

## Electrochemical conversion of greenhouse gas CO<sub>2</sub> to renewable energy and there by control air pollution in a robotic controlled fuel cell

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Received: October 04, 2021; Accepted: October 18, 2021; Published: October 25, 2021

### Abstract

Greenhouse gas CO<sub>2</sub> is increasing at alarming rate, making our earth hotter everyday. The temperature in the western has crossed all records, reaching above 400 C. There is a threat to melting of north pole ice which may create to wakeup of dormant virus whose vaccine ,today, is not available . Thus it is a high time to consume and convert the excess CO<sub>2</sub> in the environment to any form of non polluting useful product. The present works investigates electrochemical conversion of CO<sub>2</sub> in the polluting smoke to ethanol in a fuel, controlled by Robotic automation. The level of CO<sub>2</sub> and other harmful gases are monitored by robot controlled gas sensors. Electrodeposited Nickel acts as electrocatalytic cathode for CO<sub>2</sub> conversation and Carbon anode at anode chamber oonized H<sub>2</sub> to 2H<sup>+</sup> which reacts with cathodic organic product generated from CO<sub>2</sub> to form ethanol.

The presence of ethanol is detected by UV-Vis spectrophotometer. In addition the electrochemical reaction in the fuel cell produces pure electrochemical energy in the form of current and potential with no polluting products. The steady state current delivered is around 20mA per cm<sup>2</sup> of the electrode surface area. This is more than enough to drive a motor, if a battery of 10 cells ( each having 100cm<sup>2</sup> electrode area ) is fabricated.

**Keywords:** Greenhouse gas ; Robotics; Fuel Cell; Electro catalytic Nickel; Ethanol; Electrochemical Energy

### Introduction

Since the Industrial Revolution, the use of machines by humans has produced gases and chemicals that are released into the environment. Today, CO<sub>2</sub>, is the most prevalent greenhouse gas emitted by the chemical combustion of fuel to heat energy to mechanical work to finally electrical energy. Thus cars and airplanes, as well as electricity generated for homes and businesses, release copious amounts of carbon dioxide into the environment. The level of minimum CO<sub>2</sub> on earth is increasing steadily. With the rise of CO<sub>2</sub> levels , the lives of humans, plants and animals become endanger.

Greenhouse gas absorbs and emits radiant energy within the thermal infrared range, causing the greenhouse effect. The greenhouse effect, combined with increasing levels of greenhouse gases and the resulting global warming, is expected to have profound implications, according to the near-universal consensus of scientists. If global warming continues unchecked, it will cause significant climate change, a rise in sea levels, increasing ocean acidification, extreme weather events and other severe natural and societal impacts. Concerns over world climate change are contained in the Kyoto Protocol document and the United Nations Framework Convention on Climate Change (UNFCCC) which emphasizes the importance of reducing CO<sub>2</sub> emissions and their

**Citation:** Subir Paul. Electrochemical conversion of greenhouse gas CO<sub>2</sub> to renewable energy and there by control air pollution in a robotic controlled fuel cell. Int J Chem Sci. 2021;19(10). © 2021 Trade Science Inc.

absorption from the atmosphere. Similarly, the United Nations Conference on Environment and Development (UNCED) in 1992 in Rio Janeiro, Brazil, which produced two general declarations, one of which also emphasized efforts to reduce global climate change.

The fact creates a challenge to scientists and engineers to reduce the carbon footprint on Earth. Research is needed that can convert  $\text{CO}_2$  into other safer forms of compounds that can be utilized for the welfare of mankind. Currently there are many studies that try to produce a compound by using  $\text{CO}_2$  as its base material. Metallic electrocatalysts in fuel are capable of electrochemically converting  $\text{CO}_2$  into more than 30 different products, including carbon monoxide (CO), formic acid ( $\text{HCOOH}$ ), methane ( $\text{CH}_4$ ) and ethylene ( $\text{C}_2\text{H}_4$ ) or ethane ( $\text{C}_2\text{H}_6$ ). This is one of many ways to overcome  $\text{CO}_2$  hazard aside from minimizing its source of production.

For electrochemical conversion through a fuel cell, electrodes having high electro catalytic properties are required. Platinum is already known as a good electro-catalytic material for many fuel cell applications, but due to its high cost, a non-platinum based low cost electrode is the urgent need of research. Endeavours are being made to develop Non-Pt based inexpensive metals, alloys and oxides electrocatalytic materials in battery and fuel cell for future energy synthesis and storage.

Electro synthesized  $\text{MnO}_2$  has been found to act as good electro catalytic anode material for alcoholic based fuel cell. Addition of Nano carbon to  $\text{MnO}_2$  further enhances the electrical energy obtained through the electro oxidation of the fuel.  $\text{ZnO-Al}_2\text{O}_3$  composite oxides have performed as very good electrode materials for oxidation of methanol.

Among the metallic systems. Ni based alloys have shown promising future energy materials for low temperature fuel cells in cars and automobiles.

The present work is based on application of electrochemical method to convert  $\text{CO}_2$  gas or greenhouse gases to alcohols by electrochemical reduction of the gases over Nickel electro catalytic cathode material and combining the product with  $\text{H}^+$ , produced at anode, to ethanol as shown below .

**Cathodic reaction:**  $4\text{CO}_2 + 6\text{H}_2\text{O} + 4\text{e}^- \rightarrow 2\text{CH}_3\text{CH}_2\text{OH} + 2\text{OH}^- + 5\text{O}_2$  (1)

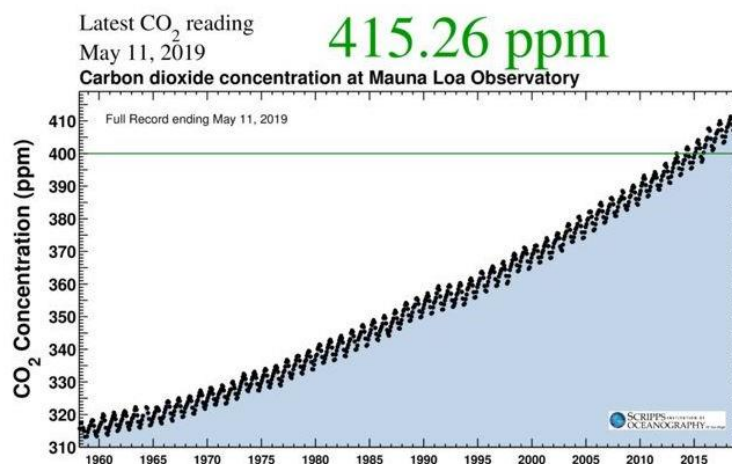
**Anodic Reaction:**  $2\text{H}_2 \rightarrow 4\text{H}^+ + 4\text{e}^-$  (2)

**Overall reaction:**  $4\text{CO}_2 + 6\text{H}_2\text{O} + 2\text{H}_2 \rightarrow 2\text{CH}_3\text{CH}_2\text{OH} + 5\text{O}_2$  (3)

The above reactions not only convert polluting  $\text{CO}_2$  to ethanol, but it will also produce electrical in the form of current and potential, given by cell current and cell potential respectively.

## Materials and Methods

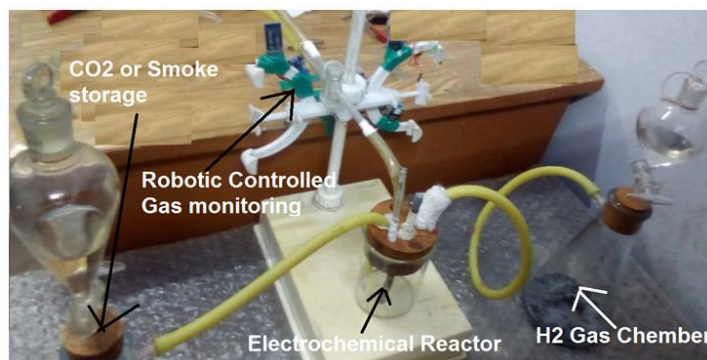
Nickel, electro coated on low carbon steel, was used as electro catalytic cathode material, over which  $\text{CO}_2$  gas was electrochemically reduced to ethanol with high Faradaic efficiency. Carbon was used as anode over which  $\text{H}_2$  gas was electrochemically oxidized to  $\text{H}^+$  ions. The conversion process is carried out in an electrochemical synthesis reactor. The performance of the cell was characterized by Cyclic-voltammetry (CV) and Chronoamperometry (CA), with a three electrode system, graphite rod as counter electrode, saturated calomel electrode (SCE) as reference electrode and the test sample as working electrode, in DY2300 Potentiostat and Gamry electrochem Impedance analyzer. The test is done to find out optimum potential and current to convert  $\text{CO}_2$  to ethanol with a fixed flow rate of  $\text{CO}_2$  gas. Presence of ethanol and its concentration were estimated by UV Spectrophotometer. Concentration of  $\text{CO}_2$  and other gases on the smoke or air were determined by Robotic controlled gas sensors (Figure 1).



**Figure 1:** Showing of minimum  $\text{CO}_2$  level on earth during the last 60 years.

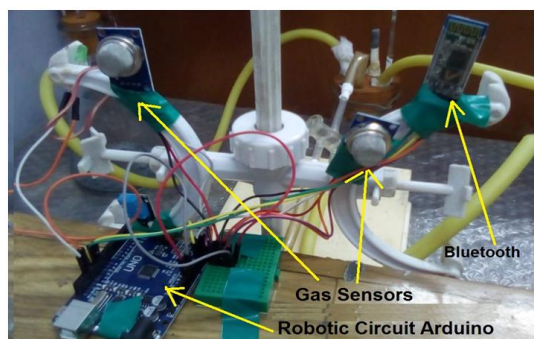
Cyclic-voltammetry (CV):- is a type of potentiodynamic electrochemical measurement. In CV, the potential was scanned from -1V

vs. SCE to 1V vs. SCE with scan rate 0.05mV/second to find out the  $I_{max}$  (current amplitude). The experiments were carried out for single cycle and multiple cycles (where the cycles of ramps in potential may be repeated as many times as needed). The current at the working electrode is plotted versus the applied voltage (that is, the working electrode's potential) to give the cyclic voltammogram trace. Cyclic voltammetry is generally used to study the electrochemical properties of an analyte in solution or of a molecule that is adsorbed onto the electrode (Figure 2).



**Figure 2:** Experimental setup of Electrochemical conversion of  $CO_2$  in smoke at cathode and  $H_2$  at anode to Ethanol solution, with robotic controlled gas monitoring in the smoke inlet.

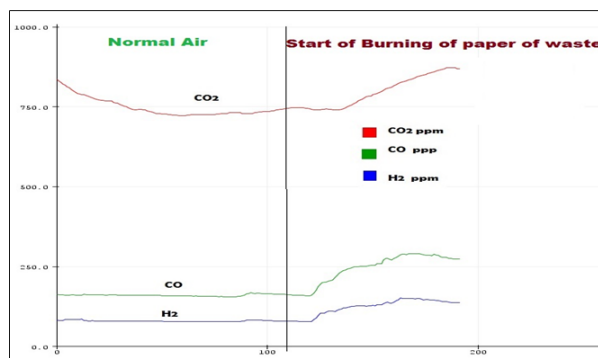
Chronoamperometry (CA) is an electrochemical technique in which the potential of the working electrode was tested at different fixed potentials, selected near or around the cell potential, in the same machine with different software. The current  $I$  was monitored as a function of time  $t$  to find out how long current is delivered from the cell. Chronoamperometry generates high charging currents, which decay exponentially with time as any RC circuit. CA can therefore be used to measure current-time dependence for the diffusion controlled process occurring at an electrode (Figure 3).



**Figure 3:** Showing arrangement of gas sensors with connection to robotic circuit and gas analysis data are transferred to Android mobile phone with bluetooth.

### UV/VIS spectroscopy

Ultraviolet-visible spectroscopy or ultraviolet-visible spectrophotometry (UV-Vis or UV/Vis) refers to absorption spectroscopy or reflectance spectroscopy in part of the ultraviolet and the full, adjacent visible spectral regions. The absorption or reflectance in the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum, atoms and molecules undergo electronic transitions (Figure 4).



**Figure 4:** Showing gas analysis in ppm with time, determined by robotic controlled gas sensors. In the normal air and smoke generated by burning waste.

The basic principle of UV/VIS is based on Beer-Lambert law, which states that the absorbance of a solution is directly proportional to the concentration of the absorbing species in the solution and the path length. The Beer-Lambert law (or Beer's law) is the linear relationship between absorbance and concentration of an absorbing species. The general Beer-Lambert law is usually written as:

$$A = a(\lambda) \cdot b \cdot c$$

where  $A$  is the measured absorbance,  $a(\lambda)$  is a wavelength-dependent absorptivity coefficient,  $b$  is the path length, and  $c$  is the analyte concentration. When working in concentration units of molarity, the Beer-Lambert law is written as:

$$A = \epsilon \cdot b \cdot c$$

Thus, for a fixed path length, UV/Vis spectroscopy can be used to determine the concentration of the absorber in a solution. The absorbance changes with concentration. This can be taken from references (tables of molar extinction coefficients), or more accurately, determined from a calibration curve.

## Results and Discussion

Consumption of  $\text{CO}_2$  gas, generated from conventional energy synthesis process from coal and petroleum fuels, is the key to reduce environmental pollution and greenhouse gas effect. It has been found that  $\text{CO}_2$  can be converted electrochemically over an electrocatalytic cathode material such as Ni, through the reaction. The electron needed for the reaction is supplied by the reaction where  $\text{H}_2$  gas is ionized to release electron. The electron may be obtained by other reaction or method electrically, but here  $\text{H}^+$  ions generated is utilized to combine with the products of reaction to produce ethanol (reaction 3), which is a useful product. In addition electrical energy is produced from the cell potential  $E_{\text{cell}}$  and flowing current  $I$  (Figure 5).

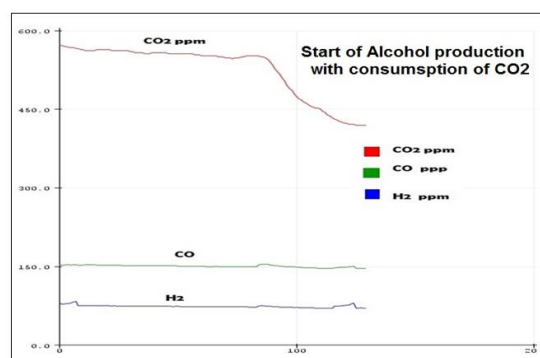


Figure 5: Showing gas analysis in ppm with time, determined by robotic controlled gas sensors, after the start of electrochemical conversion of  $\text{CO}_2$  to ethanol. It shows decrease in  $\text{CO}_2$  concentration.

Since automation is needed to control the flow of  $\text{CO}_2$  gas or smoke generated from burning of fuel as well as analysis of gas composition in the smoke, a Robotic controlled circuit with gas flow arrangement and analysis of gas data, have been fabricated. Fig.1 shows the experimental setup with  $\text{CO}_2$  gas or smoke generated /storage at the left flask, together with  $\text{H}_2$  gas generated /storage at the right flask. The electrochemical reactor or fuel cell is at the centre, receiving gas flow from two sides. Nickel cathode is used at cathode chamber and Carbon anode at the anode chamber. The electrolyte is water where a few drops of acid is added to increase the ionic conductivity of the electrolyte. This shows the robotic circuit with gas sensors, MQ135 at the left for analysis of smoke or burnt fuels in the air and MQ8 for  $\text{H}_2$  gas measurement. The MQ135 gas sensor can also give data for a few organic generation such as ethanol, acetone, butanol (Figures 6 and 7).

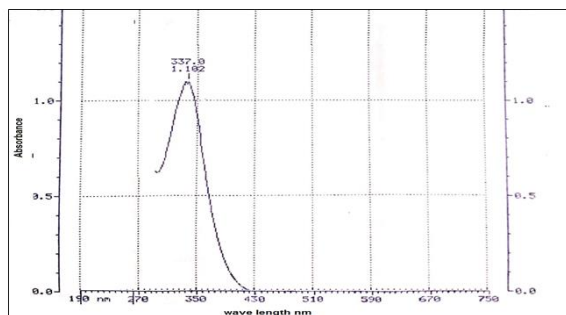
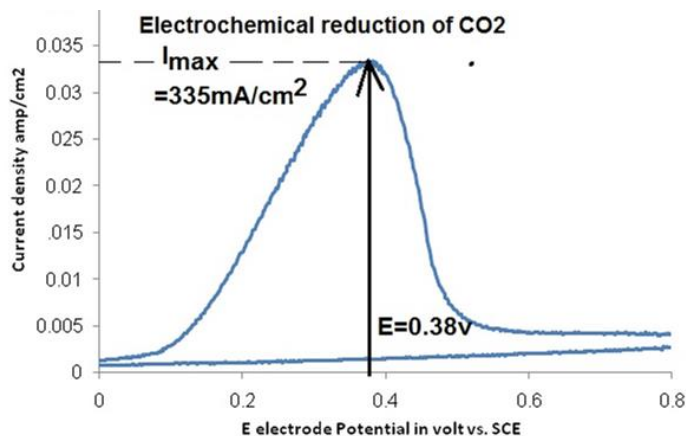
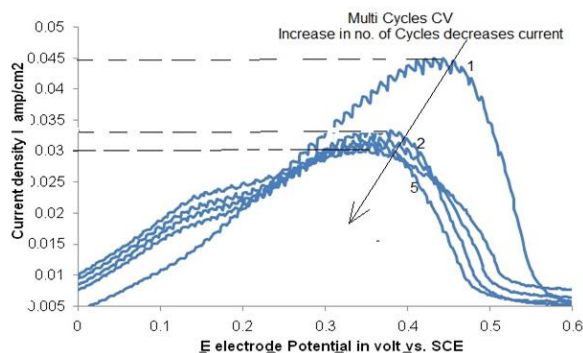


Figure 6: UV-Vis Spectrophotometry study of the product formed after electrochemical reduction of  $\text{CO}_2$  at cathode and oxidation of  $\text{H}_2$  at anode. The peak of the absorbance at the wave length 337 nm confirms that ethanol has formed.

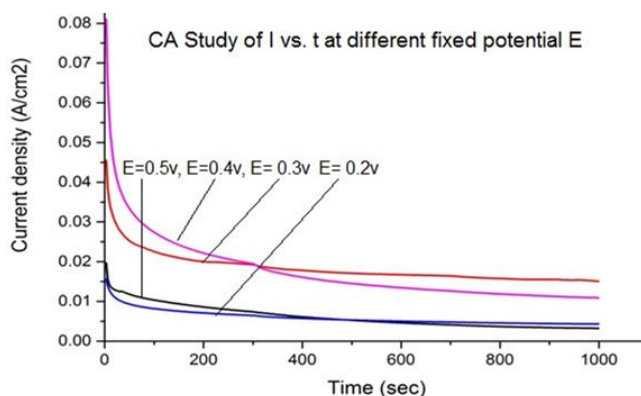


**Figure 7:** Cyclic voltammetry study of electrochemical reduction of CO<sub>2</sub> over Ni electrode.

The analysis of gases in the air before and after burning of the fuel is shown in fig.3. It is seen that the concentration of CO<sub>2</sub>, CO and H<sub>2</sub> increases with the onset of burning of the fuel. With the start of fuel cell in operation, it is seen that CO<sub>2</sub> concentration decreases due to consumption of it by the electrochemical cathodic reaction, with the production of ethanol. The presence and production of the ethanol in the fuel cell reaction is detected by the UV vis spectrophotometry analysis, with an absorption peak at 336nm wave length which matches that of ethanol (Figures 8 and 9).



**Figure 8:** Multiple cycles of CV study of electrochemical conversion CO<sub>2</sub> to alcohol over electro catalytic Ni.



**Figure 9:** Showing Chronoammetry study of electrochemical conversion of CO<sub>2</sub> at different fixed electrode potential E vs. SCE.

Fig 6 shows the cyclic voltammetry (CV) study which at what potential the electrochemical reaction occurs. This is indicated by the current jump. So electrical energy in the form of current and potential is produced during the consumption CO<sub>2</sub> gas in the fuel cell. This energy is pure, pollution free green energy. It is an additional benefit. The similar study under multi cycles CV is shown. It is seen that with repletion of cycles, I max decreases and hence energy, since the electrodes may corrode a little initially but a few cycles steady state is achieved. Having achieved the current hump and the potential, it is essential to investigate that how long the current lives and hence the reaction proceeds. This shows CA study of the system at different fixed potential around the reversible potential of the reaction. It is seen that at the potential E=0.3 volt vs SCE, current is high and remains steady state. The steady state current delivered is around 20mA per cm<sup>2</sup> of the electrode surface area. That is an electrode surface of 100 cm<sup>2</sup> (2 inch by 4

inch plate , both side ) can produce as high as 2 amps current which is wonderful and can drive a motor. A battery of 10-15 parallel cells can produce 110 volt and 2 amps current.

## Conclusion

It is possible to consume and convert the rising CO<sub>2</sub> level in the atmosphere, due to energy synthesis from coal based fuels and consumption of petroleum fuels in the transportation sectors. Robotically controlled electrochemical conversion of smoke in fuel cell can generate alcoholic liquids which are non pollutants and useful organic products. In addition renewable electrical energy is produced through the above conversion with no polluting products.

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