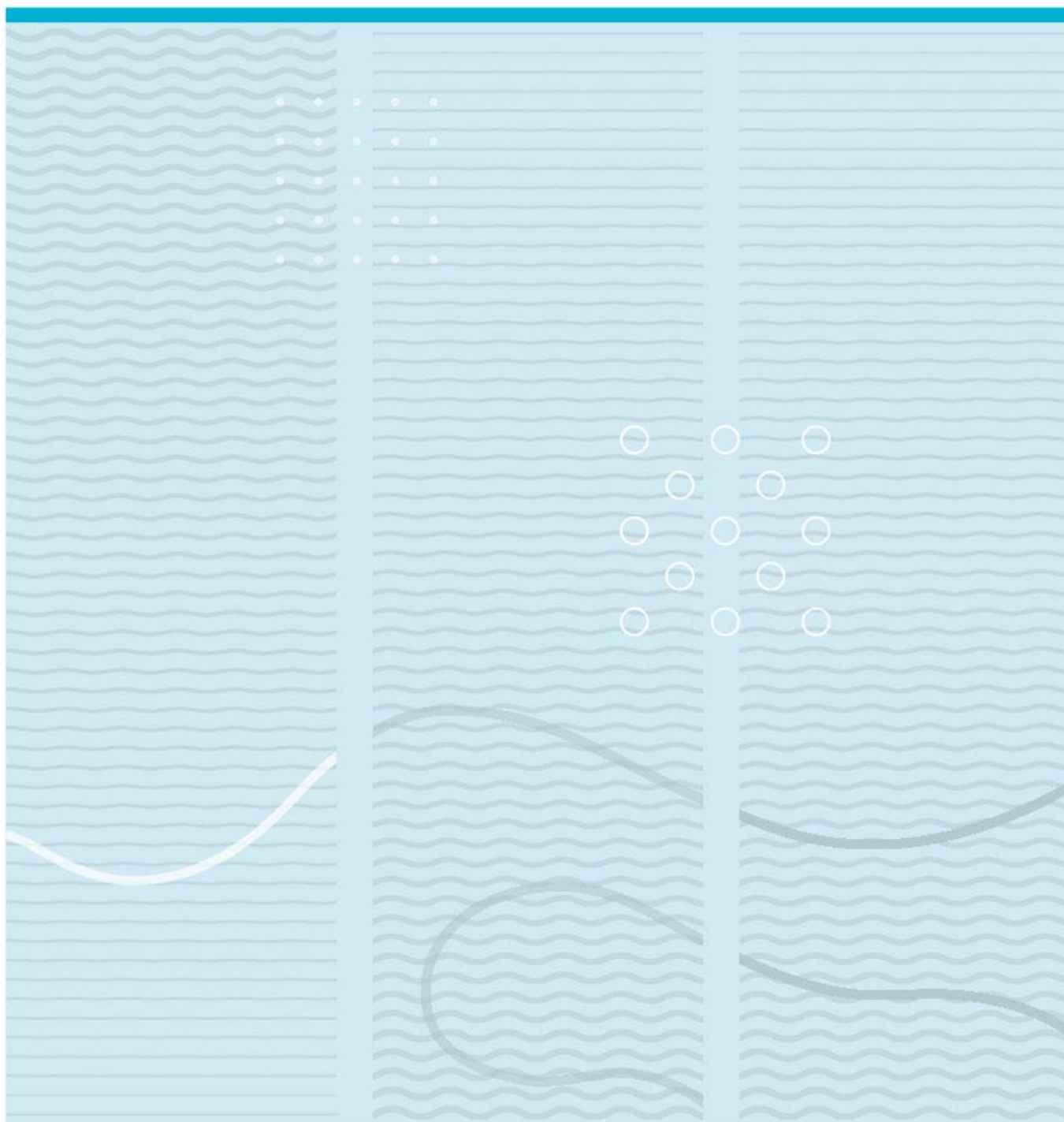


Md Fazle Rabby

# Bio-electro chemical process for power to gas application

Synthesis, Characterization, and Application



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## Summary

Fossil fuels are non-renewable resources, so their scarcity will increase day by day. Extracting and using fossil fuels also have an impact on the environment. This challenge needs to be solved by developing sustainable Biofuel production techniques. By using power-to-gas technology, by-products of fossil fuel carbon dioxide can be converted into biofuel. Research and development in this sector can open a door to the sustainable production of biofuel.

This thesis presents research on the growth of carbon nanotubes on copper foam using chemical vapor deposition (CVD) process and its application in a bio-electrochemical system. The CVD process was optimized to achieve a high growth rate and uniform distribution of carbon nanotubes on the copper foam. The modified copper foam was then characterized by Scanning electron microscope (SEM) for checking its properties. We also use it in a bio-electrochemical system to evaluate its bio-electrochemical performance. Results showed that the modified copper foam exhibited improved electrocatalytic activity and higher reductive current compared to unmodified copper foam. The study also revealed that the modified copper foam has the potential for providing a novel bio-electrode in bio electrochemical systems producing methane.

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Norway, 24<sup>th</sup> January 2023

Md Fazle Rabby

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## List of Acronyms

P2G: Power to Gas

IEA: International Energy Agency

BES: Bio-Electrochemical System

MFC: Microbial Fuel Cell

MEC: Microbial Electrolysis Cell

EET: Extracellular Electron Transfer

CV: Cyclic Voltammetry

CNT: Carbon Nanotube

CVD: Chemical Vapor Deposition

SEM: Scanning Electron Microscope

EDS: Energy Dispersive X-ray Spectroscopy

SWNT: Single Walled Nanotube

CO<sub>2</sub> : Carbon dioxide

O<sub>2</sub>: Oxygen

H<sub>2</sub>: Hydrogen

CH<sub>4</sub>: Methane

C<sub>2</sub>H<sub>2</sub>: Acetylene

AgCl: Silver chloride

# 1 Introduction

The growth of carbon dioxide (CO<sub>2</sub>) and other greenhouse gases within the atmosphere can be quite a major reason of global warming and climate change [1]. The European Union's goal of decarbonization includes reduction of greenhouse gas emissions by 40% in 2030 and also planned to reduce to 95% in 2050, they also planned to increase the use of renewable energy to at least 27% for their final energy consumption within 2030 [2]. Within 2050 they planned to power all grid electricity from renewable energy [3]. Nevertheless, some of the sectors which are hard to avoid, such as freight haulage, airlines and shipping lines are not completely electrified [4]. The EU Renewable Energy Directive planned to use advanced biofuels for transport of at least 3.5% in 2030 and to use biomethane in 10% gas grids on a volume basis in 2040 [5] [6]. According to International Energy Agency (IEA)'s assessment, 20% of worldwide gas demand can be covered by sustainable biomethane [6]. As a result, for reducing greenhouse gases and meeting the future demand of biofuels, research needs to be done for the advancement of CO<sub>2</sub> reduction and biofuel production.

## 1.1 Power to Gas Technology

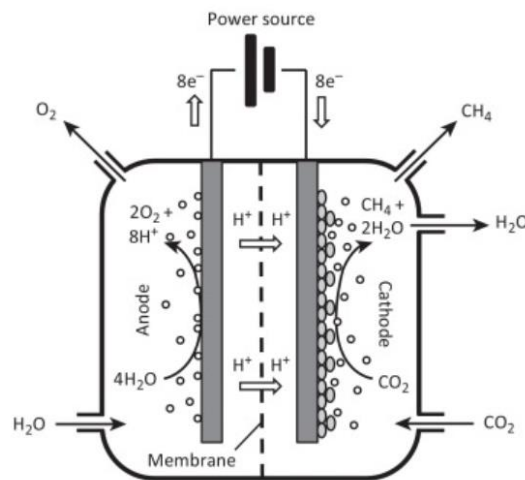
Power-to-gas (P2G) technology is a cutting-edge energy conversion process that transforms electricity into gas that can be utilized for heating or power generation purposes [7]. This innovative technique provides a cleaner and more efficient alternative to traditional fossil fuel-based energy production methods.

In a P2G system, electricity from renewable sources such as wind, solar, or hydropower is fed into an electrolyzer, which splits water into hydrogen and oxygen. The hydrogen can then be combined with carbon dioxide to produce methane, a natural gas, which can be stored, transported and used as a source of energy [8]. power-to-gas (P2G) technology offers numerous advantages to the energy sector, including the ability to store excess renewable energy, decrease reliance on non-renewable sources, and minimize the release of greenhouse gases. Furthermore, P2G can help regulate electricity grids by offering a storage solution for unused energy during low-demand periods and releasing it during high-demand times [9]. Power-to-gas technology represents a promising solution for the clean and efficient generation of energy. Its ability to store and convert renewable energy, reduce reliance on fossil fuels, and cut

greenhouse gas emissions makes it a valuable component in the quest for a more sustainable energy future.

## 1.2 Bio-Electrochemical System

Bio-Electrochemical system (BES) is a promising technology for producing methane by microbial conversion of carbon dioxide and electrical energy. It contains an anode and a cathode, which are separated by an ion-selective membrane. Oxidation reaction happens in the anode side, it moves the electrons to the electrode and the protons at the electrolyte, and the reduction reaction happens in the cathode side shown in Fig 1-1 [11]. BES can be categorized as two types, it can function as a microbial fuel cell (MFC) where it can produce electric energy or it can function as a microbial electrolysis cell (MEC) where it requires electric energy to perform cathodic reaction [12].



*Fig 1-1 Schematic diagram of a two-chamber methane producing bio-electrochemical system [10]*

## 1.3 Extracellular Electron Transfer:

BES utilizes extracellular electron transfer (EET) of microorganisms for catalyzing the anodic or cathodic behavior [13]. In this process microorganism utilized in metal reduction, can transfer electrons extracellularly [14]. Extracellular electron transfer can be characterized into following types: (a) direct electron transfer, (b) mediators-shuttled, and (c) extracellular polymeric substances of biofilms [10] [12]–[15].

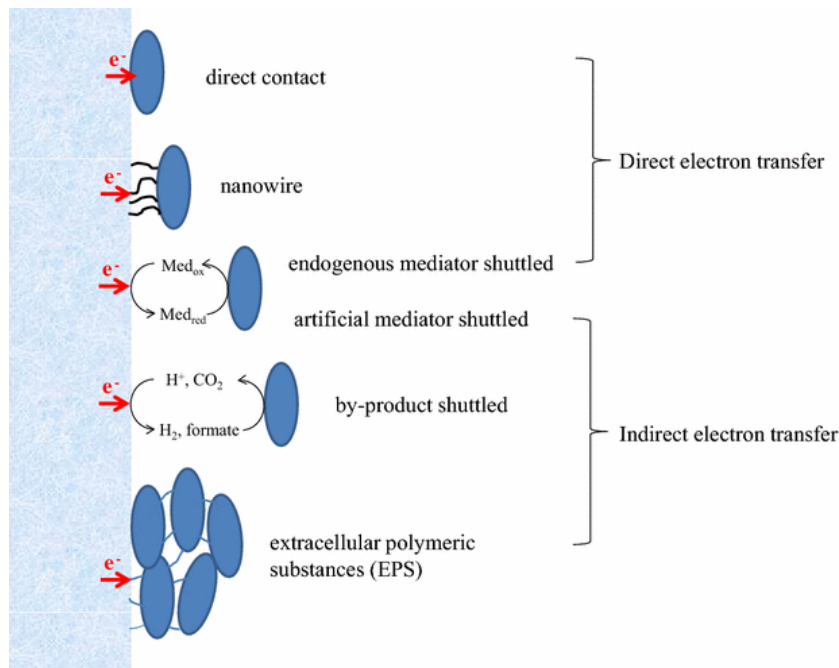


Fig 1-2 Types of extracellular electron transfer [13]

## 1.4 Methanogenesis:

Methanogenesis is the process of producing methane connected to energy conservation by utilizing microbes also known as methanogens [19]. In this process organic compounds like glucose, oxidized to  $\text{CO}_2$  and  $\text{O}_2$  is reduced to  $\text{H}_2\text{O}$ . For hydrogenotrophic methanogenesis  $\text{H}_2$  is oxidized to  $\text{H}^+$  and  $\text{CO}_2$  reduced to  $\text{CH}_4$  (methane), this process has some exclusive advantages such as high where organisms can do biological methane production [20].

## 1.5 Biocathode:

Bio-cathode, also known as microbial cathode, is an innovative technology used in bio-electrochemical systems (BESs) that harness the power of microorganisms to generate electricity. These cathodes are different from traditional cathodes in that they use microorganisms to catalyze the reduction of an electron acceptor, such as oxygen or nitrate, instead of chemical reactions [21]. One of the key features of bio-cathodes is their ability to convert organic matter, such as wastewater, into electrical energy in a sustainable and cost-effective way. Additionally, the use of bio-cathodes can also help to treat and purify wastewater while generating electricity [22].

## **1.6 Cyclic Voltammetry**

Cyclic voltammetry (CV) is an analytical technique used to study the electrochemical behavior of a wide range of materials. It is based on the principle of measuring the current and potential of a sample as it is repeatedly cycled through a range of potentials [23]. The technique involves applying a linear potential sweep to an electrode in contact with a sample solution. As the potential is swept, the current flowing through the electrode is measured, and a plot of current vs. potential is obtained. This plot, known as a voltammogram, provides valuable information about the electrochemical properties of the sample, including the redox behavior of its species, and the charge transfer kinetics [24]. In this study, cyclic voltammetry has been used for comparing the electrochemical behavior of modified and unmodified copper foam electrode.

## **1.7 Background of Carbon Nanotubes**

During the technology progress from microtechnology to nanotechnology, the discovery of Carbon nanotubes (CNT) is a milestone to remark the new era of low dimension materials. Developing new functional materials based on CNTs becomes popular and attracts research efforts from many scientists for new inventions. Scientists can create functioning materials, devices and systems with physical, chemical, biological, electrical, etc., properties [25]. CNTs are the key components of nanotechnology, which were developed in the Ando lab and were introduced by Iijima and Ichihashi in 1991 [26]. It was a single-walled CNT [27]. CNTs are made of one or several layers of graphene, Single walled and multi-walled CNTs diameters are usually 0.8 to 2nm and 5 to 20nm, respectively, but multi-walled CNTs can be less than 100nm to 0.5m [28]. CNTs have high thermal, electronic conductivity, and very good mechanical strength. Because of these properties CNTs can be used in sensors, electrodes, conducting composites and supercapacitors [29].

## **1.8 Scope of Thesis research**

The scope of this master's thesis is focused on the development of a novel bio-electrode for use in a bio-electrochemical system (BES) for power-to-gas technology. Recent studies showed ununiform distribution of carbon nano tubes on copper foam. So, the

thesis aims to investigate the growth of carbon nano tubes on copper foam using chemical vapor deposition (CVD) process, with the goal of optimizing the CVD process for high growth rate and uniform distribution of carbon nano tubes. The modified copper foam will be characterized using scanning electron microscope (SEM) and then tested in a BES reactor, where it will be compared to plain copper foam in terms of its ability to produce methane. The study will also explore the potential of the modified copper foam as a bio-electrode in power-to-gas technology.

## **1.9 Organization of thesis structure**

This section provides a summary of the organization of the thesis content, guiding the reader through the project's structure.

Chapter 1 outlines the motivations behind the research and the primary objective of the project, it includes simple explanation of the background topics like power to gas technology, Bio-electrochemical system, carbon nano tubes, etc. This chapter also explains the scope of the project.

Chapter 2 shows the materials utilized for fabrication process and explains the methods of fabrication process of carbon nano tubes.

Chapter 3 shows the application of modified copper foam in BES reactor and explains the operation of BES reactor.

Chapter 4 describes the equipment used for characterization and working principal of Scanning Electron Microscope (SEM)

Chapter 5 explains the results obtained from fabrication, characterization, and gas chromatography, also discuss about the challenges and optimization of the CVD process.

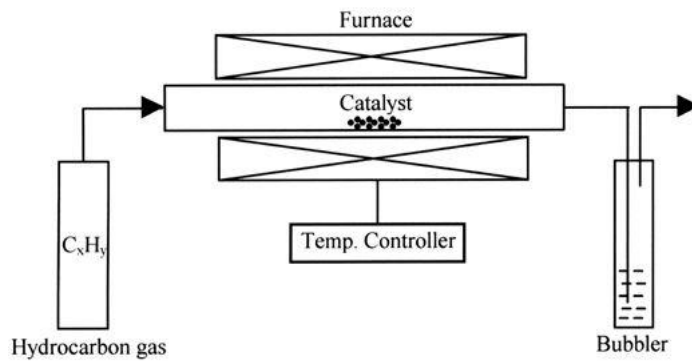
Chapter 6 includes conclusion of the project and consists of some future recommendations.

## 2 CNT Fabrication process

Producing CNTs with desired properties is challenging. There are many methods of growing CNTs. Three common methods for CNT synthesis are Arc discharge method, laser ablation method, and chemical vapor deposition (CVD) [27]. Comparison of these methods shown in Table 2-1.

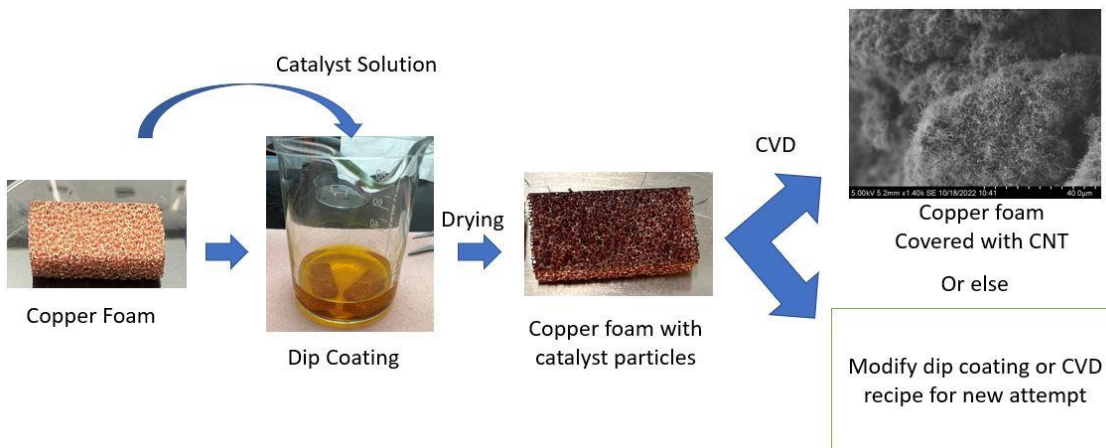
*Table 2-1 Comparison between common methods of CNT synthesis [30]*

<b>Method</b>	<b>Arc Discharge</b>	<b>Laser Ablation</b>	<b>Chemical Vapor Deposition</b>
<b><i>Process</i></b>	Arc evaporation of graphite with the presence of inert gas, CNT forms on the electrode while quenching.	Vaporization of graphite targeted by laser, CNT forms on the receiver while quenching.	Decomposition of hydrocarbons over transition metal catalyst to form CNT.
<b><i>Operating Temperature</i></b>	>3000 °C	>3000 °C	<1200 °C
<b><i>Operating Pressure</i></b>	50-7600 Torr, under vacuum	200-750 Torr, under vacuum	760-7600 Torr
<b><i>Advantages</i></b>	High Quality	High Quality, Single conformation, SWNT forms	Easy for large Scale, Able to synthesize on a template.
<b><i>Disadvantages</i></b>	Difficult for large scale	Difficult for large scale, expensive	Quality is not that high



*Fig 2-1 Schematic diagram of a CVD setup [31]*

CVD is a popular method for producing CNTs. Compared to any other methods CVD is simple and economic, in this method hydrocarbon vapor is thermally decomposed in presence of a metal catalyst [25]. Fig 2-1 shows an illustration of a CVD setup. In this experiment CVD process has been used, because of the advantages discussed in Table 2-1.



*Fig 2-2 Schematic illustration of the CNT synthesis process*

In this experiment copper foam has been used as the base material, because for CO<sub>2</sub> reduction coppers performance is well balanced in binding strength of reaction intermediates to stabilize COOH, CO and CHO [32]. As electrode material copper foam is also cheap. For performing CVD process the metal foam needs to be coated with catalyst material because for growing CNT, it is necessary to have catalyst nanoparticle that can function as a pattern for implementing the CNT [33]. Fig 2-2 shows an illustration of the CNT synthesis process. For loading catalyst particle on copper foam



Nickle Nitrate  $\text{Ni}(\text{NO}_3)_2$  and Ferrocene  $\text{Fe}(\text{C}_5\text{H}_5)_2$  solution has been used. Simple dip coating method was utilized for loading the catalyst particle on the copper foam [34]. Copper foam was dip coated and dried in the oven binder for several times. Substrate preparation, dip coating and drying process is explained in detail in the next chapters. For observing particle deposition on copper foam, the samples were annealed in high temperature tube furnace. As explained earlier for growing CNTs, catalyst particles are required. After annealing the sample was characterized by using SEM microscope for observing catalyst particle deposition [35] and by doing EDS analysis catalyst material can be detected too. After confirmation of catalyst deposition, CVD process can be done for growing CNTs [36]. Both annealing and CVD process was performed at atmospheric pressure [37]. After CVD process the sample was observed by SEM. In this experiment for attaching microbes on the electrode full coverage of CNTs was a requirement. If CNT coverage was not satisfactory, then the dip coating process and parameters of CVD process like temperature, gas flow etc was modified and the whole process was repeated.

## 2.1 Substrate Preparation

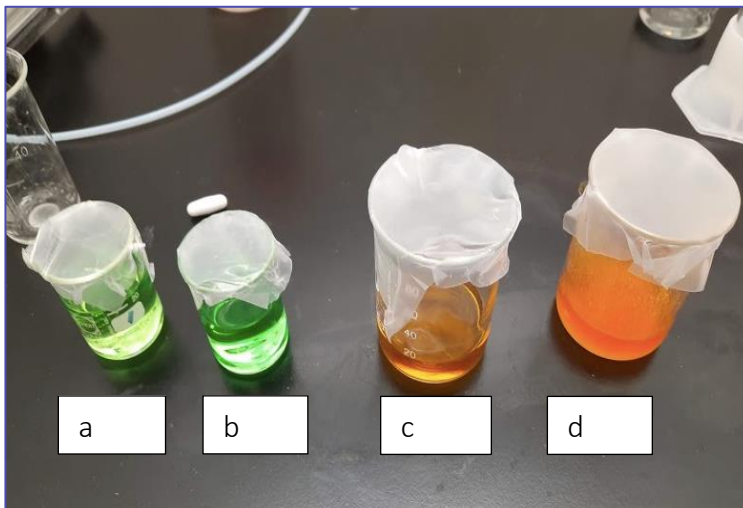
For dip coating the copper foam, ferrocene and Nickel Nitrate solution was prepared with ethanol. Nickel Nitrate and Ferrocene was in powder form. The solution was made by diluting the powder in Ethanol solution by using magnetic stirrer shown in fig 2-3. These solutions are source of Ni and Fe particles. Tabe 2-2 shows the formula and molar mass of Nickel Nitrate and Ferrocene.

*Table 2-2 Chemicals used for dip coating*

Sl. no	Chemical Name	Formula	Molar Mass
1	Nickel Nitrate	$\text{Ni}(\text{NO}_3)_2$	182.703 g/mol
2	Ferrocene	$\text{Fe}(\text{C}_5\text{H}_5)_2$	186.04 g/mol



*Fig 2-3 Ferrocene solution diluting by Magnetic Stirrer*



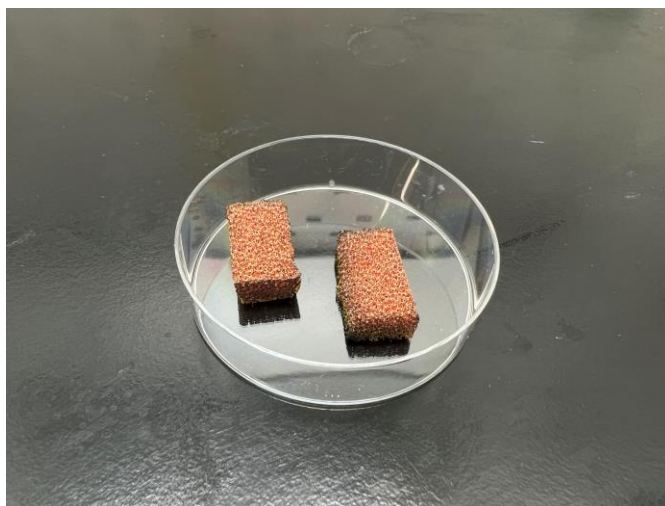
*Fig 2-4 Different concentrations of solutions a) Nickel Nitrate 50 mM b) Nickel Nitrate 100 mM c) 50 mM Ferrocene and d) 100mM Ferrocene*

For dip coating, by using ferrocene and Nickel Nitrate two different concentration 50mM and 100mM was prepared with absolute ethanol solution.

For ferrocene 100mM was not Diluted. In Fig 2-4, 'a' and 'b' are 50mM and 100mM Nickel Nitrate solution, respectively, 'c' and 'd' is 50mM and 100mM Ferrocene Solution. 100mM ferrocene was not diluted. So, later 'b' because of higher concentration and 'c' diluted solution were used for copper foam dipping process.

## 2.2 Copper Foam Dipping Process

Before dipping in the solutions, Copper foam was cut in to 1X3cm pieces shown in Fig 2-5. After that it was cleaned with Ethanol and deionized water, then the foam was cleaned with Ultrasonic cleaner shown in fig 2-7, this process cleans the contaminant.



*Fig 2-5 Plain Copper foam*



*Fig 2-6 Ultrasonic Cleaner*

After cleaning, the foam was dipped in Nickel Nitrate solution for 5min and dried in the oven (fig 2-8) for 5min in 80°C, this process was repeated for 10 times.

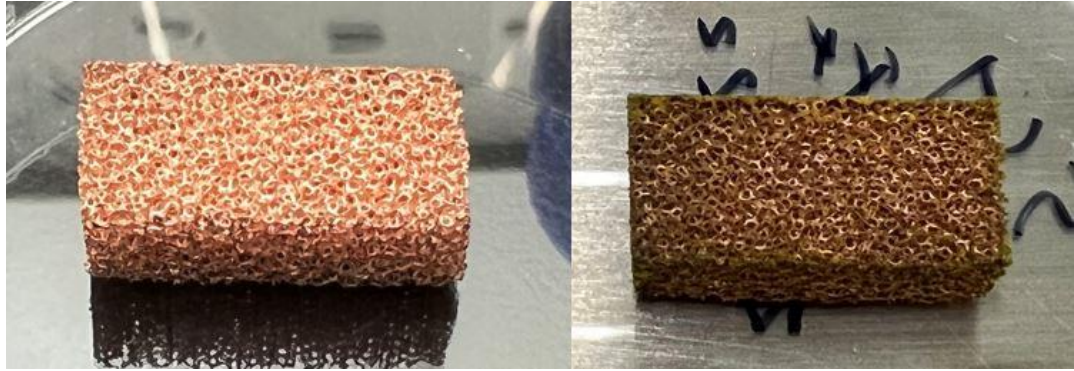


*Fig 2-7 Copper foam dipped in ferrocene Solution*

Similarly, like Nickel Nitrate solution it was dipped and dried 10 times with Ferrocene solution. Fig 2-7 shows copper foam dipped in ferrocene solution. Comparison between the plain sample and dip coated dried sample shown in Fig 2-9.



*Fig 2-8 Oven binder used for drying samples*



*Fig 2-9 Plain and dip coated copper foam*

### **2.3 Annealing Copper foam sample**

This step was performed in the clean room. It was done before doing the CVD to check the catalyst particle deposition on copper foam. As discussed earlier for getting CNTs on the sample, catalyst particle is required. For annealing and CVD process, the sample needs to be heated in high temperature [38]. In this experiment for heating, high temperature tube furnace has been used shown in fig 2-10. This furnace is also used for CVD. The tube furnace is connected with  $O_2$ ,  $N_2$ ,  $C_2H_2$ ,  $CO_2$ ,  $H_2$  gases. This furnace can reach at maximum peak temperature of  $1100^\circ\text{C}$  and maximum temperature ramping rate is  $20^\circ\text{C}$  per minute.





*Fig 2-10 High temperature tube furnace*

Copper foam sample was inserted in the tube furnace on a quartz sample holder. Temperature was ramped 20°C to 580°C in 55 minutes while passing 500 sccm of Argon gas. Temperature ramping rate was 10°C per minute. After reaching 580°C 60 sccm hydrogen gas was introduced for 90 minutes. Here hydrogen used as reducibility gas [37]. Then temperature was ramped to 750°C in 18 minutes, after reaching 750°C temperature was steady in 750°C for 10min with 10 sccm hydrogen and argon gas. After that temperature was turned down and furnace tube was cooled naturally. Natural cooling takes 4 hours. Then, the samples were removed from the furnace. After doing annealing, particle deposition on the samples were checked by SEM and EDS characterization, results explained in detail in results and discussion part.

## **2.4 Chemical Vapor Deposition (CVD) process**

After annealing process, SEM images and EDS analysis showed catalyst particle on the copper foam sample. Then CVD process was performed for growing CNTs. CVD process is similar like annealing but in this process along with hydrogen and argon, Acetylene ( $C_2H_2$ ) gas was introduced for the growth of CNTs [39]. This process was also done in high temperature tube furnace shown in fig 2-10. For CVD,

1. temperature was ramped to 580°C in 55 minutes while passing 500 sccm of Argon gas. After temperature was stabilized at 580°C and followed by the passing 60 sccm hydrogen for 90 minutes. Here hydrogen used as reducibility gas [37].

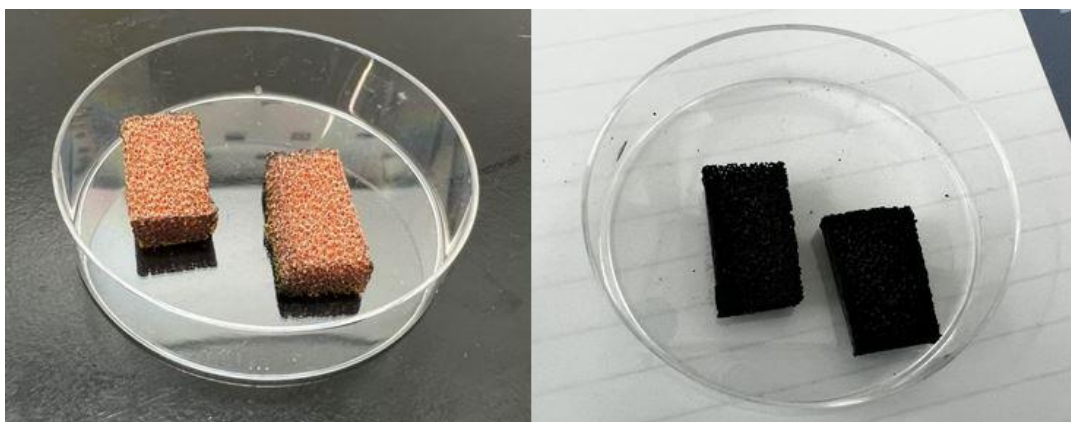
2. After that temperature was ramped to 750 °C in 18min while passing 500scm argon.



*Fig 2-11 Atmospheric pressure indicating in pressure gauge of the tube furnace*

3. When The temperature was stabilized at 750 °C, 20 sccm  $C_2H_2$  was introduced along with 10 sccm hydrogen and argon for 30minutes.  $C_2H_2$  was introduced at last for growing CNTs [37].
4. After CVD process the furnace was then cooled down to room temperature under 100sccm argon gas flow. Both annealing and CVD process was done at atmospheric pressure shown in fig 2-11. After that, the samples were removed from the furnace and then taken for SEM characterization.

Fig 2-12 shows copper foam before and after CVD process.



*Fig 2-12 Copper foam before and after CVD process*

### 3 Application of modified electrode in BES Reactor

After modifying the copper foam electrode, it has been tested in a BES reactor. In this chapter, all the steps for setting up a BES reactor and its operation has been explained.

#### 3.1 Microbial source

For attaching microbes on modified electrode, microbial source has been required [40]. For this experiment 500ml digested sludge of anaerobic digester has been sourced from NIBIO. Before putting in the incubator, storage bottle was flushed with nitrogen for avoiding oxygen contamination. The sludge was filtered and stored in 35°C for 3 weeks.

#### 3.2 Electrolyte preparation

Following chemicals has been diluted in 1 liter deionized water for preparing electrolyte [41].

Table 3-1 Eelectrolyte recipe

Chemical Name	Amount
$KH_2PO_4$	2.72 g/L
$Na_2HPO_4 \cdot 2H_2O$	3.55 g/L
$NH_4Cl$	0.28 g/L
$CaCl_2 \cdot 2H_2O$	0.0076 g/L
$MgSO_4 \cdot 7H_2O$	0.001 g/L
$MgCl_2 \cdot 6H_2O$	0.09 g/L

#### 3.3 Reactor setup

For testing the modified electrode, two chamber H-shaped BES reactor has been assembled. Anode and cathode side has been connected, in the middle of anode and cathode a cation exchange has been placed. In the anode side graphite plate has been hanged with platinum wire [42].

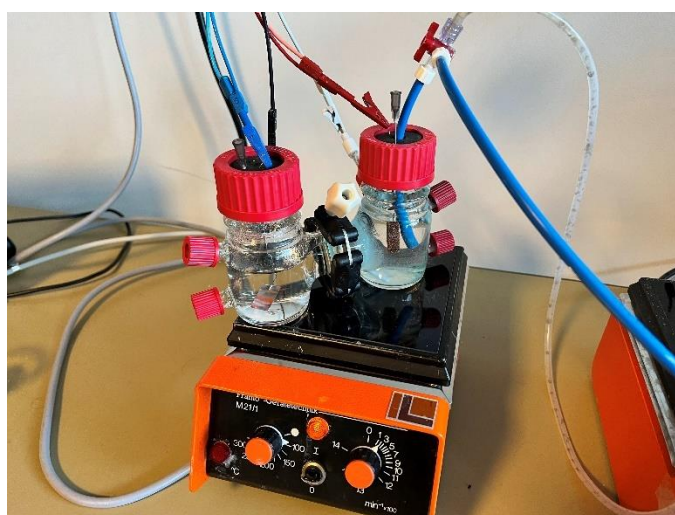




*Fig 3-1 Assembling reactor*

In the cathode side reference electrode Ag/AgCl 3.5M has been installed and modified copper foam also inserted in the cathode of the reactor using platinum wire. Another duplicate reactor has been assembled for using as control reactor, only difference is in control reactor, plain copper foam has been inserted in the cathode side using platinum wire.

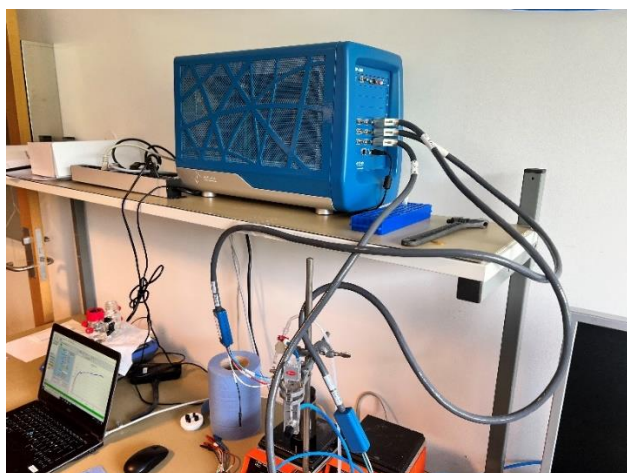
### **3.4 Operation of Reactor**



*Fig 3-2 Two chamber reactor*

For  $\text{CO}_2 - \text{CH}_4$  conversion different types of reactors can be used. In this experiment For testing the modified electrode small scale Two chamber H-shaped (two chamber) BES reactor has been used, because in single chamber reactor there is possibility of

oxygen contamination [40]. Two reactors were constructed, one for control experiment by using plain copper foam as cathode electrode and 2<sup>nd</sup> one for testing the modified copper foam electrode. In this reactor two chambers were separated by cation exchange membrane [43]. The total capacity of this reactor was 250ml. The anode side was filled with only electrolyte and the cathode side was filled with electrolyte and 30% sludge. One reference electrode Ag/AgCl was installed in the cathode side [44]. For the control reactor, plain copper foam was inserted in cathode side and for the testing reactor, modified copper foam was inserted in the cathode side. It was connected with CO<sub>2</sub> gas, 5ml per minute. The reactor was connected with Potentiostat (Biologic, France) for performing cyclic voltammetry, supplied 1.3V and for collecting Electrochemical data, potentiostat was on for 24hour period and data was analyzed with EC-Lab software.



*Fig 3-3 Potetiostat connected with reactor*

### 3.5 Gas Chromatography

For analyzing produced methane gas THERMO Scientific TRACE™ 1300 Gas Chromatograph has been used showed in Fig 3-4. Produced gas was collected from the reactor and was injected in Trace 1300, and it analyzed the gas and showed analysis report. Shown in results and discussion part.



*Fig 3-4 Trace 1300 gas chromatograph for gas analysis*

## 4 Equipment Utilized for Characterization

Characterization of the samples were done with Scanning Electron Microscope (SEM) and Energy dispersive X-ray Spectroscopy (EDS), this chapter explains the working principal of this equipment.

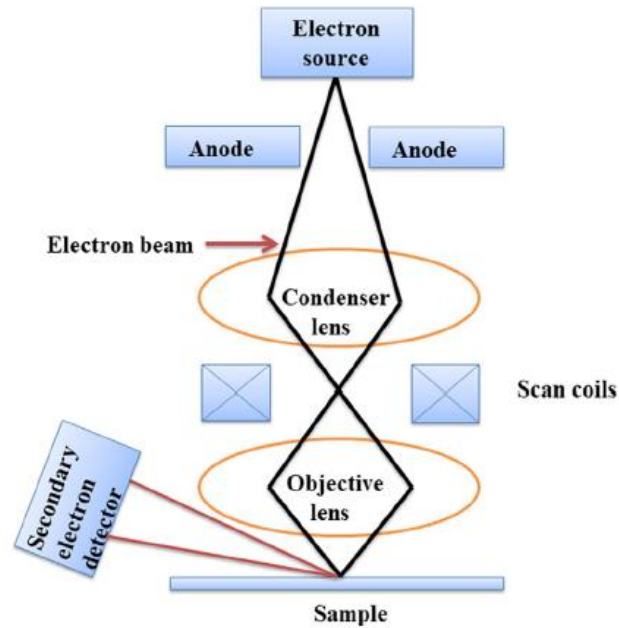
### 4.1 Scanning Electron Microscope (SEM)

Scanning electron microscope (SEM) is kind of an electron microscope which can produce pictures of a sample surface by focused beam of electrons [45]. Lab setup of Hitachi SU3500 SEM shown in Fig 4-1.



*Fig 4-1 Hitachi SU3500 Scanning Electron Microscope*

An electron gun located at the top of the device emits a highly focused beam of electrons. The gun can be of two types: field emission, which uses a strong electric field to extract electrons from atoms, or thermionic, in which heating a filament causes electrons to be emitted [46]. The scanning electron microscope (SEM) examines the surface of a sample with high-energy electron beams [47]. This method of imaging contrasts with traditional light microscopes, which employ light waves to create magnified images.



*Fig 4-2 Working Principal of SEM [46]*

A diagram illustrating the operation of a scanning electron microscope (SEM) is displayed in Fig 4-2. The electron column includes scanning coils, through which the electron beam is directed to the final lens, this allows the beam to be deflected horizontally and vertically to scan a rectangular area of the specimen's surface. Signals emitted from the scanned area are detected and amplified by electronic devices, which display them as images on a cathode ray tube. The raster scanning is coordinated with the microscope, resulting in a map of the signal intensity emitted from the scanned area of the specimen to be displayed [46].

## **4.2 Energy Dispersive X-ray Spectroscopy (EDS)**

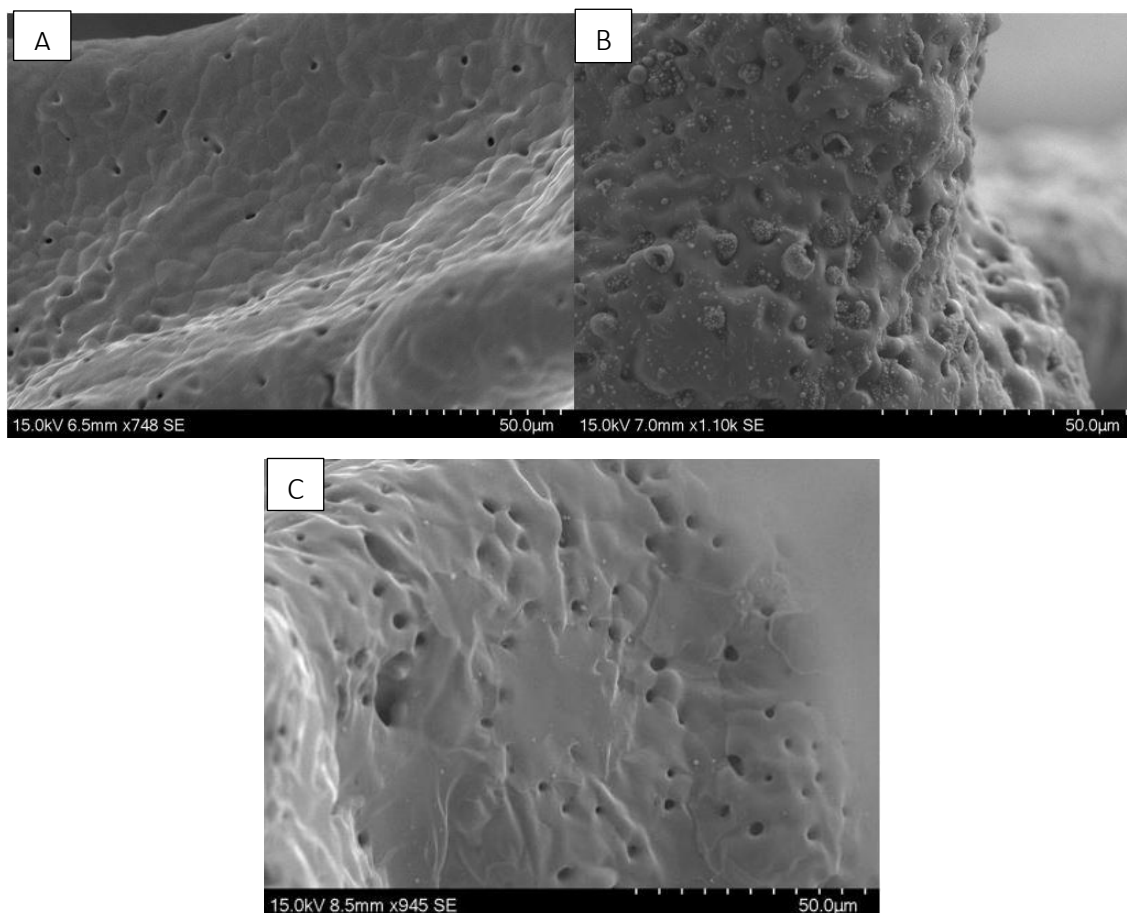
EDS is also a function of SEM, when used in conjunction with a Scanning Electron Microscope (SEM), it is possible to create a map of the surface elements of a sample and evaluate the relative proportions of those elements at different locations [48]. In this study for checking catalyst particle deposition this function has been used.

## 5 Results and Discussion

In this chapter, experimental results obtained by characterization and gas chromatography has been presented and analysed.

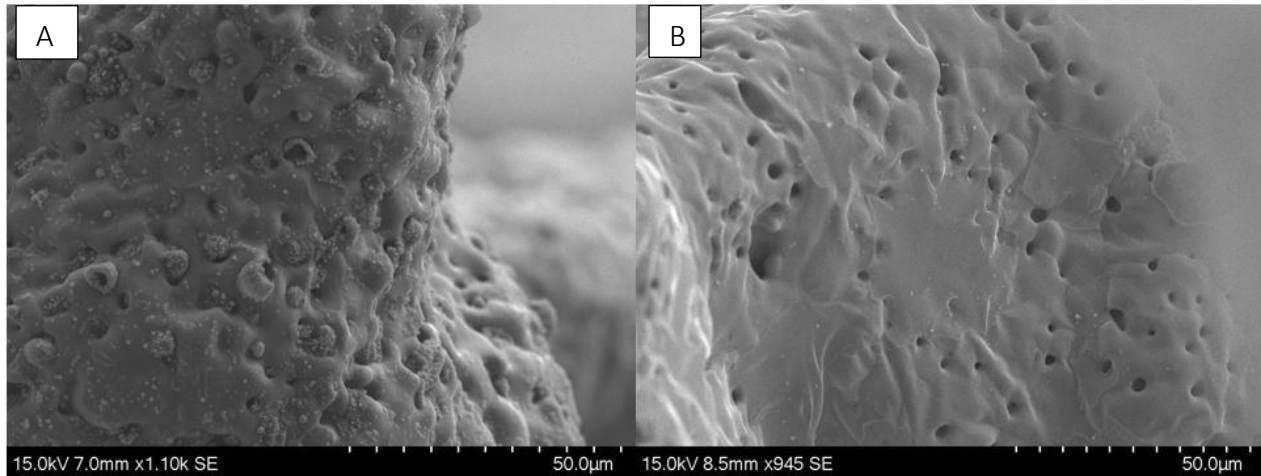
### 5.1 Catalyst loading

After annealing, dip coated samples were analysed by SEM and EDS characterization. Below SEM images fig 5-1, shows comparison between plain copper foam, Nickel Nitrate and Ferrocene dip coated copper foam after annealing. Fig 5-1 A) shows smooth surface of plain copper foam, fig 5-1 B) shows Nickel nitrate dipped copper foam shows the surface is not smooth like plain copper foam it shows deposited particles, Fig 5-1 C) Ferrocene dipped copper foam also shows some deposited particles after annealing.



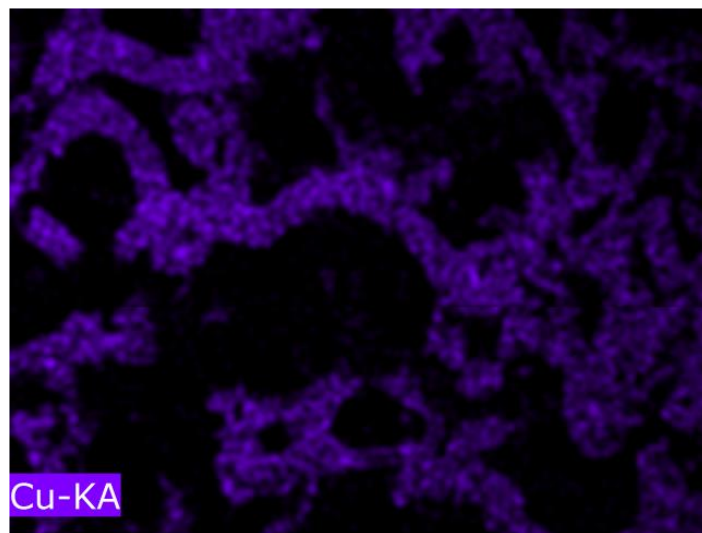
*Fig 5-1 Comparison by SEM images of deposited catalyst particle A) Plain Copper foam B) Nickel Nitrate dip coated Copper foam and C) Ferrocene coated copper foam*





*Fig 5-2 Comparison of A) Nickel Nitrate and B) Ferrocene coated copper foam*

Fig 5-3 shows the comparison between Nickel Nitrate and Ferrocene dip coated copper foam side by side. After putting it side by side, it clearly shows that Nickel Nitrate coated sample is loaded with more catalyst particle. Study of Y.Y. Wei, et al shows CNT coverage on the sample depends on the catalyst particle [49]. So for doing CVD process, Nickel Nitrate coated sample has been used.



*Fig 5-3 Xmap image of copper foam after Annealing*

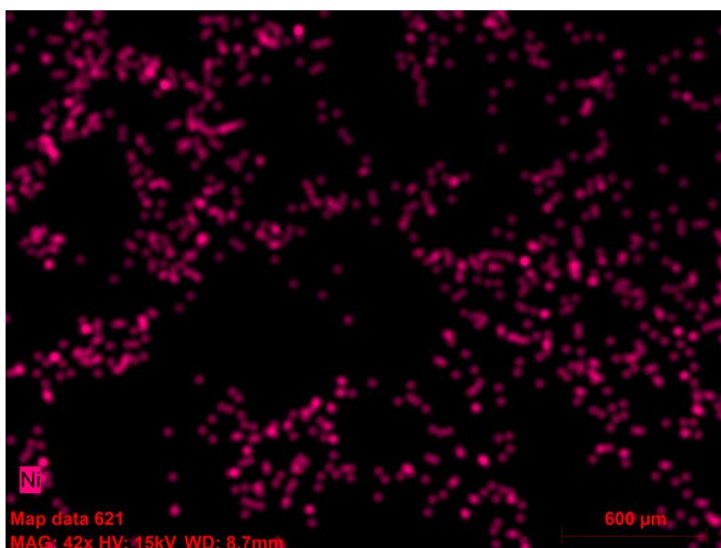


Fig 5-4 Xmap image shows Nickel coverage after annealing on copper foam

Fig 5-3 shows Xmap pattern of copper and Fig 5-4 shows Xmap pattern of Nickel catalyst basis. Pink points corresponds to Nickel Particle. In fig 5-3 blue points shows the base copper foam.

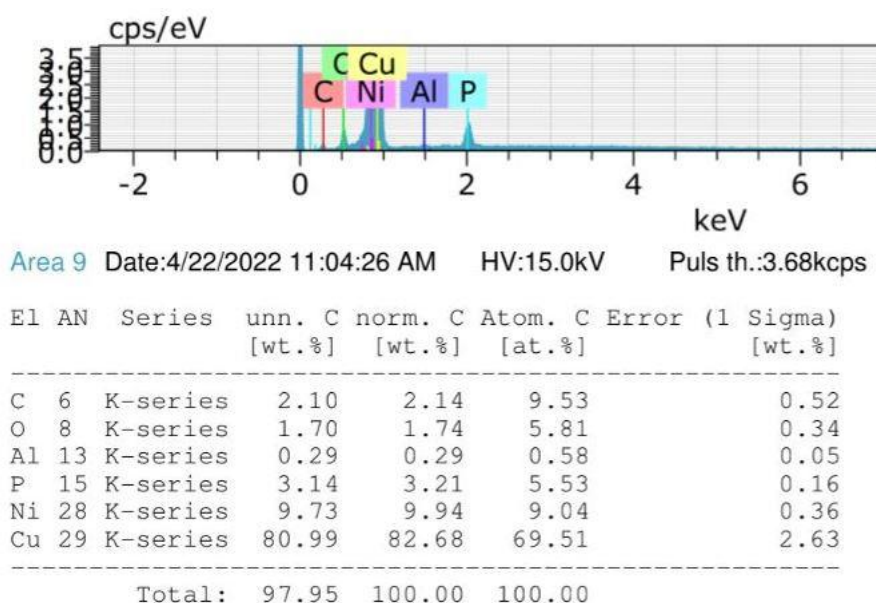


Fig 5-5 EDS data for Nickel Nitrate dip coated Copper foam after annealing

In fig 5-5, shows EDS data for Nickel Nitrate dip coated copper foam, it shows 9.73 atomic percentage of Nickel and also pick for Nickel in the graph and fig 5-6 shows EDS data for Ferrocine dip coated copper foam but it couldn't detect Iron particle. Similarly the SEM image showed little catalyst particle on Ferrocene coated copper foam, so it



confirms Nickel particle was attaching on the copper foam but Ferrocene wasn't. So the experiment continued with Nickel Nitrate coated copper foam.

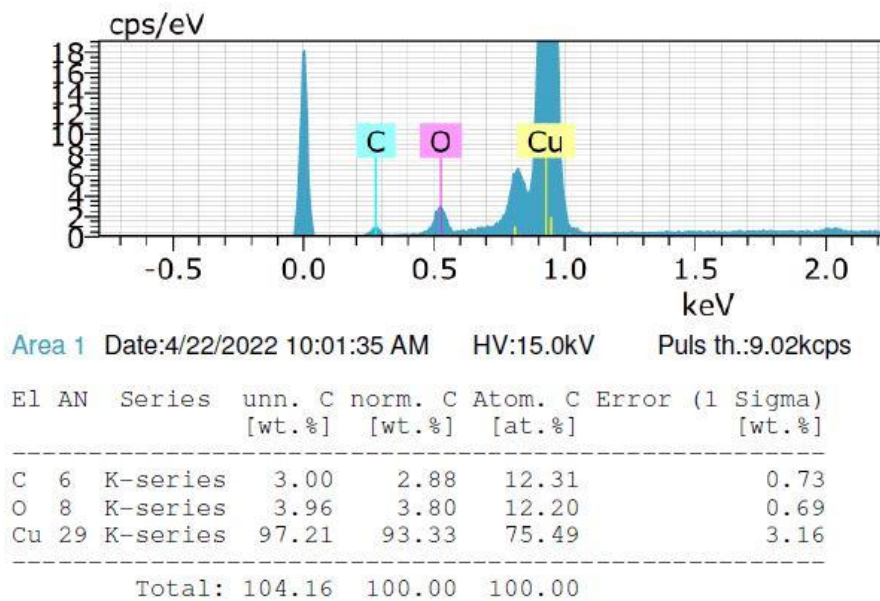
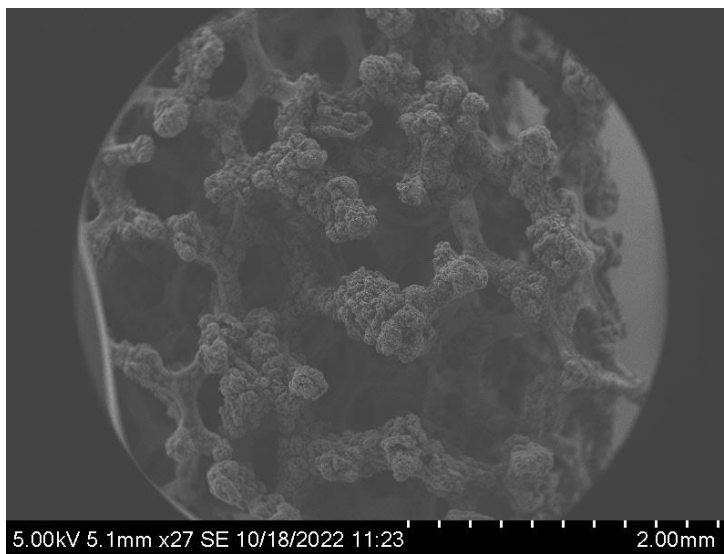


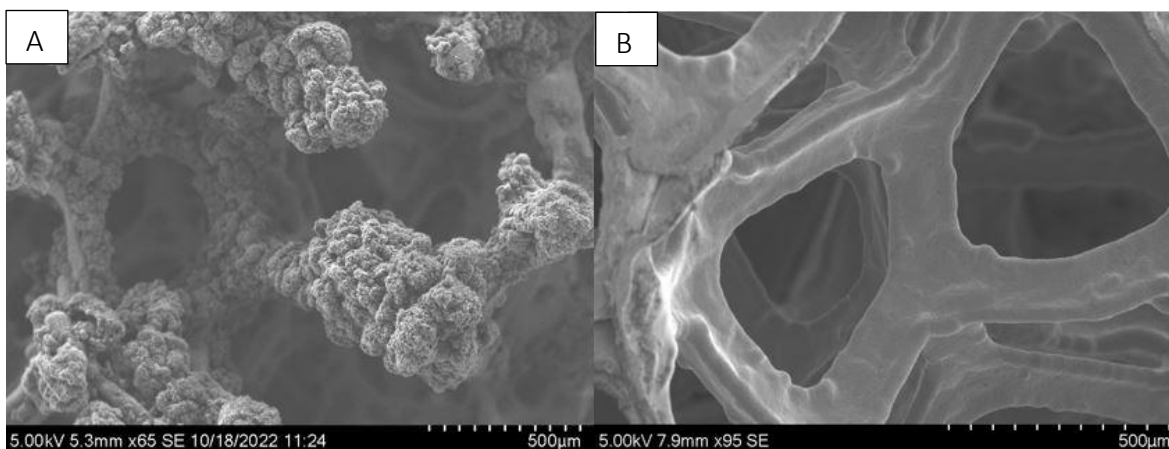
Fig 5-6 EDS data for Ferrocene dip coated Copper foam after annealing

## 5.2 CNT grown after CVD process



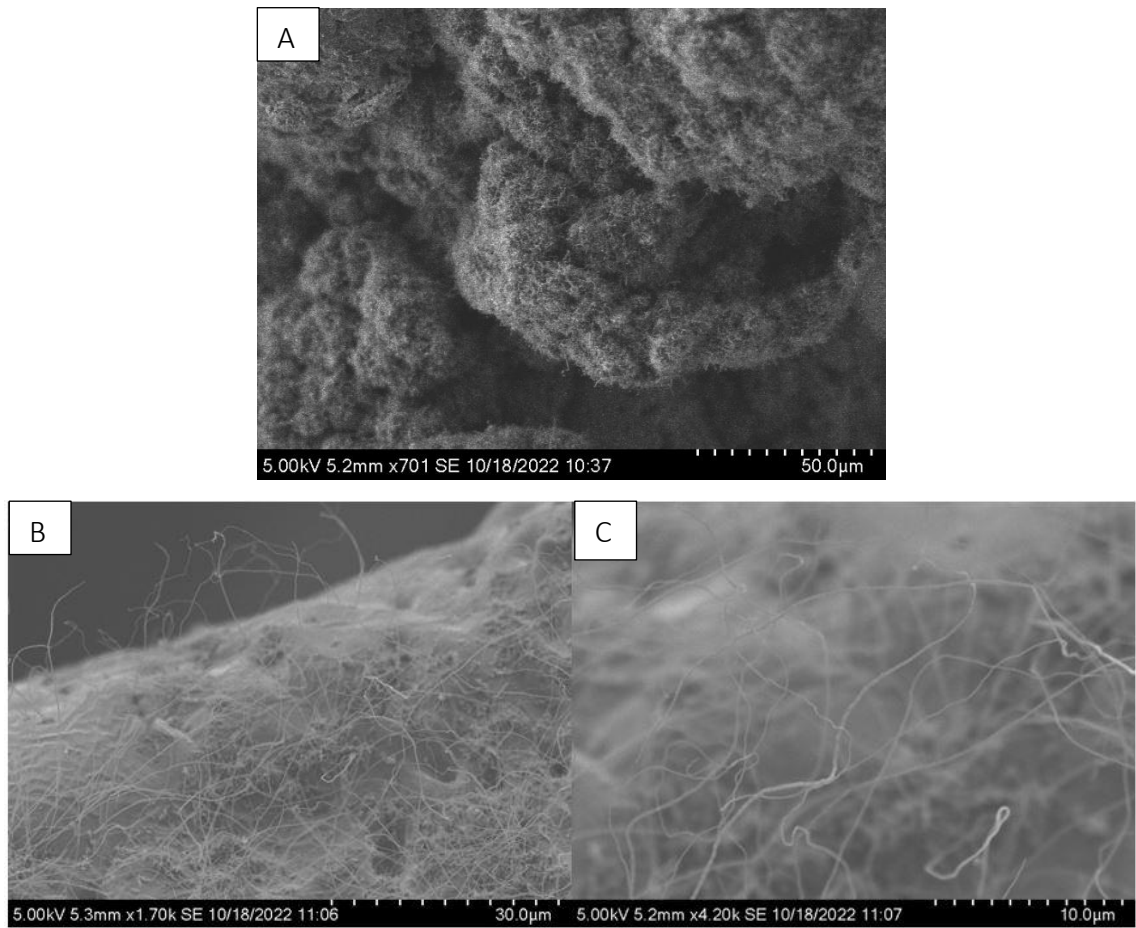
*Fig 5-7 SEM image of Nickel loaded Copper foam after CVD*

Fig 5-8 shows uniform coverage of CNTs on copper foam. As previously discussed, it is required to cover the copper foam because good coverage of CNTs because it exert attaching microbes on the electrode according to the study of Hanyue Ma, et al [50].



*Fig 5-8 SEM image of A) Nickel loaded Copper foam after CVD, Coverd with CNTs comaparing with B) plain Copper foam with dimension of 500 micrometer*

Fig 5-8 shows the surface difference of copper foam with and without CNTs. Comparison is done between CNT loaded copper after CVD and a plain copper foam.



*Fig 5-9 SEM image of Nickel loaded Copper foam after CVD, Covered with CNTs with dimension of A) 50 micrometer, B) 30 micrometer and C) 10 micrometer*

Fig 5-9 shows zoomed SEM images of the modified copper foam; surface covered with CNTs. Moreover, the CNTs appeared well distributed and long in size. This uniform coverage creates a rough surface [51]. The result shows that CNTs increased the surface area of copper foam, it will increase electron transfer efficiency according to the study of Liu et al [52].

### 5.3 Results from Biologic Potentiostat

Data taken from Biologic Potentiostat by using EC-Lab software shows modified copper foam has higher reductive current compared to plain copper foam, CNTs act as conductive medium according to the study of Zhang et al [53]. Fig 5-10 shows for plain copper foam reductive current is average -9 to -10mA and for modified copper foam in fig 5-11 reductive current is average -14 to -15mA. It shows surface modification of copper foam has influence on BES system [54].

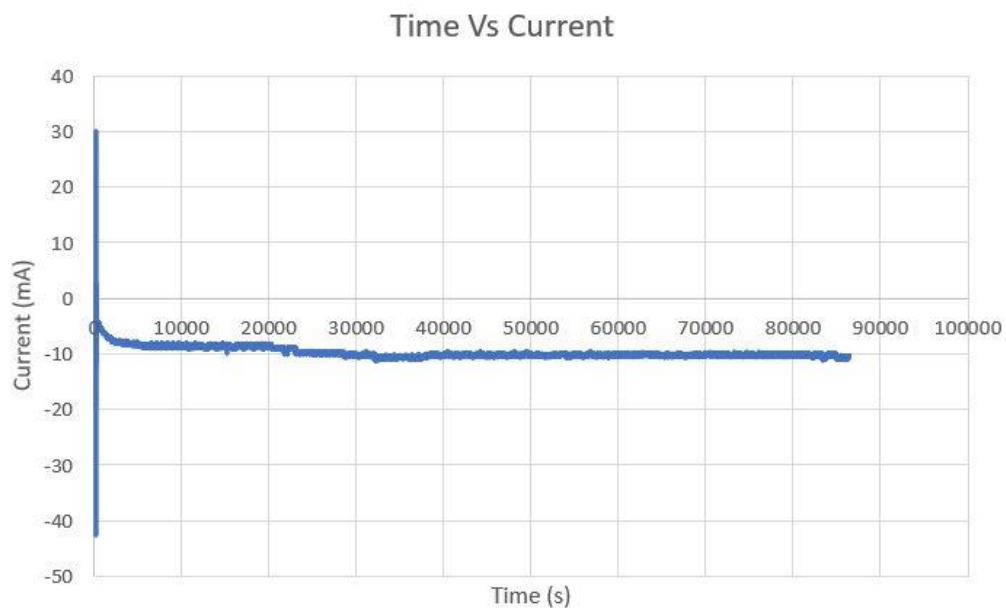


Fig 5-10 Time vs Current graph for plain Copper foam sample

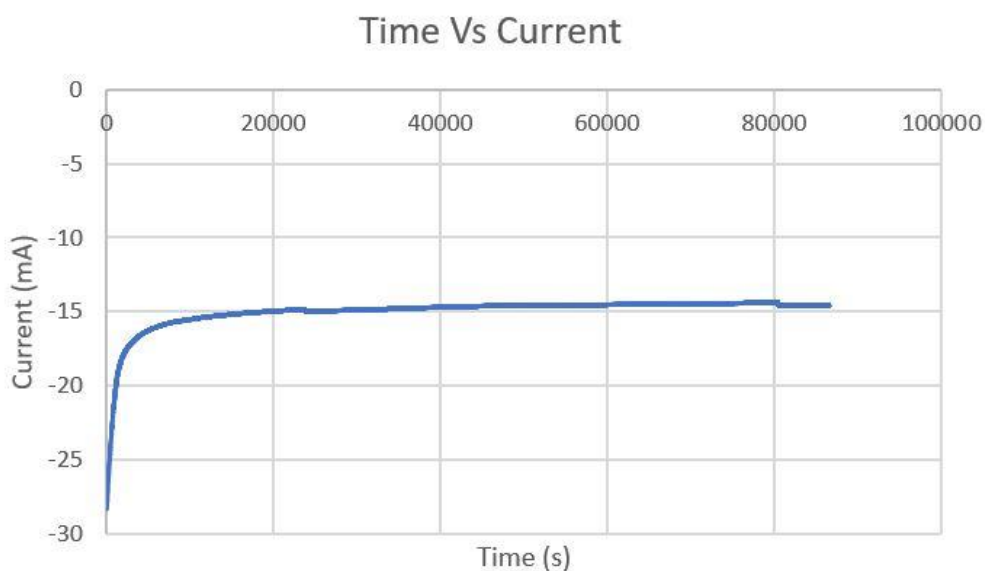


Fig 5-11 Time vs Current graph for CNT grown copper foam

## 5.4 GAS Chromatography

After injecting gas sample from modified copper foam inserted reactor below graph has been extracted from THERMO Scientific TRACE™ 1300 Gas Chromatograph. It shows methane pick in the middle shown in fig 5-12. Fig 5-13 shows the graph for gas sample of plain foam inserted reator. It didn't show any pick for methane because plain foam has anti microbial proerties according to the study of Aryal et al [55]. It shows modification of copper foam surface is effective for methane production.

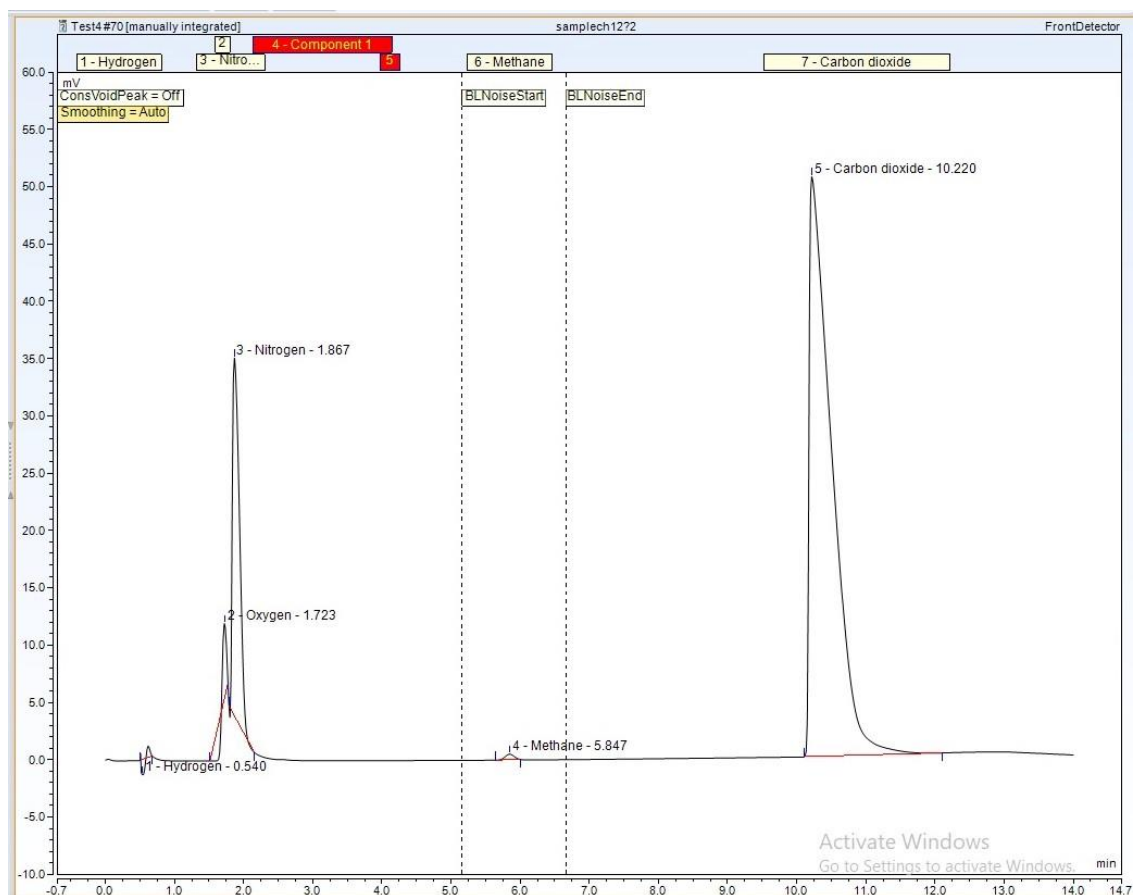


Fig 5-12 GCE graph for gas sample of modified copper foam inserted reactor

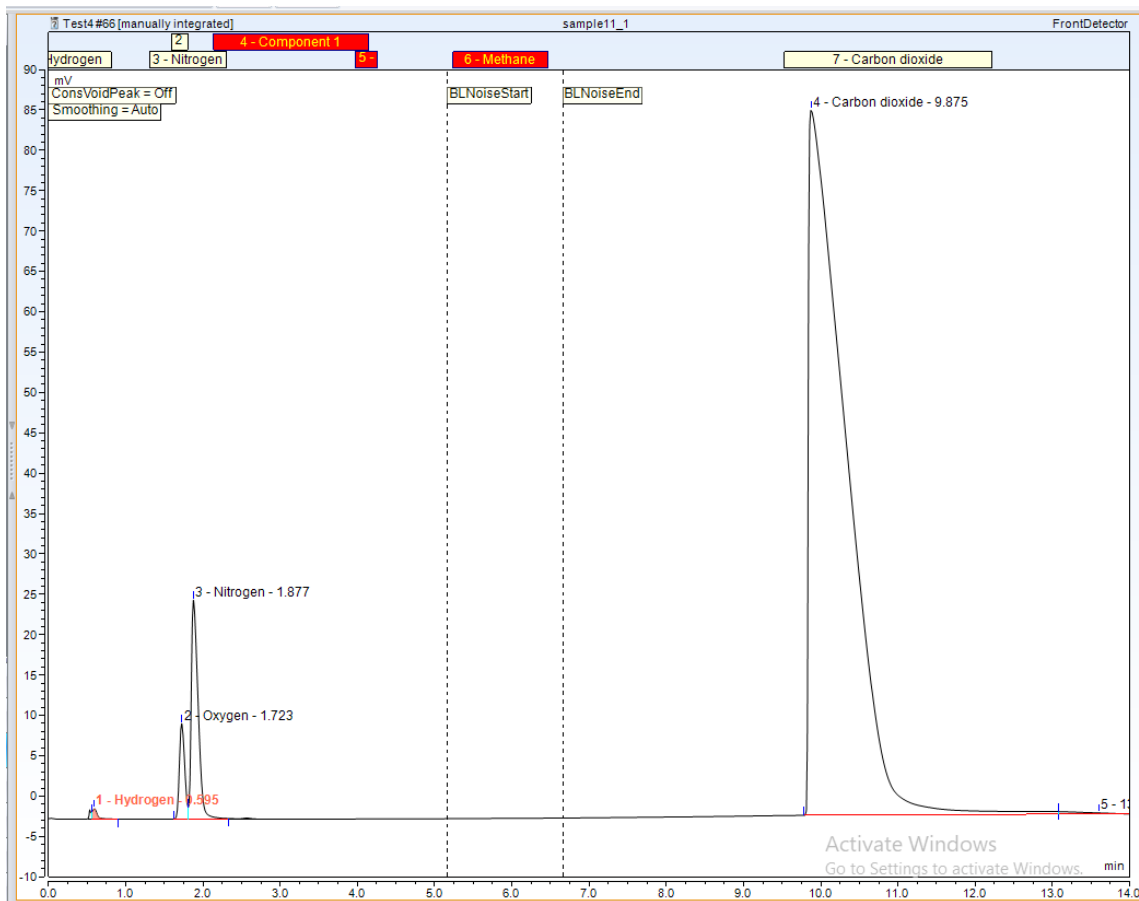
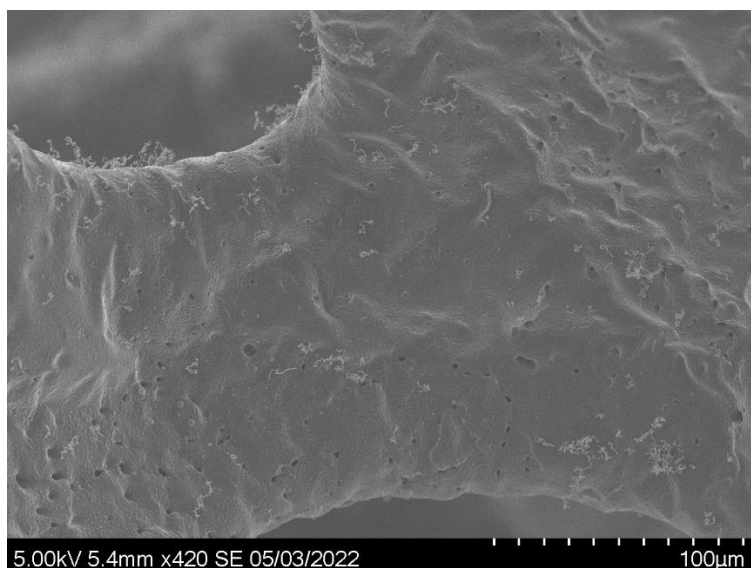


Fig 5-13 GCE graph for plain copper foam inserted reactor

## 5.5 Optimization of CVD process

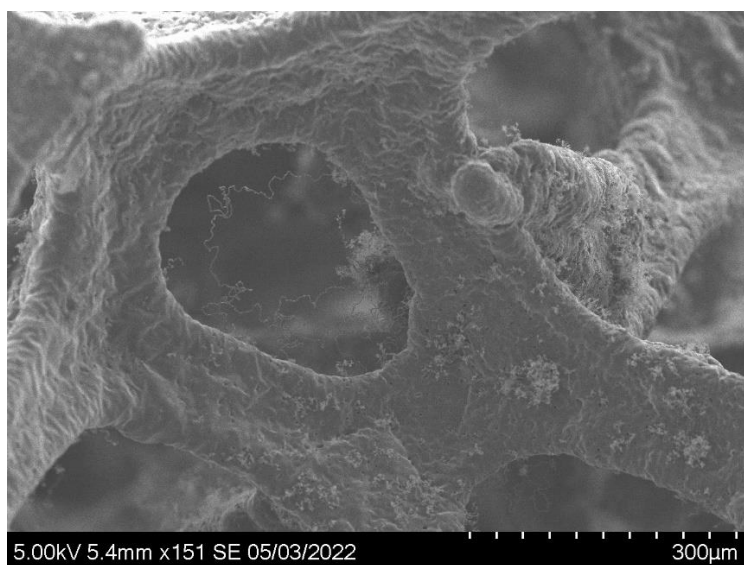
Initially getting CNTs over copper foam was challenging. After many attempts with different CVD recipe by modifying the parameters of dip coating recipe, temperature, gas, flow expected result has been achieved. In this chapter some of the initial attempt's recipe has been discussed. At the beginning of the experiment, annealing time was shorter, gradually it was increased, discussed in method part, fig 5-14 shows less CNT coverage because of short annealing time. short CVD recipe is given below:

1. temperature was ramped to 750 °C in 75 minutes while passing 400 sccm for of Argon gas.
2. The temperature was stabilized at 750 °C and followed by the passing 60 sccm hydrogen for 20 minutes then  $C_2H_2$  was introduced for 20minutes.
3. The chamber was then cooled slowly to room temperature under 100 sccm of Arron gas flow.

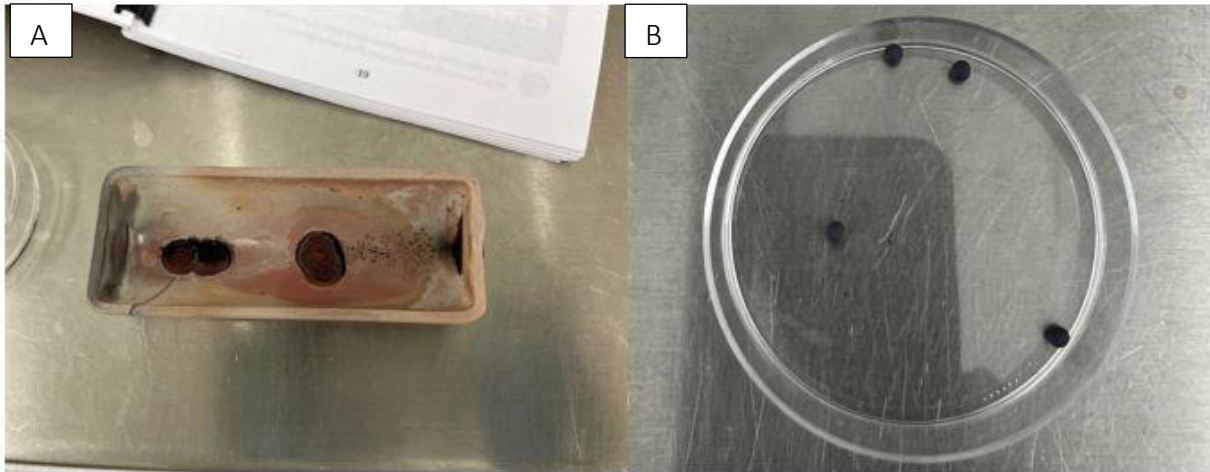


*Fig 5-14 Little coverage of CNT on Copper foam result of shorter annealing time*

CVD process was also done with Ferrocene dipcoated copper foam, but due to less CNT coverage the experiment was continued with Nickel Nitrate dipcoated copper foam shown in fig 5-15.

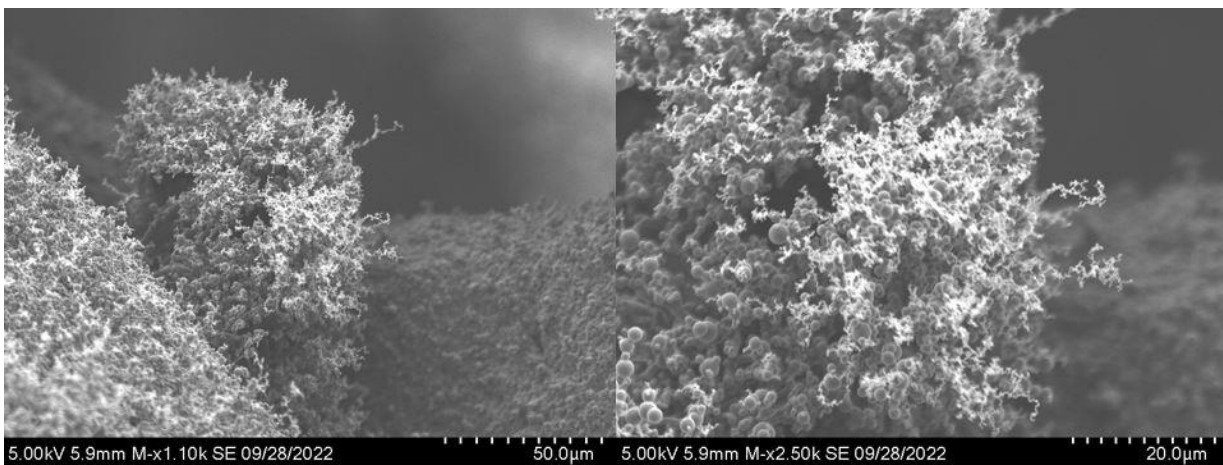


*Fig 5-15 Less CNT coverage on Ferrocene dipcoated copper sample*



*Fig 5-16 A) Damaged quartz boat and B) Damaged copper foam*

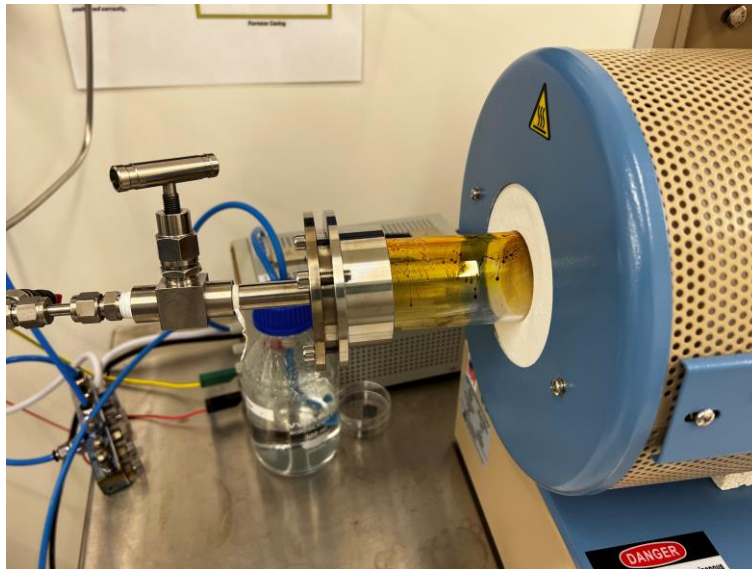
Fig 5-16 shows damaged quartz boat and melted copper foam due to high annealing temperature, for improving CNT growth temperature was increase from 750°C to 800°C, but it damaged the sample though melting point of copper in 1085°C [56], so later annealing temperature was kept 750°C for avoiding damaged sample.



*Fig 5-17 Tubular structure on Copper foam due to leakaged*

Ensuring proper sealing of tube furnace was important. Accidental leakage happened during one attempt, and it showed tubular structures instead of CNTs shown in fig 5-17 also showed stains in the tube furnace shown in fig 5-18.



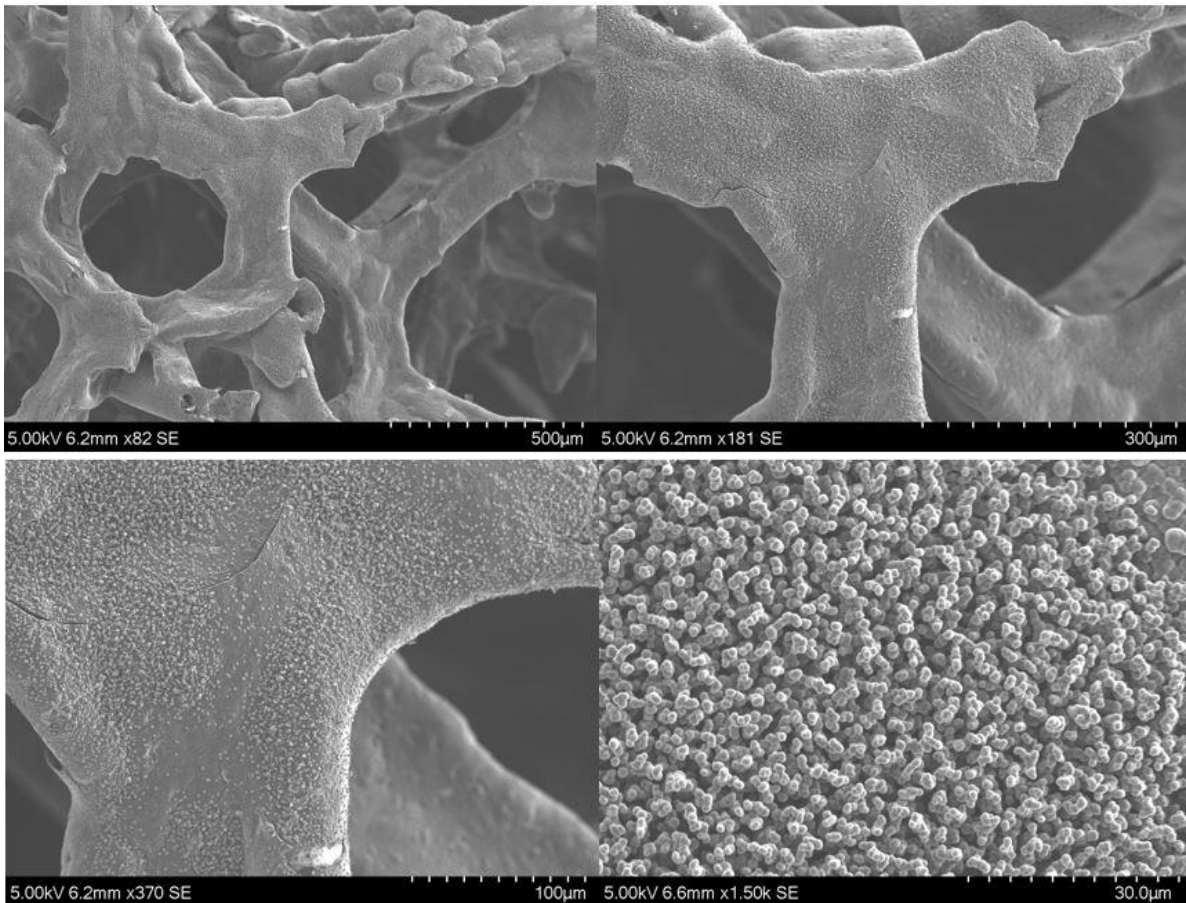


*Fig 5-18 Stains in Tube Furnace due to leakage*

During CVD process, during the step of growing CNT while passing  $C_2H_2$ , Hydrogen and Argon gas should be supplied, one attempt without the presence of Hydrogen and Argon gas showed black film on the quartz sample holder and also on the copper foam sample shown in fig 5-19. SEM images shown film like structure on the copper foam and some tubular structures instead of CNTs shown in fig 5-20.



*Fig 5-19 Black film formed on Quartz sample holder*



*Fig 5-20 Film like layer and tubular structure on copper foam due to (Acetylene)  $C_2H_2$  gas supply in CVD process without the presence of Hydrogen and Argon gas*

For avoiding this kind of black film and tubular structure showed in Fig 5-20 instead of CNTs, in all the experiments hydrogen and argon gas was supplied along with  $C_2H_2$  (Acetylene) gas.

## 6 Conclusion

Two different chemical solutions have been tested as catalyst Ferrocene and Nickel Nitrate. CNT synthesis on copper foam by using Nickel Nitrate catalyst has been showed good result. Simple and cheap dip coating process worked on copper foam sample; it was fully covered with CNTs.

For modifying copper foam with CNTs, long CVD recipes showed good result. Catalyst particle deposition on copper looks relatable with the amount of carbon nano tubes. As catalyst, Nickel Nitrate showed more deposition than Ferrocene.

The aim was to use the modified electrode in a BES system, and it performed accordingly. In comparison with the plain copper foam, modified copper foam showed high reductive current in cyclic voltammetry experiment. Moreover, by using gas chromatography technique, gas sample from the modified and plain copper foams BES reactor has been tested, modified copper foams gas sample showed methane but for plain copper foam there was no methane, it shows power to gas application is functioning with the developed electrode.

### 6.1 Future Recommendations

More dip coating recipe and catalyst solution can be explored in future. By studying material characteristics new base material as electrode can be discovered. Long term performance of copper foam in BES reactor can be done by long cyclic voltammetry experiment. New CVD recipe can be explored for finding controlled CNT growth, and performance of different CNT characters can be tested in BES reactor, and methane production performance can be tested by gas chromatography.

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