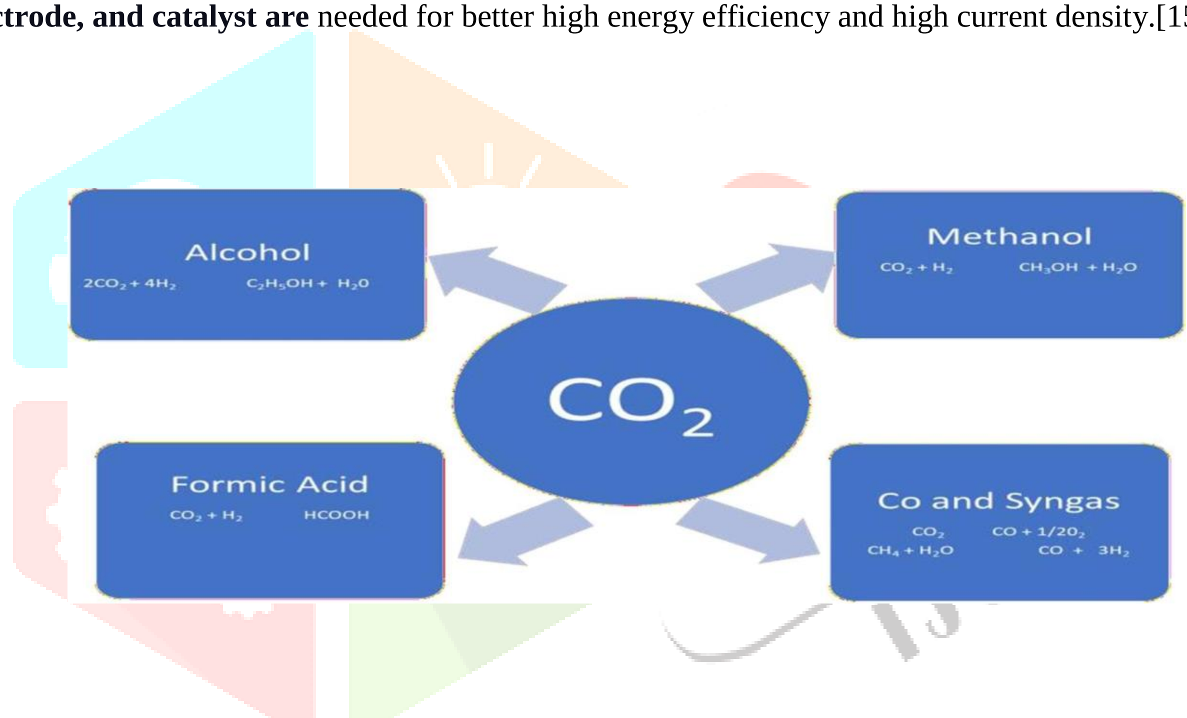
This method retains the $CO_2$ can fulfil the 40% percentage of global energy requirements in industries and plants.

This method becomes easy to implement and reduces the complexity of rection.

This process works on the combination of CCS and CCU, so it is easy to develop new carbon- based products by this method.[10]

**Electrocatalytic $CO_2$ conversion**

The production of $CO_2$ by various manufacturing processes and industries is collected or stored and utilized by **electrochemical reduction that** produces chemicals and fuels like **methanol, formic acid, and other hydrocarbons** by using electricity as a source of energy. This process can be efficiently conducted at room temperature and low pressure. The energy source is taken from renewable energy like solar, wind, geothermal, hydroelectric, and thermoelectric. However, ERC needs an electrocatalyst that works at **low electro potential** and gives **high current density**. By ERC, techniques mainly methanol and formic acid are produced due to their high efficiency. Hydrocarbon and syngas are also efficient options to carry by the ERC method. The electrode plays a key role in the formation of any product by $CO_2$. The two classes of electrodes are aqueous and non-aqueous. Metallic electrodes in aqueous supporting electrolytes are **In, Sn, Hg, and Pb**, and non-aqueous media are **Zn, Au, and Ag**. Major Electrochemical $CO_2$ conversion focuses on **copper** as an electrode for the remarkable result due to its **high electrocatalytic activity** in the production of hydrocarbons, aldehydes, and alcohols. Copper is also used as an alloy, electrocatalyst, and more in ERC. The factor like ERC is **the optimum design, electrode, and catalyst are** needed for better high energy efficiency and high current density.[15]




| COMPOUND | CARBON PERCENTAGE | CATALYST | YIELD | MAX EFFICIENCY | ELECTRODE |
|---|---|---|---|---|---|
| **Formic Acid** | 26.08% | Sn, Cu, Zn-Phthalocynammics | 53% | < 90% | Hg, Pb, In, Sn |
| **Alcohol** | 52.2% | Copper | | 70-90% | cu |
| **Hydrocarbon** | 87.7% | Copper | 5-17% | 75% | PtGDEs |
| **Co And Syngas** | 42.9% And 30-60% | Ni, Co, Sn, Phthalocynammics | 59.5% | 25-50% and 50.52% | - |
| **Methanol** | 37.5% | Copper And Palladium | 40% | 90% - | cu |

**Biological Conversion**

Microalgae can digest $CO_2$ and are considered a sustainable derivative for biomass production. They provide carbon fixation and wastewater treatment at the same time thereby enhances the competitiveness of process.

**Photocatalytic Conversion**

The reduction of $CO_2$ can be conducted photo-catalytically on a catalyst-based measure and light-based measure. The process needs photocatalysts with narrow bandgaps as UV light only accounts 4% of solar light. The light harvesting can be conducted by cation/anion dopants in semiconductors to form new valence bands resulting in narrow bandgaps or through the modification of surface sensitivity of semiconductors with bandgaps in the range of 2–4 eV (WBG semiconductors), dye molecules and platinum metals.

## METHANOL PRODUCTION: -

Looking at the current scenario of $CO_2$ emission many countries have come across a Ways to utilize $CO_2$ as source of energy. Countries like Iceland, Japan, China, USA are currently working on a utilization of $CO_2$ as a storage of electricity. One of the most effective utilizations is to produce methanol from $CO_2$. Currently countries like Iceland, Japan and Korea have executed the plant of $CO_2$ utilization means conversion of $CO_2$ to methanol using ccu (captured carbon) and renewable hydrogen.[7] First ever plant was established in 2011 in Iceland and named as carbon recycling international(cri). Cri plant took into the consideration the catalytic reaction to form methanol from $CO_2$ and $H_2$. Also, the countries like USA, Japan have executed that electrochemical reduction of $CO_2$ and $H_2$ oxidation will also lead to production of methanol.as we know methanol have large potential as an energy source can be used in transportation sector.[8] The target of many countries is to replace gasoline by methanol and replace diesel by dimethyl ether. In present situation methanol is currently used as feedstock in production of formaldehyde, methyltertbutylether and acetic acid.[7][8]

**Process: -**

Once the $CO_2$ is captured, the process is carried out to transform into methanol. This process involves reactor, distillation, hydrolysis etc. Captured $CO_2$ is feed in feedstock according to the requirement of methanol to be synthesized [7]. $H_2$ in inlet stream corresponds to the stoichiometric ratio of $CO_2$ and $H_2$ in the given following reaction: -

$$CO_2 + 3\,H_2 \Longleftrightarrow CH_3OH + H_2O \text{ .............. (3)}$$

Water in the outstream is recycled to $CO_2$ plant in order to convert CO into $CO_2$. Water obtained in outstream can be also utilize in hydrolysis in order to increase the efficiency of plant. Hydrolysis or co to $CO_2$ conversion can be carried out by following reaction

$$CO_2 + H_2 \Longleftrightarrow CO + H_2O \text{ .................. (4)}$$

Catalyst used during the process are generally doped metals. Cu/ZnO catalyst used in reaction 3 attacks on al203 substrate, and they follow the Langmuir-Hinshelwood-Hougen-Watson formalism. figure given below represent the simplified version of the methanol production.

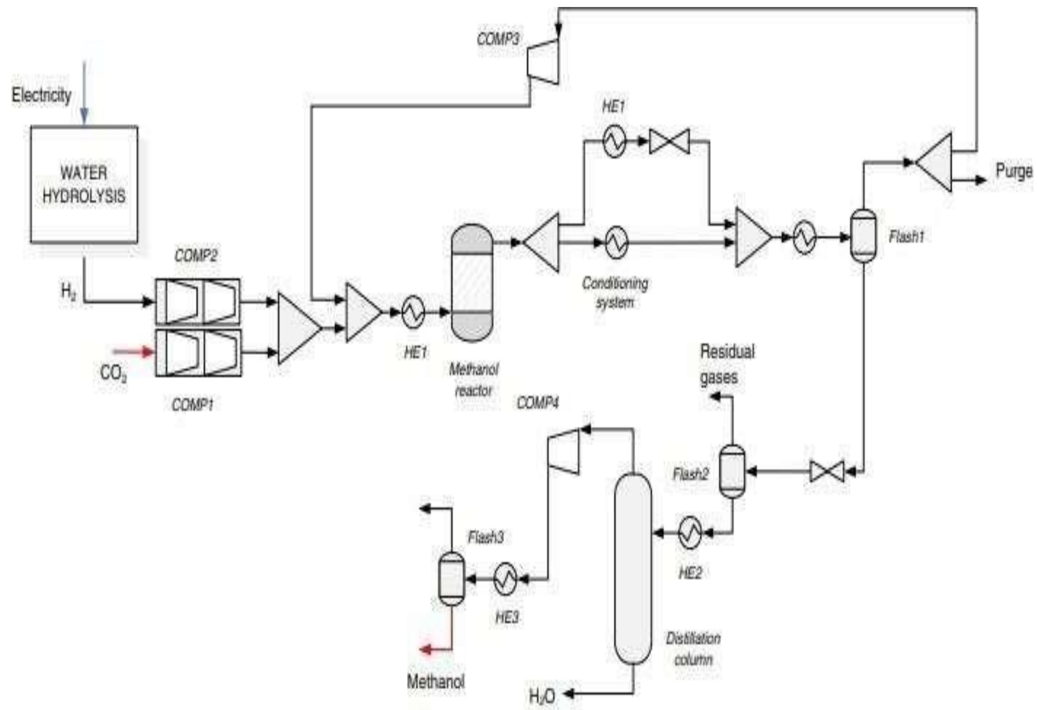



Fig. 2. Flow diagram of the methanol synthesis process [13,14].

$H_2$ after electrolysis at 30 bar enters into the system. $CO_2$ is pressed up to 78 bar. Fixed bed reactor know as methanol reactor is introduced in system. $CO_2$ and $H_2$ stream mixture is heated up to the temperature of methanol reactor. In order to cool down the methanol and water mixture to 35 degrees centigrade and 73.4 bar pressure. Heat exchanger in downstream is integrated in the system with reboiler and he2. $CO_2$ is recycled back to inlet of $CO_2$ and $H_2$ . Compressor is used to increase the pressure. At atmospheric pressure distillation column works and it separates the methanol and water. Further with the help of he3 and compressor 4 the purification of methanol is carried out. Methanol obtained is at atmospheric pressure and 20 degree centigrade.

The system which is specified above produces approx. 1300 tons per day methanol of 98%wt. Also, system generates 0.56 t H20/tch3oh. Error generated in the system is around 15% after considering the flowrates and compositions of the compound. Key performance index of this system/process is specified in table given below

kips evaluated for the methanol synthesis process.

kips

Product purity (Wt%) 98%

$CO_2$ convr (%) 28%

$CO_2$ convp (%) 94%

$CO_2$used (ton/h) 74.1

Heat duty (MW per hour/ton $CO_2$ used)
1.2 (cooling needs)

Electricity requirement (MW per hour/ton of $CO_2$used) 8.3

$CO_2$ emissions (ton of $CO_2$/ton of $CO_2$used)
6.8 (0.5 w/t electrolysis)

Investment cost (meur2010/(ton of $CO_2$used/h)) 1.6

Affect and market

Before year 2020 market price of methanol was on an average 270 euros per ton in European markets. But due to pandemic year 2020 and 2021 the market price of methanol has reached its peak level. Currently the production of olefin requires huge amount of methanol. Thus, countries like Iran and US estimates that future of methanol is not positive. But the probability of producing methanol by captured CO2 have given a hope to the market of methanol.

Economic analysis: -

| | |
|---|---|
| Plant lifetime: | 20 years |
| Opex of pemel | 45 €/kw |
| Equivalent operating hours: | 8500 h |
| Opex of ccu | 7 €/tCO2 |
| Wacc | 5% |
| Opex of methanol unit | 25 €/tch3oh |
| O2 selling price | 150 €/ton |
| Tci factor | 2.2 |
| El. Energy cost | 50 €/MWh |
| Catalyst cost | 160 €/kg |

Looking to current situation in whole country, every manufacturing company requires an economic plant. So, methanol production from CO2 should have a significant impact basis on economy. As we are using methanol as an alternative of biofuel. Here above-mentioned table specifies the detail analysis of economy of methanol. Using the principles of thermodynamics this table is formed to know the impact of methanol production plant. Also, H20 generated as a byproduct in the system can be sold which can have economic impact on the production cost.

## METHODOLOGY

1. Electrode Preparation

The Copper – Iron Electrode plate was cut to the size of 1.5 X 4 cm then it was rubbed using sandpaper to remove the dirt on the electrode. After that both the electrode strips were washed using dilute Hydrochloric acid and were dried by wiping a tissue over them.
Copper electrode is used as Working electrode Iron electrode is used as Counter Electrode Ag/AgCl solution is used as Reference Electrode.

2. Carbon dioxide conversion process to methanol

1. By keeping both the electrolytes same

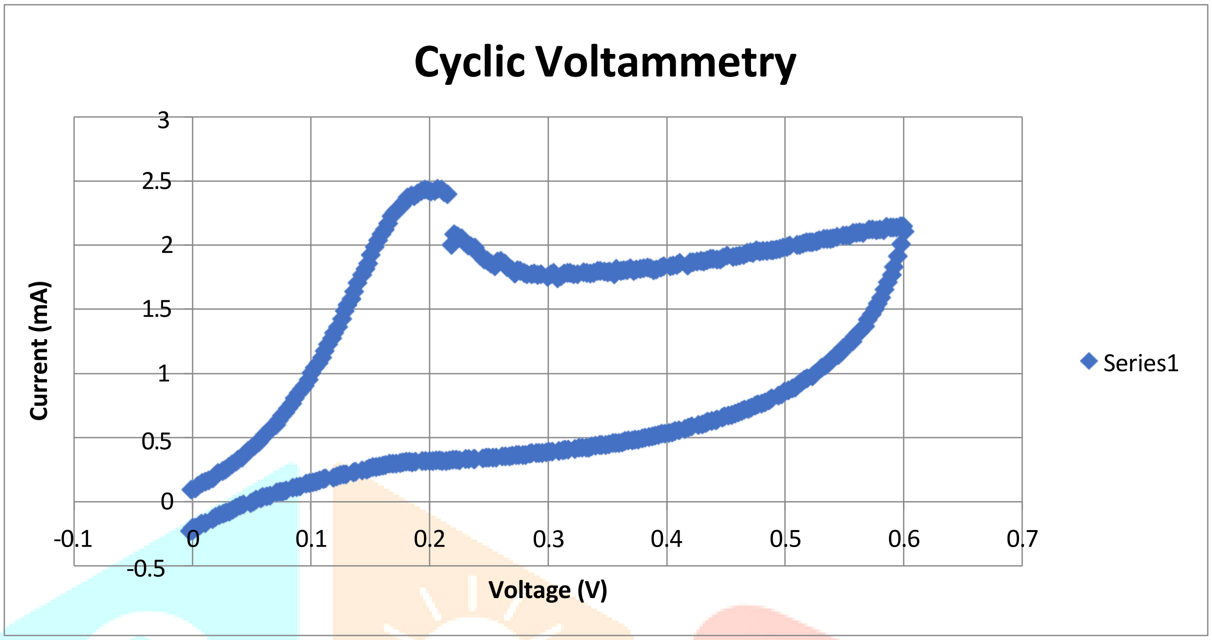
- On the variation of the time of bubbling of $CO_2$ in $NaHCO_3$, 50ml of 0.1N $NaHCO_3$ solution is incorporated in the cell chamber consisting of counter electrode and then the $CO_2$ gas is passed in the cell chamber containing the reference electrode and the working electrode. The optimum time for $CO_2$ absorption was studied by varying the time as 5min, 10min and 15min. Subsequently, the resultant solution obtained through electrochemical synthesis is absorbed in organic solvent n- Hexane and is sent for analysis by gas chromatography to determine the optimum time for $CO_2$ absorption.

2. By taking counter electrode side electrolyte as HCl

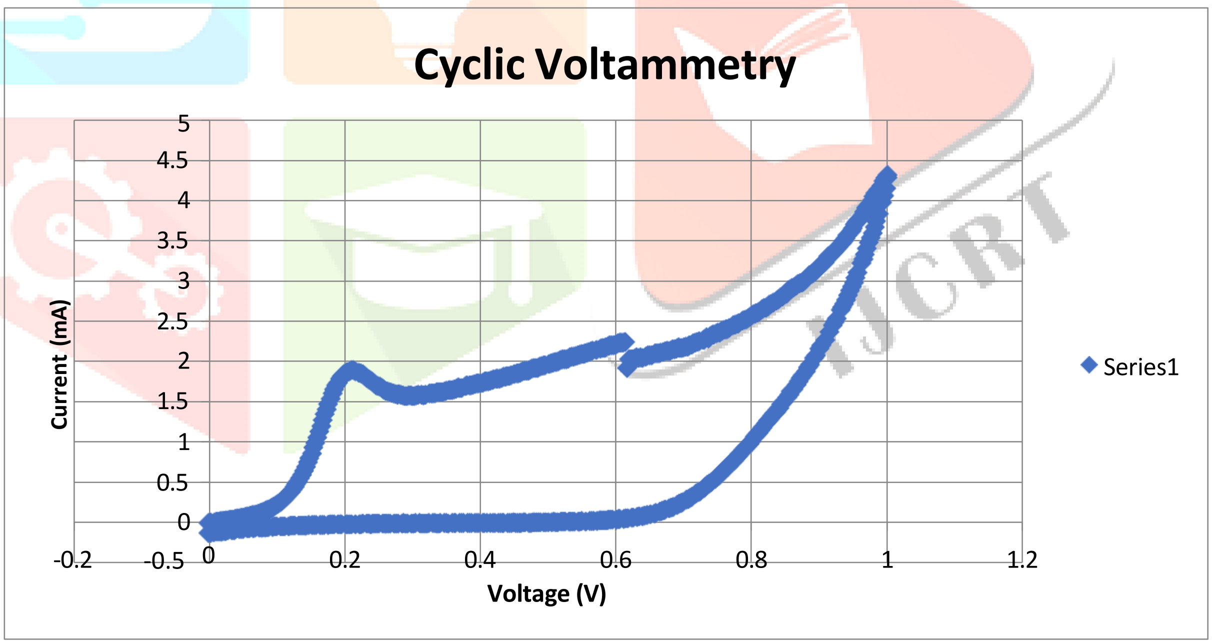
- On the variation of counter electrolyte, 50ml of 0.1NHCl is incorporated in the counter side electrode and then the $CO_2$ gas

3. is passed in the cell chamber containing the reference electrode and the working electrode. The optimum time for $CO_2$ absorption was studied by varying the time as 5min, 10min and 15min. Subsequently the resultant solution obtained through electrochemical synthesis is absorbed in organic solvent n- Hexane and is sent for analysis by gas chromatography to determine the optimum time for $CO_2$ absorption.

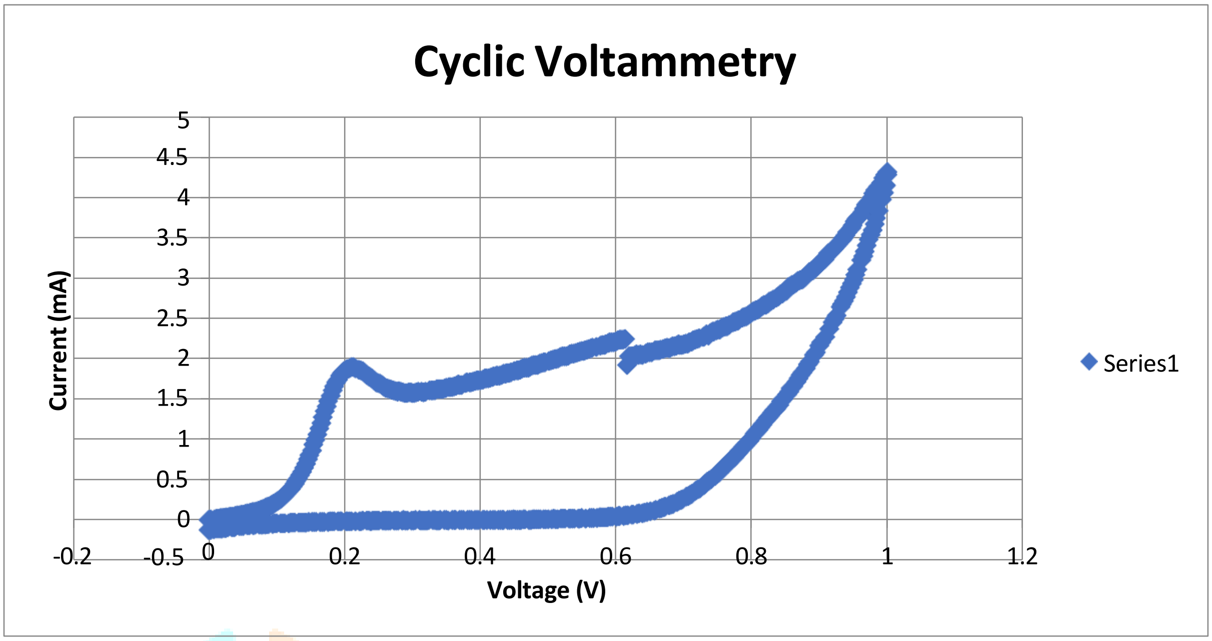
# RESULT & CONCLUSION



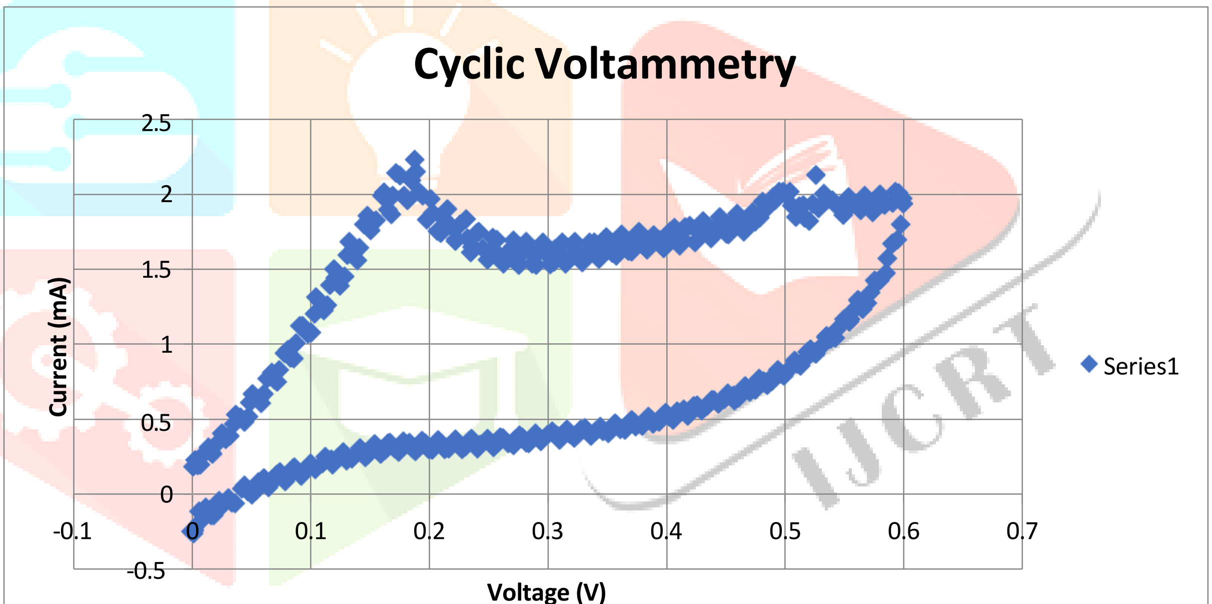

Working Electrolyte – $NaHCO_3$, Counter Electrolyte – HCl, Time for $CO_2$ absorption – 5 min



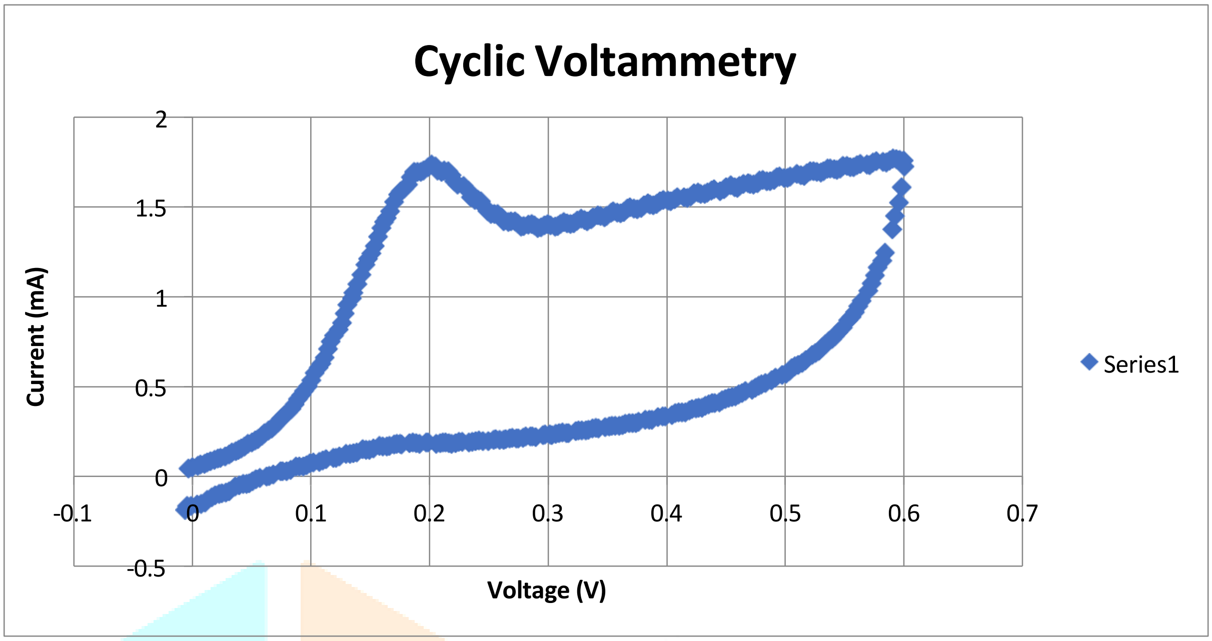

Working Electrolyte – $NaHCO_3$, Counter Electrolyte – $NaHCO_3$, Time for $CO_2$ absorption – 5 min



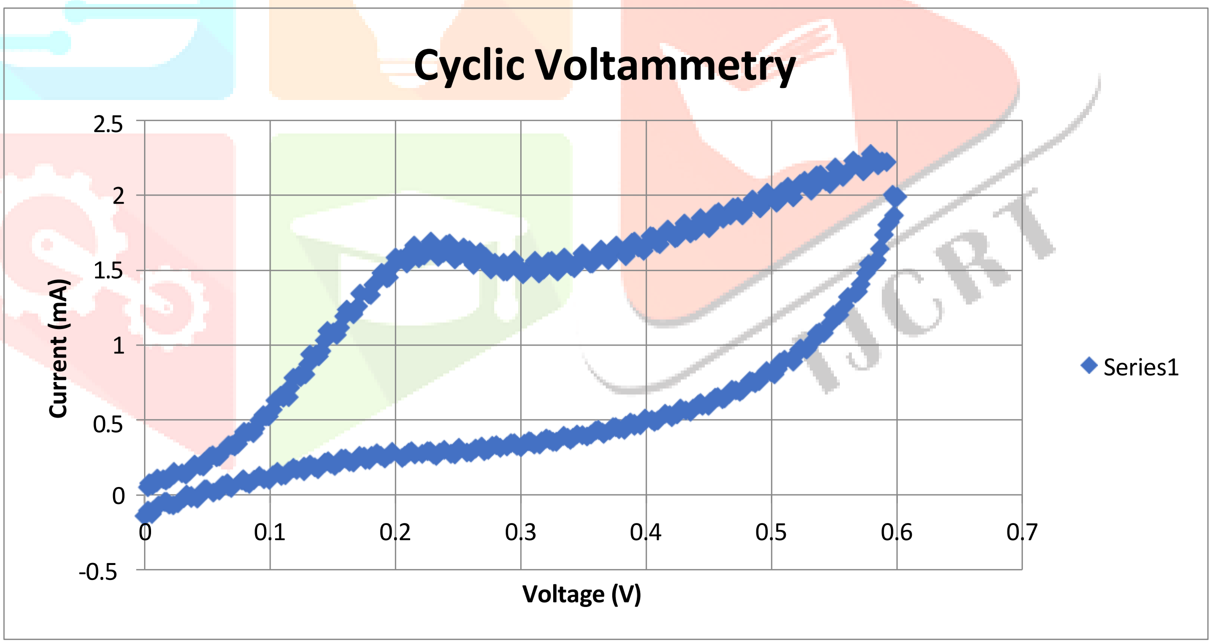

Working Electrolyte – $NaHCO_3$, Counter Electrolyte – $NaHCO_3$, Time for $CO_2$ absorption – 5 min



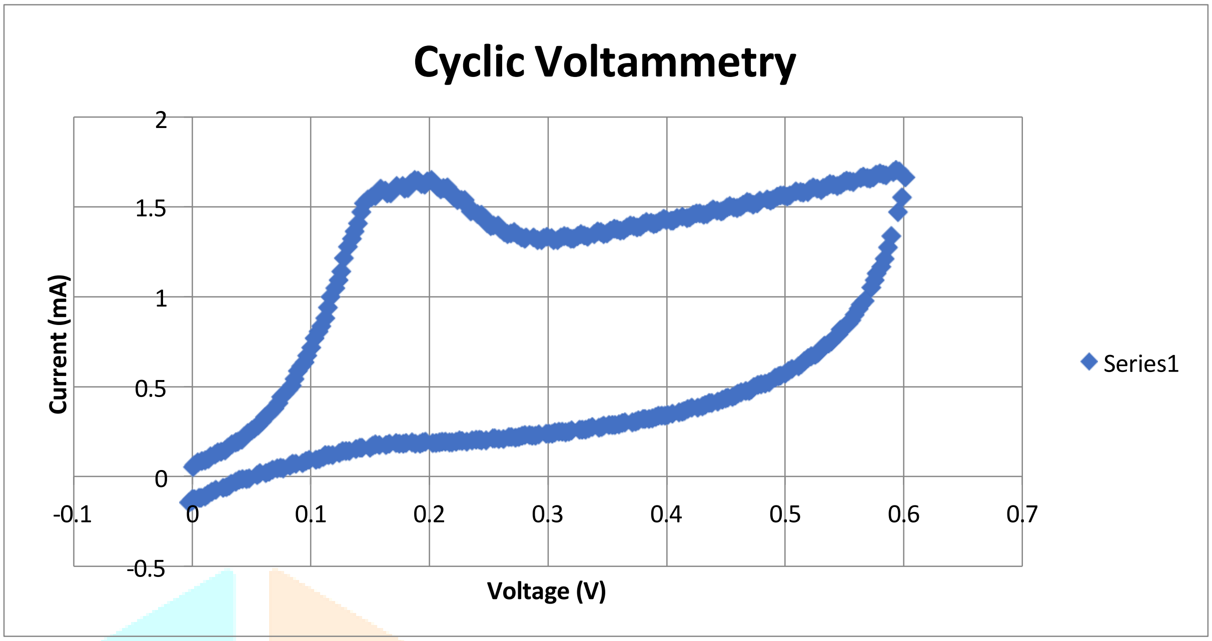

Working Electrolyte – $NaHCO_3$, Counter Electrolyte – HCl, Time for $CO_2$ absorption – 10 min




Working Electrolyte – $NaHCO_3$, Counter Electrolyte – $NaHCO_3$, Time for $CO_2$ absorption – 10 min

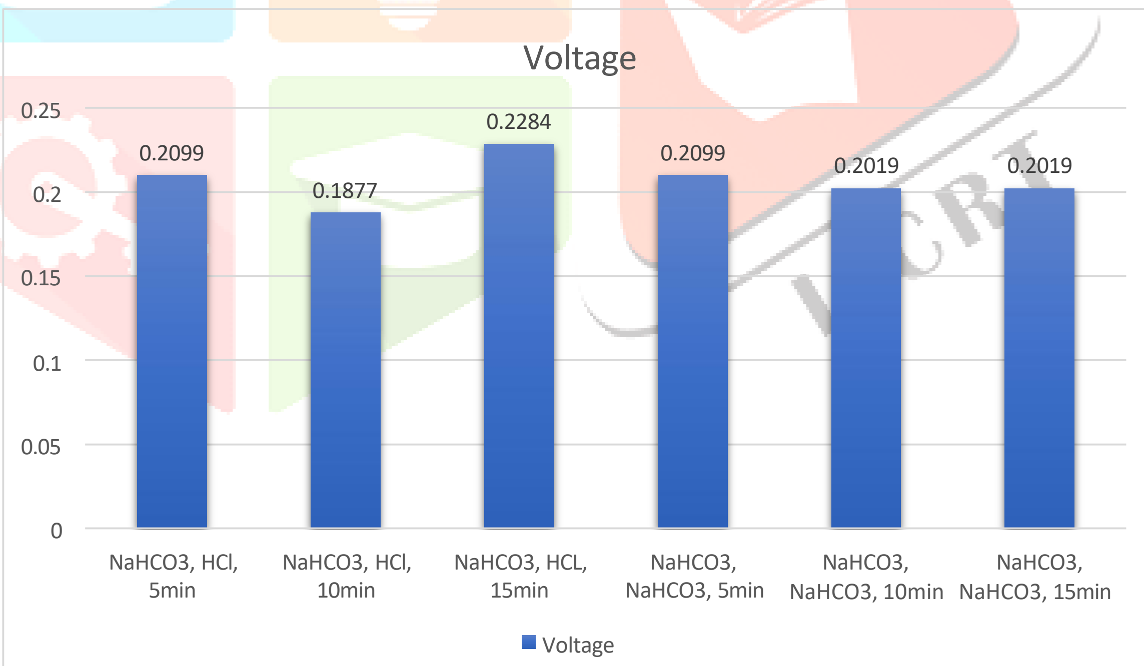



Working Electrolyte – $NaHCO_3$, Counter Electrolyte – HCl, Time for $CO_2$ absorption – 15 min




Working Electrolyte – $NaHCO_3$, Counter Electrolyte – $NaHCO_3$, Time for $CO_2$ absorption – 15 min

In the above graphs the upper peak obtained shows us the optimum voltage to conduct the reaction and we are still working on the lower peak.



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