

**CATALYST DEVELOPMENT FOR CO₂ REDUCTION USING
SUSTAINABLE SOURCES**

by

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**KOÇ
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Catalyst development for CO₂ reduction using sustainable sources

Koç University

Graduate School of Sciences and Engineering

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ABSTRACT

Global warming is one of the major threats to humanity at present. The major cause is utilisation of fossil fuels which results in CO₂ production. Present work establishes an understanding on the two molecules i.e. CO₂ and H₂O which are at the core of solution for the CO₂ problem with an aim to develop catalytic surfaces for CO₂ reduction reaction using sustainable sources. Researchers are working on developing surfaces which can help reduce these molecules effectively. All sorts of materials and techniques are under consideration from metals to semiconductors to nanomaterial and photo-electro-thermal catalysis. Our study points out one major finding, which is that the binding energy of an intermediate during any reduction process depends on the morphology of the material.

Chapter 1 presents an overall picture of the CO₂ dilemma with an emphasis on where we stand globally. It begins by first discussing thermodynamics and kinetics related to CO₂ and H₂O with a more subtle reading on hydrogen evolution reaction due to its simplicity. The same understanding can be applied to CO₂ which results in more complex array of products such as methane, carbon monoxide, methanol etc. It also discusses the mechanism of HER and CO₂R which is followed by text on plasma CO₂ reduction. This chapter also deals with discussion of materials selection for reduction processes and also presents reports in tabulated form on the earth abundant materials presently being utilised for reduction purposes.

Chapter 2 discusses HER on metallic copper nanowires, this is the first report on making nanowires using DBD plasma process. These nanowires are characterised by using SEM, XRD, XPS and Raman spectroscopy, followed by application in HER. These nanowires showed excellent performance in comparison to bulk copper surface form; by reaching the specific current density of 10mA/cm² with an overpotential half the present value on bulk surfaces, also the exchange current density increase to at least six times.

Chapter 3 presents findings on the use of metallic copper nanowires for CO₂ reduction, we used a conventional two chamber electrolytic cell with separate counter electrode compartment to study CO₂ reduced species. The products are analysed by using GC2014 with a column MS5A and nitrogen is used as carrier gas. We found that metallic nanowires are more selective to overall gaseous products as compare to their bulk counter part(flat copper surface). As the applied potential was increased to more higher values, the proportion of CH₄ and CO is increased which is not observed in flat copper surface.

Chapter 4 discusses the utilisation of DBD plasma technique for CO₂ reduction on Cu and Ni oxide loaded supports (Al₂O₃ and SiO₂). Inhouse system is built to carryout the CO₂ reduction reaction. We observed the formation of saturated hydrocarbons on copper oxide loaded alumina while nickel oxide loaded silica showed preference for unsaturated hydrocarbons.

Chapter 5, presents details on the use NiS and CuS for HER. Both surfaces after synthesis are treated with plasma and showed altered morphology. On comparison between plasma and non plasma treated metal sulphides, there is almost 100mV difference in overpotential to reach specific current density.

In the end, main conclusions and future work are listed followed by references used in this study. Overall, in this thesis, new surfaces and techniques are evaluated for energy conversion processes with a goal of efficient energy conversion and we found that metallic copper nanowires are more efficient than bulk copper surface during HER reaction, the overpotential required to reach specific current density decreased by half; when metallic nanowires are used instead of bulk copper surface. When the same nanowires are tested for ECO₂R, 30% increase in overall gaseous product is observed. During plasma reduction of CO₂ on metal-oxide loaded supports, it is concluded that CuO loaded samples are selective towards saturated hydrocarbons while NiO loaded samples are selective towards unsaturated hydrocarbons with a total CO₂ conversion efficiency of up to 30%.

ÖZETÇE

Küresel ısınma, günümüzde insanlığa yönelik en büyük tehditlerden biridir. Bunun başlıca nedeni, CO₂ üretimi ile sonuçlanan fosil yakıtların kullanılmasıdır. Mevcut çalışma, CO₂ sorununa çözüm olacak iki moleküle yoğunlaşarak, CO₂ indirgeme reaksiyonu için sürdürülebilir kaynaklar kullanarak katalitik yüzeyler geliştirmeyi amaçlar. Son yıllarda CO₂ indirgeme reaksiyonu üzerine etkili olabilecek yüzeyler üzerine bir çok araştırma bulunmaktadır. Metallerden yarı iletkenlere, nanomalzemelere ve foto-elektro-termal katalizlere kadar her türlü malzeme ve teknik üzerine çalışmalar bulunmaktadır. Bu çalışmada ortaya çıkarılan önemli nokta, indirgenme reaksiyonları sırasında oluşan reaksiyonların malzemenin morfolojisine bağlı olduğudur.

Bölüm 1, küresel olarak nerede durduğumuzu vurgulayan CO₂ ikileminin genel bir resmini sunmaktadır. Önce CO₂ ve H₂O ile ilgili termodinamik ve kinetik konseptler basitliği nedeniyle hidrojen evrimi reaksiyonu hakkındaki bilgileri tartışarak başlar. Daha sonra, metan, karbon monoksit, metanol vb. gibi daha karmaşık bir ürün dizisine neden olan CO₂ indirgenme reaksiyonları tartışılır. Ayrıca, Hidrojen evrimi reaksiyonu (HER) ve CO₂ indirgenme (CO₂R) reaksiyonları tartışıldıktan sonra plazma ile CO₂ indirgenme reaksiyonları mekanizması da tartışılır. Bu bölümde ayrıca, indirgeme süreçleri için malzeme seçiminin önemi de tartışılmakta ve halihazırda indirgeme amacıyla kullanılan malzemelere ilişkin raporlar da sunulmaktadır.

Bölüm 2’de metalik nanoteller ile HER mekanizması tartışılmaktadır. Metalik nanotellerin oluşturulması plazma işlemini kullanarak yapılmıştır ve bildiğimiz kadarı ile bu çalışma bu konudaki ilk rapordur. Bu nanotellerin SEM, XRD, XPS ve Raman spektroskopisi, ardından HER’de uygulanması karakterize edilir. Bu nanoteller, düz metal bakır yüzey formuna kıyasla mükemmel performans gösterdi ve 10mA / cm² spesifik akım yoğunluğunda, düz bakır elektrotlara göre %50 daha az aşırı potansiyel gösterdi. Ayrıca değişim akımı yoğunluğu en az altı kat artış gösterdi.

Bölüm 3 CO₂ indirgenmesi için metalik bakır nanotellerin kullanımına ilişkin bulgular sunar, CO₂ indirgenme reaksiyonları sonucunda açığa çıkan türleri incelemek için ayrı bir karşı elektrot bölmesine sahip geleneksel iki odacıklı elektrolitik hücre kullandık. Çıkan ürünler, bir gaz kromatografisi ile analiz edildi. Bu çalışmada metalik nanotellerin genel olarak gaz

halindeki ürünlere, düz bakır yüzeylere kıyasla daha seçici olduklarını bulduk. Uygulanan potansiyel daha yüksek değerlere yükseltildiği için, düz bakır yüzeyinde gözlenmeyen CH_4 ve CO oranlarının arttığını gördük.

Bölüm 4, Cu ve Ni oksit yüklü destekler (Al_2O_3 ve SiO_2) üzerinde CO_2 indirgenme reaksiyonu için dielektrik bariyer boşalma (DBD) ile plazma tekniğinin kullanımını tartışmaktadır. CO_2 indirgenme reaksiyonunun gerçekleştirilmesi için bir reaktör sistemi tasarlanmıştır. Bu çalışmada bakır oksit yüklü alümina üzerinde doymuş hidrokarbon oluşumunu gözlemledik, nikel oksit yüklü silika ise doymamış hidrokarbonları tercih etti.

Bölüm 5, HER için NiS ve CuS kullanımıyla ilgili ayrıntıları sunmaktadır. Sentezden sonra her iki yüzey de plazma ile muamele edildi ve bu işlem sonucunda değiştirilmiş morfoloji gösterildi. Plazma ile işlem görmüş ve görmemiş metal sülfürler kıyaslandığında, spesifik akım yoğunluğuna ulaşmak için aşırı potansiyelde neredeyse 100mV fark bulunduğu gösterildi.

En son bölümde ise, sonuçlar özetlenmiş ve gelecekte planlanan çalışmalar listelenmiştir. Genel olarak, bu tez çalışmasında, verimli bir enerji dönüşümü amacı ile enerji dönüşüm süreçleri için yeni yüzeyler ve teknikler değerlendirilmiş ve metalik bakır nanotellerin HER reaksiyonu sırasında düz bakır yüzeyden daha verimli olduğunu ve özel akım yoğunluğuna ulaşmak için gereken aşırı potansiyelin yarı yarıya azaldığını bulduk. Aynı nanoteller CO_2 R için test edildiğinde, düz bakır yüzeye göre toplam gaz miktarında % 30 artış gözlemlendi. Metal oksit yüklü desteklerde CO_2 'nin plazma indirgenmesi sırasında, CuO yüklü numunelerin doymuş hidrokarbonlara karşı seçici olduğu, NiO yüklü numunelerin ise toplam % 30'a varan bir CO_2 dönüşüm verimliliği ile doymamış hidrokarbonlara karşı seçici olduğu sonucuna varılmıştır.

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ABBREVIATIONS

BET; Brunauer–Emmett–Teller
CV; cyclic voltammetry
DBD; dielectric barrier discharge
DFT; density functional theory
DI; deionised water
EIS; electrochemical impedance spectroscopy
GC; Gas chromatography
HER; hydrogen evolution reaction
LSV; linear sweep voltammetry
MS5A; molecular sieve column
OER; oxygen evolution reaction
RHE; real hydrogen electrode
 R_s ; solution resistance
SEM; scanning electron microscopy
UV; ultraviolet
wrt; with respect to
XPS; X-ray photoelectron spectroscopy
XRD; X-ray diffraction

Chapter 1- Introduction

1.1 Brief

It is a well-established fact that rising CO₂ levels are adversely affecting our climate by increasing the global average temperature^{1,2} which results in melting of polar ice caps and glaciers and this in return is causing floods and loosing coastal areas to rising sea levels. Not only this, the depletion of ozone layer and rising instances of skin cancer is also another issue which can be related to CO₂ increase in earth atmosphere. Another related problem is an all-time decreasing crude oil reserves³⁻⁵ which if used at current pace will be consumed by the following century⁶ so we have to divert our attention to other fuel sources such as but not limited to hydrogen. Because if we replace carbon based fuels in transportation and energy sector with hydrogen technology, rising CO₂ level will be suppressed and thus reduction in adverse effects on climate change, with a long term solution of global reliance on carbon based fuels will be diverted to hydrogen.

The main aim of this thesis is to build an understanding of energy conversion and shed some light on the use of earth abundant resources for the purpose of energy conversion. Most portion of global energy needs is fulfilled by using carbon based materials; mainly organics, which on burning yield CO₂. This thesis incorporates the study of energy conversion area with a special focus on problems related to CO₂. One, rising level of CO₂ due to burning of fossil fuels and other the shortage of fuel which can affect global economic bubble. The equation seems simple, to balance the adverse effects on our atmosphere, usage of organic fuels should be stopped immediately but it cannot be done since the term global village came into existence due to industrial revolution lead by coal and eventually crude oil. Now the question is, since we cannot immediately halt the use of crude oil, what would be the feasible solution. The first solution that is being studied; is fixing atmospheric CO₂, the other is utilising atmospheric CO₂ to make fuels that can be used in a cycle of fuel to CO₂ conversion and vice versa. The other is planting more trees. The other part of the problem is searching alternative of carbon-based fuel and thus hydrogen comes under the observation.

Now the strategy is, working on creating ways to decrease atmospheric CO₂ by, may be converting the atmospheric CO₂ to useable fuels; this study can be one direction and the other is developing ways to use hydrogen as fuel but for that we need to make cheap hydrogen.

Chapter 1- *Introduction*

So, there are two parts of this thesis, CO₂ reduction and hydrogen evolution. Now what strategy should be used to address these two issues, there are many ways and selected few covered under this thesis are as follows,

- Electrocatalysis
- Plasma catalysis

The solutions are obviously just not limited to above mentioned techniques, there are many solutions possible on which studies can be made such as,

- Thermal dissociation of CO₂ and H₂O
- Photolysis of CO₂ and H₂O
- Photocatalysis
- Thermal catalysis
- Electrocatalysis, photo electrocatalysis

Briefly, thermal dissociation is based on bond breaking energy, temperatures of up to 3000°C⁷ are required for reduction of both these molecules, which is not a very sustainable way. In case of photolysis⁸, sunlight can be focused on the molecules to break them apart, but it depends on the component of sunlight that can be used for the purpose. It has been studied that UV light can be used for the purpose but the intensity of UV in sunlight is almost 2-3% which renders the process unfeasible⁹. The rest of the techniques utilise interfaces for the reduction process. In theory, the molecule of interest interacts with a surface and breaks apart into desirable products. For instance, in case of photocatalysis, the molecule adsorbs on the surface and photons from sunlight produce an electron hole pair which may subsequently reduce or oxidise the species of interest. In case of thermal catalysis; temperature in excess of 300°C are used during the interaction of surfaces and molecules which results in reduction. In case of electrocatalysis, external electrical energy is used to carry out the reaction of interest based on the surface. There is another variant; namely photo-electrocatalysis, which combines sunlight and electricity to yield the reduction of molecule to desired products.

Before going in details of more technical research on the subject, let us have a look on what can be done in the meanwhile to address CO₂ problem or at least understand the extent of the problem. Average tree consumes 24 kg of CO₂ a year¹⁰, there is a total of 3 trillion tons of CO₂ in earth's atmosphere¹¹ (400ppm, while let's assume the safe level is around 300ppm). A recent study estimated about 3 trillion trees¹² (31%forest landmass on earth surface-20000trees per

square km) at present on earth, it will take 25 years from present level of CO₂ to reach the safe level of 300ppm, provided that we prevent anymore CO₂ formation and that the forest land mass remains the same (number of trees remain almost the same). Given that the CO₂ rise is almost 2-3ppm per year¹³, the CO₂ level by 2045 will be 350ppm. So, in the meanwhile, the technical research is in progress on CO₂ to fuel conversion for CO₂ to fuel cycle, the earth's forest mass should be kept around 35-40% with up to 4-5trillion trees. Turkey emits 300 million tons of CO₂¹⁴ which pose a need of 30billion trees to decrease its effect in ten years. At present Turkey has around 8billion trees¹⁵. For a sustainable solution, the oil producers and consumers should be taxed to maintain a healthy forest life to counter increasing CO₂ production rates. Research studies are needed to see the feasibility of such an idea.

Coming back to the research domain on CO₂ reduction and hydrogen evolution. The idea is to convert already available CO₂ in atmosphere to useable fuels, also the readily available water reserves can be used to generate hydrogen. The problem now is efficiency of the established processes and materials. The main problem with hydrogen evolution is expensive catalyst, Pt is used but its expensive, the alternative found to be MoS is almost 10th of the cost of Pt, but then comes the efficiency of the process. Electricity required to produce hydrogen is expensive, so hydrogen problem has two different areas where work is needed, number one, cheap electricity production to generate hydrogen and the other is, the surface that can efficiently produce hydrogen, for instance if we compare Pt with Cu, Pt reaches 10mA at 50mV¹⁶ of overpotential while in case of Cu the overpotential to reach similar current density is around 400mV¹⁷.

The source of cheap electricity should obviously be such a system, that comprises of solar cells that can convert photons to electrical energy for hydrogen generation. This part of research is not covered in this thesis, we have focused on finding solutions for suitable surfaces for HER.

The other part of the thesis is CO₂ reduction using two ways, one electrochemical way and the other uses hydrogen plasma. The core of the thesis is synthesizing various surfaces and testing them for HER and CO₂ reduction, along with development of testing techniques to study the same reactions. In the following texts fundamentals of CO₂ reduction and HER are discussed.

As part of understanding the technical aspects of the problem, the first step is to understand the reduction reactions of the molecules i.e. CO₂ and H₂O. CO₂ reduction results in a complicated array of products, thus let's first analyse and understand the electrochemical water reduction process (HER) and the principles can be easily extended to understand electrochemical CO₂ reduction process. Then studies will be focused on plasma CO₂ reduction in which solid surfaces are used to reduce CO₂ molecule under hydrogen plasma. To understand the reduction process of these molecules, it is necessary to look on the thermodynamics and kinetics of the reduction reactions.

1.2 Thermodynamics of HER and CO₂ reduction

Let us start the discussion by focusing on water molecule since it is easy to understand in comparison to CO₂. Water molecule has a Gibbs free energy of formation -237kJ/mol.



This means, that breaking water molecule is a non-spontaneous process and will require an equivalent of Gibb's energy of up to -237kJ/mol, in term of enthalpy; about -285kJ/mol.

Same goes for CO₂, which has a Gibbs energy for formation of up to -394kJ/mol and thus a non-spontaneous process in reverse direction through following equation,



The above discussion talk about input energy in general sense, lets discuss about a specific case of energy input, say electrical energy. In case of electrical energy, water stability diagram is the key descriptor which describes the thermodynamics, Figure 1.

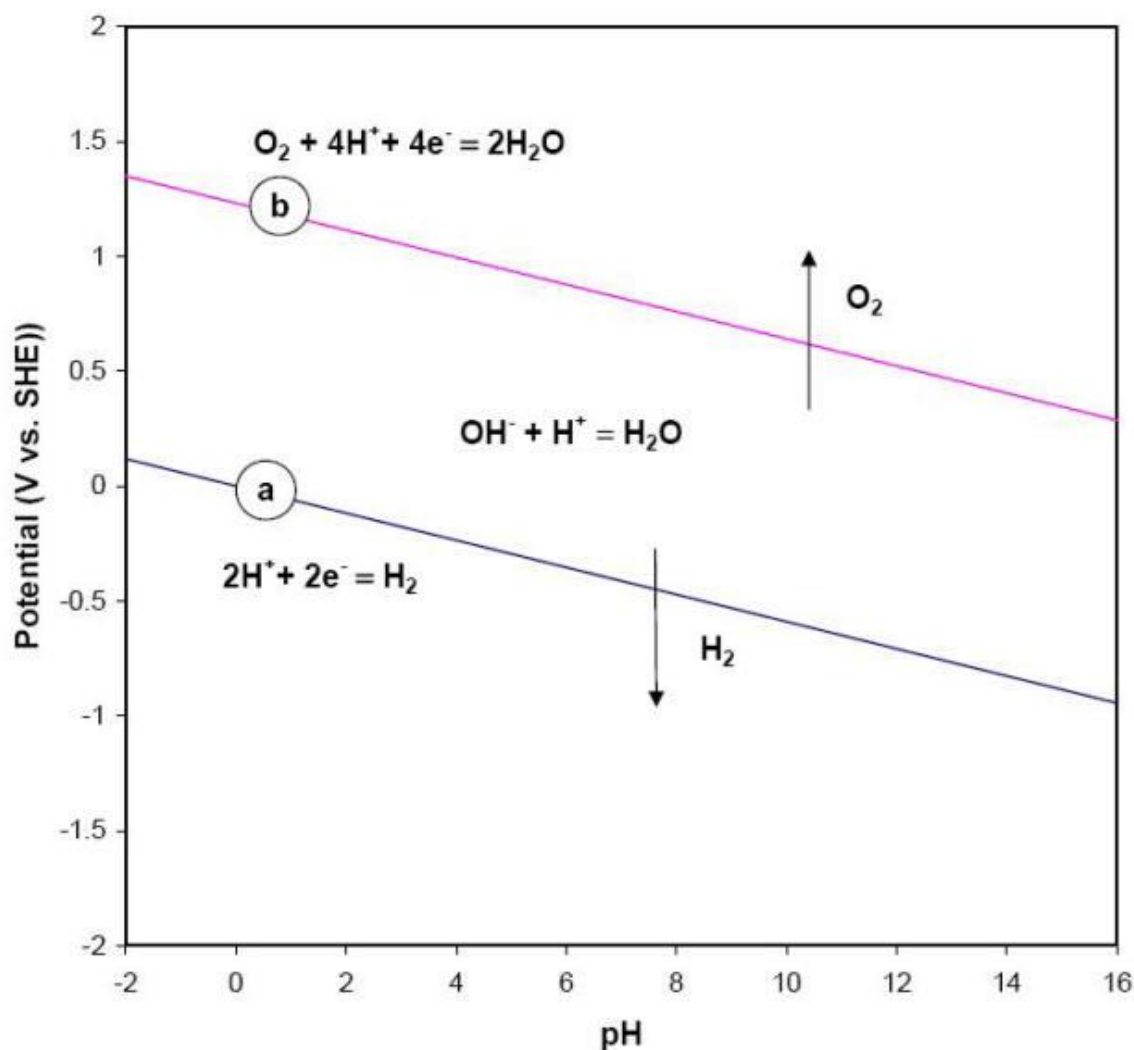
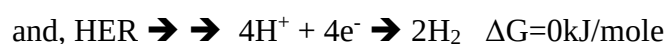


Figure 1 Water stability diagram¹⁸

Since, we are talking thermodynamics, the water stability diagram dictates the applied potential wrt to SHE, for HER and OER. The potential is obviously dependent upon the kinetic parameters such as mechanism and medium in which the reaction is carried out; which is discussed in next part. Here, we shall focus on thermodynamics. So, from thermodynamic standpoint, HER will start at 0V at pH 0 because,

$$\Delta G = -nF\Delta E$$



which translates to $\Delta E = 0 \text{ V}$.

As the pH of the solution will increase, the Nernst equation will govern the applied potential value by using following equation.

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - (0.0592/n)\text{Log}Q$$

Similar thermodynamic pathway happens for CO₂ which has a stability diagram as shown in Figure 2,

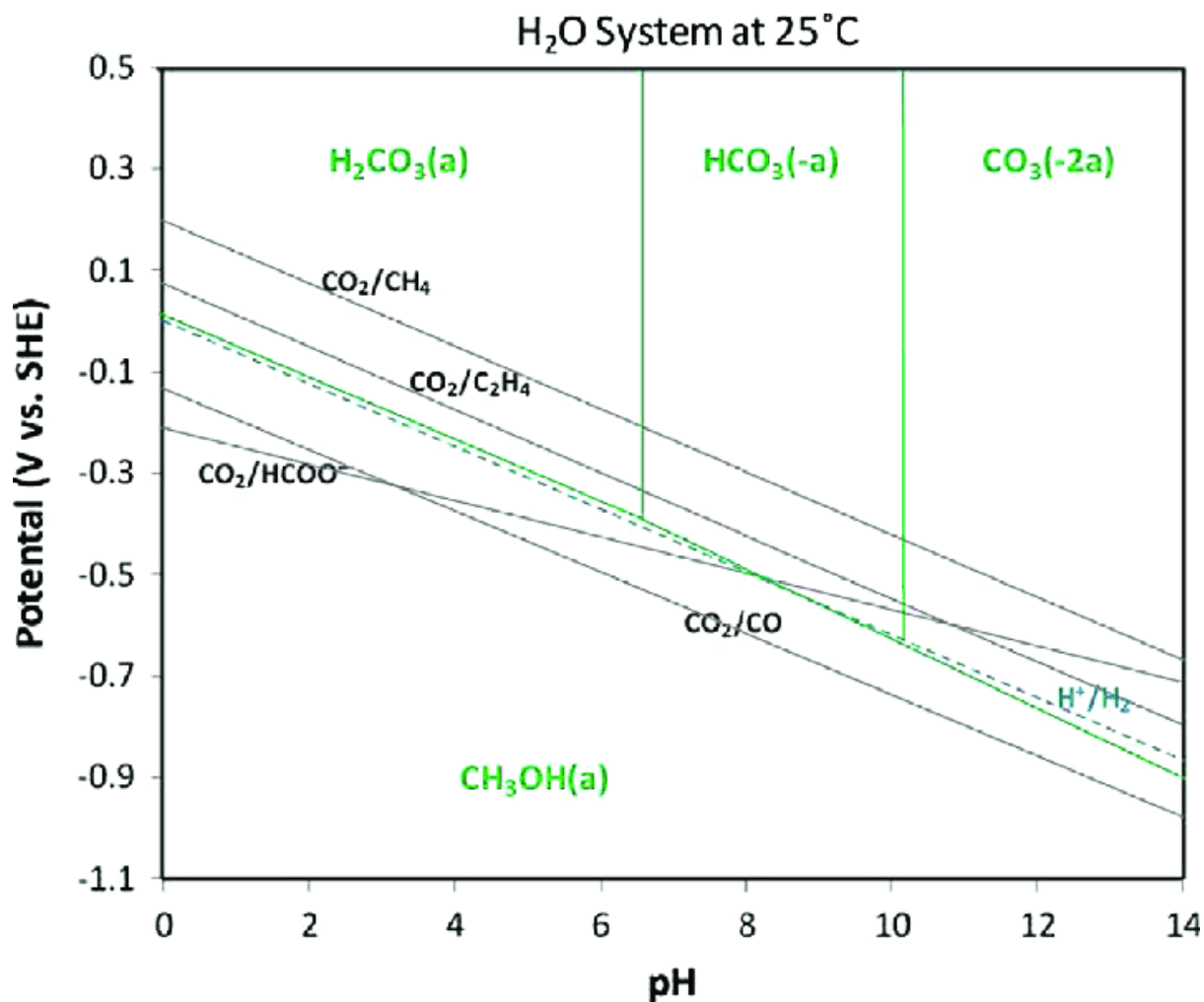


Figure 2 CO₂ stability diagram¹⁹

The lines for CO₂ reduction are governed by the chemical equations in the following Table 1. Again, the thermodynamic values are dependent upon the pathway.

Table 1 Standard potentials for CO₂ reduction reactions²⁰.

Reaction	<i>E</i> (V) vs. SHE
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	-0.41
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH}$	-0.61
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$	-0.53
$\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{C} + 2\text{H}_2\text{O}$	-0.20
$\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{HCHO} + \text{H}_2\text{O}$	-0.48
$\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	-0.38
$\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	-0.24

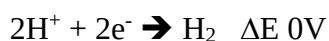
Now that it is established, to reduce these molecules; external energy will be required, we can look into kinetics of the reduction processes.

1.3 Kinetics of HER and CO₂ reduction

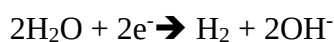
The kinetics deals with the mechanism by which reduction process takes place, so the energies required for the non-spontaneous reduction process may require a little more or large amounts of extra energies compare to the thermodynamic values to reach a certain rate of reaction, depending on interaction of reduction species with the surface over which the reaction is being carried out.

To understand this, let's consider an example of electrochemical reduction of hydronium ion and water molecule on a somewhat excellent electrode.

Hydronium ion requires 0V wrt Hydrogen reference electrode at pH=0.



We will need to increase the electrode's energy by electrical equivalent of -237kJ/mol and this reaction will occur. In basic environment, the activity of hydrogen is minimal and water molecule will reduce instead of hydronium ion. Thermodynamically the reaction will happen at -0.82V wrt Hydrogen reference electrode.



Chapter 1- Introduction

It is evident that energies required for the reduction process is dependent on the mechanism by which reduction takes place.

Now let us consider a case for reduction of same species (hydronium ion) on different surfaces. Consider a case for Pt and Cu. On Pt, the rate of reaction at thermodynamic potential is about 1mA/cm^2 while that of Cu; is about 0.001mA/cm^2 . By considering these examples, we can establish that extra reduction energies (other than thermodynamic ones) are dependent on the surface being utilized for the reaction and the path which is adopted.

Now let's divert our attention to why there is a difference in the rate of reaction for hydronium ion reduction on different surfaces, in this case, let's put our attention to Pt and Cu. To understand the difference, the key descriptor is free energy of adsorption which is almost zero kJ/mol for Pt and has a positive value for Cu. In simpler words, copper binds the intermediate (hydronium ion) more strongly than Pt, thus extra energy required to free the reduced species. Let's assume, this mechanistic description is true in almost all cases, then we can work on calculations for free energy of adsorption of hydrogen intermediate on different surfaces. First, we shall understand the experimental way to calculate the ΔG_{ads} and then we shall discuss the theoretical way being utilised.

For simplicity, let's assume hydronium ion is represented by H^+ and adsorbed specie is represented by H^{+*} , the equation for the adsorption process can be represented by,



Equilibrium constant for the process can be given by,

$$K = \frac{[\text{H}^{+*}]}{[\text{H}^+]}$$

Also, if θ is coverage, and reactant coverage follows Langmuir adsorption isotherm model, then

$$K = \frac{\theta}{(1+\theta)}$$

Using Nernst equation,

$$K = e^{\frac{-\Delta G_{\text{ads}}}{k_B T}}$$

To obtain θ , one should know the total number of active sites available for reaction and the extent to which the sites are utilised during the reduction process. To experimentally determine the coverage, the catalyst is scanned across underpotential region where hydronium ions gets adsorbed, the area under the CV curve in that region gives the total number of sites involve in adoption process. To get the total number of active sites, one needs to know total number of surface atoms available for the reaction.

Theoretically, DFT is used extensively to calculate the intermediates free energy of adsorption on different surfaces, the DFT calculations are based on the following equation²¹,

$$\Delta G_{H^*} = \Delta E_H + \Delta E_{ZPE} + T\Delta S_H$$

Where ΔE_H is Hydrogen chemisorption energy, ΔE_{ZPE} is difference between zero-point energy of adsorbate and its gas phase while ΔS_H is the entropy of hydrogen in gas phase under standard conditions.

Same principles can be extended for CO₂ reduction in electrochemical environment but in this case, there is a wide variety of products are possible such as but not limited to CO, CH₄, C₂H₆, formic acid etc. The distribution of products varies with the change in surface chemical and morphological makeup.

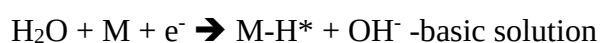
By the discussion so far, we can conclude that if we change the surface over which reduction reaction is taking place; the rate of reaction may change i.e. efficiency of the process may change.

1.4 Mechanism of HER

HER consists of several steps depending on the environment and conditions in which the reactions is carried out. Following lines summarise the understanding of mechanism for HER.

There are two distinct steps in which HER happens, adsorption of intermediates and desorption of intermediates to final product.

1. Adsorption- Volmer



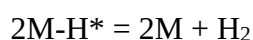
2. Desorption

Desorption process is classified in two ways, electrochemical (Heyrovsky) and chemical (Tafel)

a. Heyrovsky- Desorption



b. Tafel- Desorption



Where, X^* represents the intermediate bound to atomic site for electron transfer and M represents the metal site.

1.5 Mechanism of CO₂R

CO₂ reduction is again similar to HER and happens in multistep. The complexity arises due to the possibility to several different production formation that is not the case for HER. The key descriptor is the formation of CO₂-* and COOH* radical as an intermediate. It is understood that CO₂-* is the radical formed in the aqueous reduction of CO₂ on Cu, Ag and Au while COOH* is formed in non-aqueous environment.

The pathways adopted during CO₂ reduction are classified in three groups as follows, Figure 3. There are two main steps in CO₂R which govern the overall kinetics, 1. Formation of CO₂-* radical and 2. protonation of CO₂-. The final product formation is dependent on the rate limiting steps. If protonation is the rate limiting step CO is favoured and if CO₂-* formation is

the rate limiting steps, we shall have compounds with hydrogen in it such as but not limited to formic acid, methanol, methane etc.

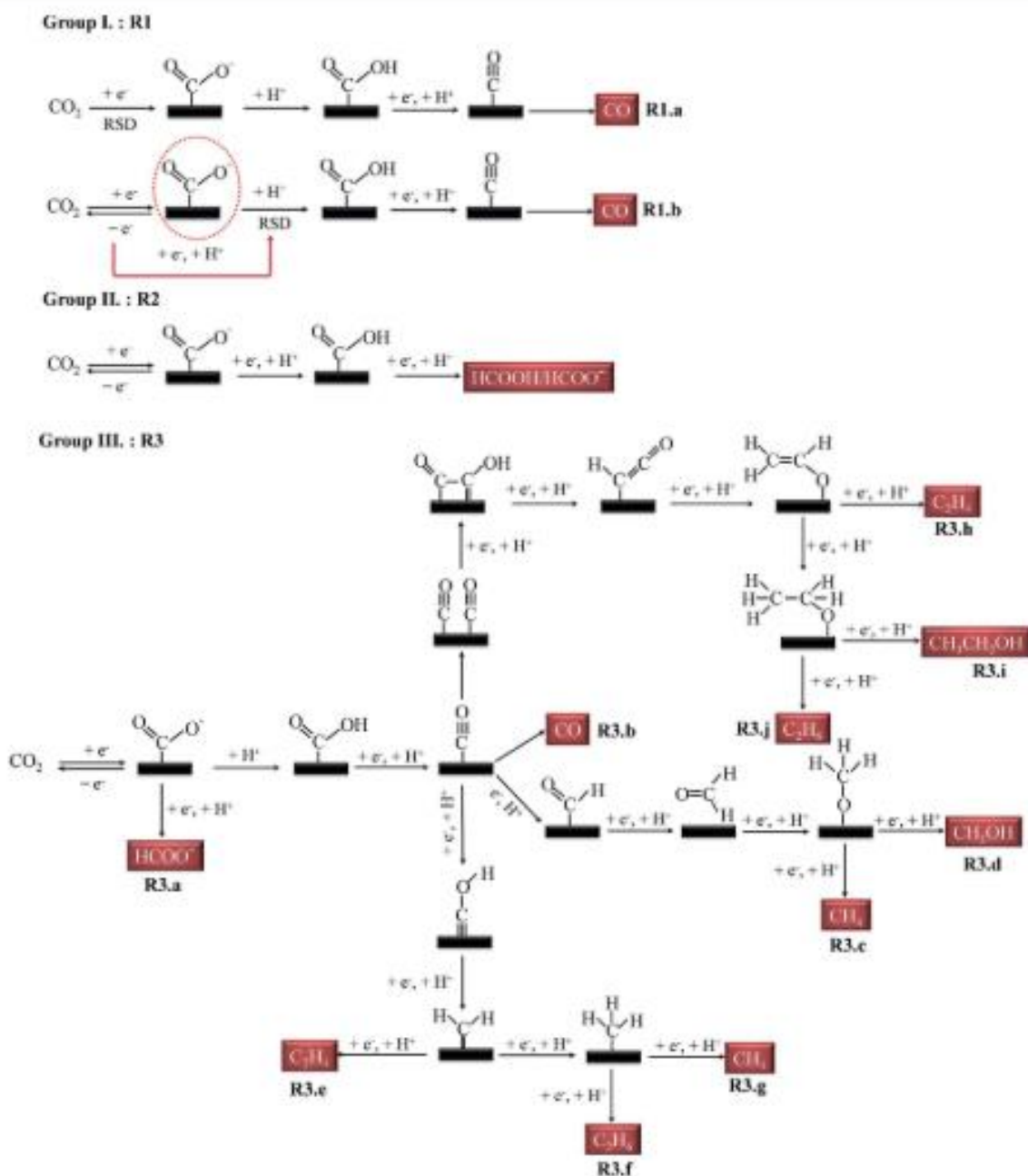


Figure 3 Various CO₂ reduction mechanisms¹

1.6 Theory and mechanism of Plasma Catalysis

1.6.1 What is Plasma

As we know it, plasma is the fourth state of matter. It is mainly constituted by charged particles and photons. In theory any gas can become plasma if provided with enough energy to take out electrons from outer shells to make ions. Plasmas usually contains, charged species both positive and negative, neutral molecules, atoms, their excited states and energy particles such as photons. Overall, plasma is a net neutral state.

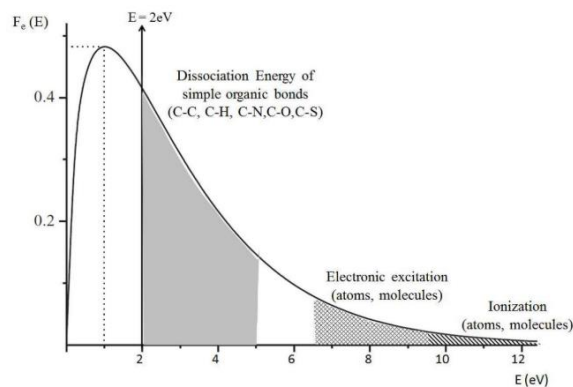
In a typical process, plasmas are created by using high voltages to excite the particles of gas to such an extent where it destabilises and charged particle such as positive ions and negative electrons coexist. The local temperature of particles such as electrons may range from room temperature to thousands of kelvins. There are two classes of plasmas, high temperature plasma with electronic temperature of less than 10^7K while low temperature plasma are subdivided into two more classes thermal plasma with temperature range of less than 10^4K and non-thermal plasma with a temperature less than 10^5K , the difference between thermal and non-thermal plasma is the energy of electrons is much higher than heavier particles in case of non-thermal plasma.

1.6.2 Uses

Plasma technology is quite established and advanced. Main applications exist in surface modification industry such as reduction of oxides and scales in steel industry. Thin films of metal and different compounds are also deposited by using plasma technology. Extensive research is in progress in using plasma technology to deal with pollutants particle such sulphur oxide, nitrogen oxide and CO_2 .

1.6.3 How Plasmas work

Since the plasma contains all sorts of particles with various kinds of energies, the chemistry will be complicated. To better understand, lets simplify the system and consider the electrons as the key source for reaction initiators. In a typical plasma, energy of electrons varies and follows a Boltzmann distribution function as indicated in Electron energy variation in plasma²².

Figure 4 Electron energy variation in plasma²²

The bond strength of organic compounds range from 2-5ev per molecule and a typical plasma system has enough particles to carry out the desired reactions. The reactions can be a result of elastic and inelastic collisions between electrons and heavy particles (ions, atoms and other constituents in plasma).

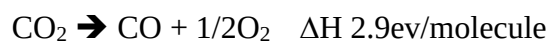
Following equations are the possible reactions of electrons in plasma with molecule of interest.

Table 2 Various different types of reactions possible in plasma reduction

Excitation	$e + M \rightarrow M^* + e$
Dissociation	$e + M_2 \rightarrow 2M + e$
Attachment	$e + M \rightarrow M^-$
Dissociation attachment	$e + M_2 \rightarrow M^- + M$
Ionisation	$e + M \rightarrow M^+ + 2e$
Dissociation ionisation	$e + M_2 \rightarrow M^+ + M^- + e$
Recombination	$e + M_2^+ \rightarrow M_2$
Decomposition	$e + MN \rightarrow M + N + e$

1.7 CO₂ reduction chemistry-Plasma Technology

The reduction of CO₂ is a non-spontaneous process. As a first step, the CO₂ molecule may dissociate into CO and O radical, this O radical can then interact with other CO₂ molecules and radicals present in the catalyst reaction chamber. Overall, the equation will be,



To determine the efficiency of CO₂ dissociation, following formula is used,

$$\eta = \frac{\chi \Delta H}{SEI}$$

The overall conversion efficiency of CO₂ is calculated by using following equation,

$$\chi = \frac{\% \text{CO}_2 \text{ converted}}{\% \text{CO}_2 \text{ in feed}}$$

Specific energy input can be calculated by using following equation.

$$SEI = \frac{P}{F}$$

Where, P = power, F = flow rate

To understand the plasma reduction, we need to have a look on thermal reduction process. The molecule of interest say, H₂O will interact with the surface and adsorbs on the surface by making an intermediate. This intermediate may interact with other intermediates and incoming molecules and make the product; in this case hydrogen. Again, we are supposed to provide external energy equivalent to Gibbs free energy of up to -237kJ/mole, the rate of reaction will be governed by the value of adsorption free energy for the surface and intermediate's interaction. If the magnitude of the value is large more energy will be required to free the adsorbed intermediate in form of final product and if the magnitude is low, small amount of extra energy will be required to carry out the reaction. In case of plasma, molecules vibrate at such a high frequency that it destabilises the molecule and molecule may form high energy radicals which may end up in interacting with other molecules, radicals and adsorb species; to generate products. In case of plasma, high temperature may or may not be used, since radicals usually have such a high energy that they may end up generating the product, but efficiency of such processes is directly proportional to plasma intensity.

In the following section, we shall discuss the surfaces being utilised for HER and CO₂ reduction in electrocatalysis and CO₂ reduction in plasma catalysis.

1.8 Materials for reduction processes- Electrocatalysis and Plasma catalysis

Before going in details, of what materials are presently being explored for the reduction of water and CO₂ molecule, through the techniques of interest, it would be a good idea to see what factors govern the selection of material for the reduction processes of these molecules.

Effective materials selection for the water splitting and CO₂ reduction depends on many factors, following text deals with material selection for electrolytic reactions involving water as solvent. There are two classes of materials that can do the job of water splitting into HER, OER and CO₂ reduction; metals and semiconductors. Generally, metals have higher electrical conductivity than semiconductors thus are suitable kinetically. But metals are in metastable state and will eventually corrode. On the other hand semiconductors, although are stable but limited in case of environment in which they can work and also limited kinetically as compared to metals (not always the case; also superiority of the surface for the reduction process depends on intermediate's binding energy i.e. not too strong and nor too weak- Sabatier's principle). These materials can be classified as,

- Metals
- Metal combinations (alloys)
- Semiconductors- metal oxides, metal sulphides, metal nitrides and doped semiconductors and others.

Main limitation of the reaction media are as follows,

- Acidic, basic, neutral (in other words; media with highest hydrogen activity, lowest hydrogen activity, along with solubility limit of CO₂)
- Concentrated, dilute solutions

1.9 Metals, alloys and other materials for HER and CO₂ electrocatalysis

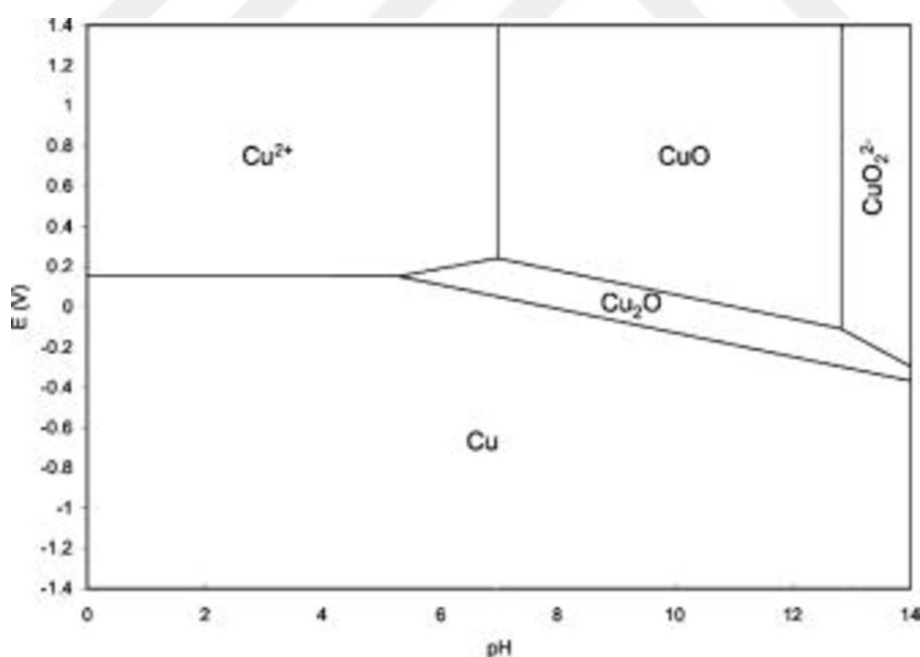
Thermodynamically water can be split into hydrogen at 0V pH (0). Thus, hydrogen evolution will be studied preferably in acidic medium.

The metals of d block elements can be considered for hydrogen evolution reactions. There are two classes in which d block metals can be divided. One with positive reduction potential then hydrogen and other negative reduction potential with hydrogen. Those metals with positive reduction potential are suitable for HER in acidic media. But mostly those metals are noble and expensive. The reduction potential map for d block is shown in following Table 3.

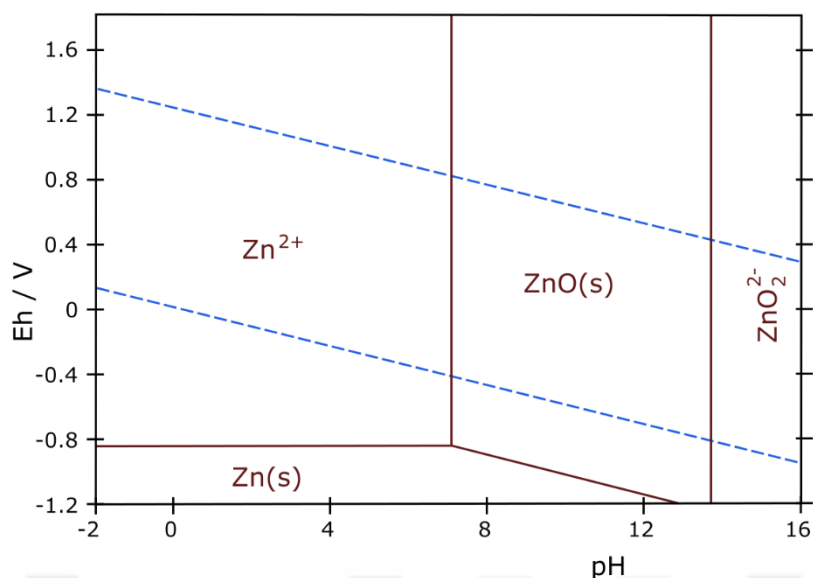
Table 3 Standard reduction potential in volts of d-block elements

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	-1.62	-1.19	-0.91	-1.18	-0.44	-0.28	-0.23	0.34	-0.76
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
	-1.45	-1.09	-0.2				0.95	0.8	-0.4
Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
			0.1			1.15	1.18	1.5	0.85

Copper is the only non-expansive metal available for HER in acidic media. Other metals with negative reduction potential will eventually dissolve in acidic media and replace Hydrogen in solution since their $E_m < E_{H_2}$. Other metals with negative reduction potentials, can be used in basic media for HER reaction, since in basic medium hydrogen activity is very low (up to $10^{-14}M$). Metal application for HER and OER can be studied by using Pourbaix diagrams. The use of Pourbaix diagram can be understood by considering example of Cu and Zn. Figure 5 shows the Pourbaix diagram of Cu and Zn.



(a)



(b)

Figure 5 Pourbaix diagram (a) Copper²³ (b) Zinc²⁴

For reaction involving solid copper, if we consider the oxidation, the Cu/Cu^{2+} boundary lies on the positive side of potential axis which means that the Cu/Cu^{2+} reaction is a non-spontaneous reaction. Thus, Copper can be used for HER in acidic medium below 0.15V under standard conditions. For Zn, the Zn/Zn^{2+} boundary lies on the negative value of potential axis which illustrates that the reaction will spontaneous i.e. in acidic environment; Zn electrode will immediately dissolve. Thus, in short, Pourbaix diagrams are a powerful tool to predict the usability of an electrode in electrochemical environment.

Similar principles can be applied for metal selection for CO_2 reduction using metals in aqueous media. For materials other than metals and alloys such as oxides, sulphides etc, the main limiting criteria is materials' suitability in medium such as if the materials is compatible in basic or acidic medium. For example, basic oxides cannot be used in acidic environment and acidic oxides cannot be used in basic environment. Amphoteric oxides can be used in either, but their efficiency i.e. rate of reaction at equilibrium thermodynamic potential of reduction reaction should be larger.

For plasma applications, the main requirement is high surface area materials, but that material should also be compatible with plasma environment. Carbon based substances cannot be used since plasma interact with carbon based functional groups and free them as gases. In literature mostly, oxides are used with loaded metals on them.

1.9.1 ECO2R materials and state of research

For electrochemical CO₂ reduction, the materials are divided into various classes. Here we present the following materials but classes of materials are just not limited to the ones, mentioned here.

- a. Metallic materials (noble metals-Pt, Au, Ag, non-noble metals-Cu)
- b. Alloys
- c. Carbon supported metal catalysts
- d. Metal free catalysts
- e. Transition metal sulphides

In the following texts, we shall present details of research on the use metallic elements along with copper and its modifications for ECO2R.

Au and Ag are extensively used to study ECO2R, especially to understand the mechanistic aspects. Both Au and Ag in bulk form have higher Tafel slopes which is an indication for the formation CO₂^{-*} which subsequently reduce to produce CO. However their modifications (especially Ag), to nanostructure such as nanoparticles, nanowires and films show a reduction in Tafel slope value from 130mV/dec to 50-60mV/dec²⁵⁻²⁸ which indicates that there is a change in CO2R mechanism and it is concluded that COOH* instead CO₂^{-*} radical is formed which subsequently reduce to CO.

In ECO2R domain, it is a well known fact that copper produces various different kinds of hydrocarbons and alcohols²⁹⁻³¹ but overpotentials are quite high with a range of upto -1V. One study showed the formation of CO and HCOOH on oxide derived copper (ODCu) with an overpotential of upto -0.5V vs RHE³². In the study, it is concluded that CO binds to the active sites of the catalyst more strongly and thus favours the formation of further reduced products such as HCOOH. People have worked on other techniques to modify the surface of the copper electrode, namely ex-situ and in-situ techniques are being utilised to modify the surface. In one study³³, Copper surface is treated with a combination of O₂ and CO₂ plasma to form a Cu₂O surface and it is concluded that Cu⁺ plays a pivotal role in producing hydrocarbons such as ethane and ethene and other multi-carbon species. In another study³⁴, a mixture of O₂ and CO₂ is used to suppress the H₂ formation at higher pH along with a formation of C₂H₄ up to 30% in a 10%O₂/CO₂ mixture.

In another study³⁵, one group studied the effects of length of metallic Cu nanowires on the formation of products, they observed that higher hydrocarbons are formed as the length of nanowires is increased. They concluded that increasing the length of nanowires giving carbon a chance to dimerize.

A clear cut mechanistic approach in formation of reduced species still missing. Further studies can be carried out on different morphologies of Cu nanowires and the effect of nanowires density can also be studied, on how they effect the reduced product formation.

1.10 Reports on HER catalysts- Electrocatalysis

Following Table 4 illustrates the catalysts developed in last three years for HER, benchmark is set as Pt.

Table 4 List of HER catalysts since 2017

Catalyst	Overpotential @5mA/cm ²	Tafel slope (mV/dec)	Year	Ref.
Nickel copper nitride	580mV @ 10mA/cm ²	67	2019	³⁶
Pd-CuPc/MOF	0.63mA/cm ² @150mV	191	2019	³⁷
CoMnZnPd/C	15mA/cm ² 50mV	@ 90	2018	³⁸
Ni-CeO ₂ Gd	3mA/cm ² 200mV	@ 102	2017	³⁹
FeCuNi	200mV	120	2018	⁴⁰
NiP on Ni foam	100mV @ 10mA/cm ²	@ 92	2019	⁴¹
Cu coating deposited on Ni foam	93mV @10mA/cm ²	175	2019	⁴²
Ni60%Co	200mV	127	2018	⁴³
NiCoS-150	232mV 10mA/cm ²	80	2019	⁴⁴

Ni foam 3	150mV	160	2019	⁴⁵
FeP	200mV	64	2018	⁴⁶
Cu ₂ S	300mV	100	2019	⁴⁷
NiCoSn	76mV	63	2019	⁴⁸
	10mA/cm ²			
Cu/Cu ₂ O/Nickel (5 min)	400mV	100	2019	⁴⁹
	10mAcm ⁻²			
Bi-NP	140mV	110	2018	⁵⁰
Cu/Al ₇ Cu ₄ Ni@Cu ₄ Ni	@10mA/cm ²			
Cu-Ni-P-MoS ₂	500mV	167	2018	⁵¹
Pt-VGNSAs/CC	60mV	30	2017	⁵²
	@10mA/cm ²			

1.11 Reports on CO₂ reduction catalysts-Electrocatalysis

Table 5 List of catalysts for CO₂ electroreduction since 2016

Catalyst	Year	Reference
Rough copper surfaces	2016	⁵³
Copper nanocrystals	2016	³²
Atomic cobalt layer	2016	⁵⁴
Molecular copper catalyst	2016	⁵⁵
Copper 100 surface	2016	³⁴
Porous hollow fibre copper	2016	⁵⁶
Pd-Au alloys	2016	⁵⁷
Pt(111)	2016	⁵⁸
Biofunctionalized conductive polymers	2017	⁵⁹
Various metal electrodes	2017	⁶⁰
Au surfaces	2017	⁶¹
Ag-Zn alloy	2017	⁶²
Stable Ag catalyst	2018	⁶³
Zn based foams	2018	⁶⁴

MOF mediated Cu	2018	65
Laser prepared Cu-Zn alloy	2018	66
TiO ₂ / MoS ₂	2018	67
MOF mediated N ₂ doped carbon	2018	68
Copper porphyrin MOF	2018	69

1.12 Reports on CO₂ reduction catalysts-Plasma catalysis

Table 6 List of catalyst for CO₂ plasma reduction, since 2016

Catalyst	Year	Reference
CeO ₂ /ZrO ₂ - Ni	2016	70
CeO ₂ /ZrO ₂ - Ni	2017	71
Ni-Ce-Al ₂ O ₃	2017	72
Ni zeolites	2017	73
Ni USY	2017	74
Ni Al ₂ O ₃	2017	75
Ni Al ₂ O ₃	2017	76
ZrO	2018	77
Ni Al ₂ O ₃	2018	78
Ni Al ₂ O ₃	2019	79

From the analysis of reports, following conclusions can be made.

- HER- Electrocatalysis: This is the most developed field and the work in this field is way ahead then CO₂ reduction. Pt is set as the benchmark in most studies. The objective is set to search inexpensive alternative of Pt. DFT studies showed MoS would be a good candidate and experimental results confirmed it. For our study, the main is to utilise earth abundant materials, so the literature was studied with a view of reviewing the literature on earth abundant materials for HER. The materials that showed excellent performance with earth abundant elements include elements such as, Cu, Ni, Mo, Co, S, N, P, OH-.
- CO₂ reduction -Electrocatalysis: Much work is done on metallic elements to understand the mechanism for CO₂ reduction. The complexity in CO₂ reduction arises due to

variation in product distribution due to the rate limiting steps of formation of either CO_2^* - (or COOH^*) or the protonation of the formed radicals. Common metals that are studied extensively, Cu, Pd, Au, Ag, Pt, Zn etc.

- CO_2 reduction- Plasma: Mostly studies are done on metals loaded on alumina and other oxide supports, the goal is either hydrogenating CO_2 with H_2 or H_2O , also methane reforming is quite common. The later makes sense in case of industrial processes. On Cu, Au and Ag, the formation COOH^* is the main step and in subsequent steps, based on rate limitations; different kinds of products form.

After thoroughly analysing the literature, it was observed that reduction performance is obviously a function of chemical makeup of the material, the subtle or hidden part was the dependence of reduction performance parameter on the morphology of the substance. Taking this observation into account, studies were performed bulk copper sheets and their modification to metallic nanowires using hydrogen plasma reduction, this study constitutes the first of its kind. Metallic nanowires were used in the study of HER and CO_2 reduction through electrolysis. Plasma CO_2 reduction studies were carried out on Cu and Ni oxides loaded on silica and alumina, in total more than 18 samples were tested for CO_2 reduction using H_2 plasma and the products were analysed through GC. Overall goal is to make energy conversion processes more efficient using earth abundant resources, for this purpose, for the first time metallic Cu nanowires are synthesised using dielectric barrier discharge (DBD) process.

Chapter 2- Electrochemical HER using metallic Cu nanowires

2.1 Introduction

Due to depleting carbon fuel sources and excess demand of energy, researchers are searching for efficient and alternative ways to develop energy. There are many research areas in this domain and one very effective way is turning to hydrogen economy, which is the future technology. Already much work is done on fuel cell technology which takes up hydrogen as a fuel and converts to electrical energy at an efficiency of up to 90%. So, the requirement is a cheap hydrogen source in place of current carbon-based fuels.

Commercial hydrogen is mainly produced by water gas shift reaction⁸⁰ and steam reforming⁸⁰⁻⁸², a small proportion is produced through electrolysis (up to 4%). Researchers are trying to find ways to increase the proportion of electrolytic hydrogen production by using suitable catalyst. So far Platinum's performance is good for HER, but it is expensive. There are two ways to find a suitable catalyst for HER, one is trying to work experimentally on different combinations of elements to find a catalyst as good as Pt, this way seems very long and tedious as different combinations of elements from periodic table will be a very big number. The other way is to work on the computational side to predict which combinations will work and here comes the DFT. A lot of work has been done on DFT in last two decades, which efficiently predicts the performance of elemental metals²¹ and other simple substances such as metal alloys^{83,84} and carbon based systems^{85,86} for HER.

One flaw with DFT is its inherent simplicity to calculate the binding energies of intermediate which mostly assumes a flat surface which is seldom a case in practical engineering applications. For instance, for copper which we have studied here in detail, it is considered as a bad catalyst for HER since it requires an overpotential of 400mV to reach 10mA/cm² ($i_0=10^{-5}$ A/cm²) but modification of copper morphology to nanowires reduced the same overpotential to 210mV, this overpotential change which strongly relies on the morphology cannot be predicted by DFT which raises flaws in the calculations. In simpler words, DFT studies are predicting free energy of adsorption for hydrogen intermediate on bulk surfaces and the calculations are made by considering various simple assumptions, but if the morphology of the substance is changed, its catalytic performance parameters also change.

DFT can only be used to identify the intermediate binding energies for bulk materials as binding energies can be changed by morphology. As far as the bulk material properties are

concerned, the best success story of DFT is its prediction of MoS as a suitable catalyst for HER⁸⁷.

Although Mo is very inexpensive as compare to platinum (12USD: 12000 USD per pound), researchers are trying to work on other earth abundant sources and copper is one of them with a price tag of 2USD per pound.

A lot of work has been done on copper and its modification to oxides, sulphides, phosphides and other forms^{36,88–98} but HER on metallic copper nanowires synthesized by plasma reduction is never reported. We have achieved up to 210mV overpotential for a 10mA/cm² current density.

2.2 Experimental

There are two ways to make copper nanowires from starting feedstock, one; coating FTOs with metallic copper using commercial Cu bath or use thin sheets of Cu. Thin sheets of Cu are utilised to make Cu nanowires. Before starting the experiments, the chemical composition of Cu sheets was determined through XRF. In all experiments, polished copper sheets are used. The sheets are cut in 2x1cm² coupons and first are ground with coarse grinding paper and then polished using fine papers. After the samples are polished, they are used in subsequent steps.

To understand the copper behaviour in different electrolytes, cyclic voltammetry is performed using EZstat Pro potentiostat, real hydrogen electrode (RHE) is used as reference electrode from Hydroflex electrode, Germany. All salts used are from Alfa Aesar (noted otherwise). To perform cyclic voltammetry, two compartment cell is used, in which the compartment are separated using PEM membrane. The system is cleaned before using. Salt solutions with a concentration of 1M are used. In the first stage, CVs are taken in three acidic, two neutral and three basic solutions. Before taking the CVs, open circuit potential is observed to reach stability. Once stable OCP is reached, CVs are started. All CVs are taken at 5mV/sec and cycled through HER to OER region, at least eight cycles are taken in each CV.

After cyclic voltammetry, linear sweep voltammetries (LSVs) are performed in three media i.e. KOH, K₂SO₄, HCl. LSVs are also recorded in the same fashion as the CVs. First the system is given due time to reach stability, once stable OCP is reached, LSVs are recorded from OCP in HER direction.

Once the bulk copper surface is characterised in electrochemical media, in the next stage, metallic nanowires are prepared. For metallic nanowires synthesis, a clean copper surface is

first polished and heated to various temperatures from 400-700°C for 30minutes each. After heat treatment, the surface morphologies of oxide films are evaluated using SEM. Once it is established that at particular temperature and time; oxide nanowires are forming, the sample are prepared for plasma reduction of oxide nanowires to metallic nanowires.

In this scheme, oxide nanowire coupons are set in a the DBD plasma generator and plasma treatment for 60minutes is found to be appropriate time for reduction process. Once the reduction process is done, the samples are analysed using SEM for surface morphology. XRD, Raman spectroscopy and XPS is carried out to further delve into chemical makeup of the material.

2.2.1 Synthesis of Metallic Copper nanowires

Copper sheets with a purity of 99.99% are used. First the sheets are polished using grinding and polishing machine and then cleaned with DI water and organic solvents. The samples are then heat treated in oxidising environment at various temperatures to form nanowires as reported in literature ⁹⁹. The samples are then reduced in hydrogen plasma by indigenously made plasma generator which takes an input of 18V, 5%DC, square wave of 0-10Vpp (15watt). The flow rate of hydrogen is set at about 50sccm and the time interval for the plasma reduction is sixty minutes.

2.3.1 Electrochemical evaluation for HER

The nanowire sheets are tested in neutral environment of K₂SO₄ (0.1M) with a pH of 7 in a typical H-cell for electrochemical experiments. The counter electrode and working electrode are in separate chambers, the reference electrode is placed with working electrode and 1 cm is maintained between reference electrode and working electrode. The hydrogen electrode (RHE) from Gaskatell is used as reference electrode. Before the test, the solution is bubbled with nitrogen gas for 15 minutes at a flow rate of 20sccm for 15minutes to remove any residual oxygen in the system. The setup is then closed using a Teflon lid. The two chambers of the cell are separated by using a proton exchange membrane. During the electrocatalytic measurements the nitrogen gas is continuously bubbled at the top of the solution at 5sccm. For the electrochemical experiments, first magnetic stirring of the solution is carried out for 5 minutes and then open circuit potential is observed until system stabilises, after that a CV is taken and then LSV data is collected. The LSV data is used to determine polarisation curve, exchange current density, Tafel slope and overpotential for 10mA/cm².

2.3 Results and discussions

XRF results of polished copper sheets are indicated in Figure 6, which indicate minor Zn and Ni impurity.

As a first step, to understand the behaviour of copper surface under various media; cyclic voltammetry studies were carried out in various electrolytes by using Real hydrogen electrode(RHE). The results are as shown in Figure 7, the CVs have three distinct regions; Copper oxidation to CuO or Cu^{2+} ions on positive potentials, HER on negative potentials and Cu^{2+} reduction on positive potentials in reverse direction from oxidation. In all condition (Figure 7a-h), Copper oxidises beyond +0.34V, thus beyond this potential catalyst surface will not take part in catalytic reaction (such as OER). For nitric acid, Copper reacts with nitric acid and oxidise to Cu^{2+} ions, the reaction is spontaneous and thus nitric acid can not be used for study of HER on copper. In case of HCl, it is observed that copper oxidises readily and reduce back to the electrode in short applied potential range, it is evident due to the presence of reversible peak. But a similar phenomenon is missing in case of sulfuric acid, which indicates its suitability for HER. Rest of the electrolytes except KCl have similar features to that of H_2SO_4 and thus are suitable for HER.

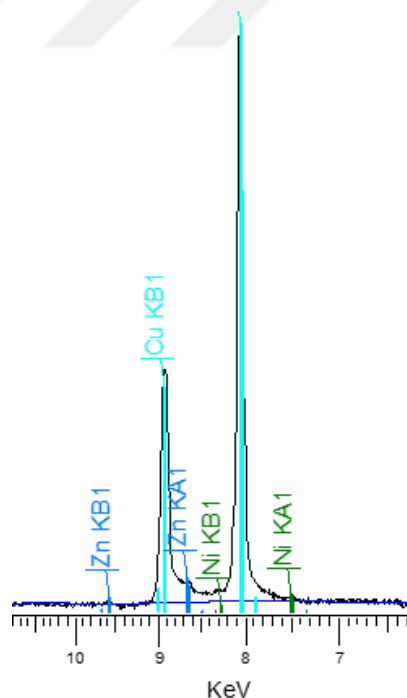
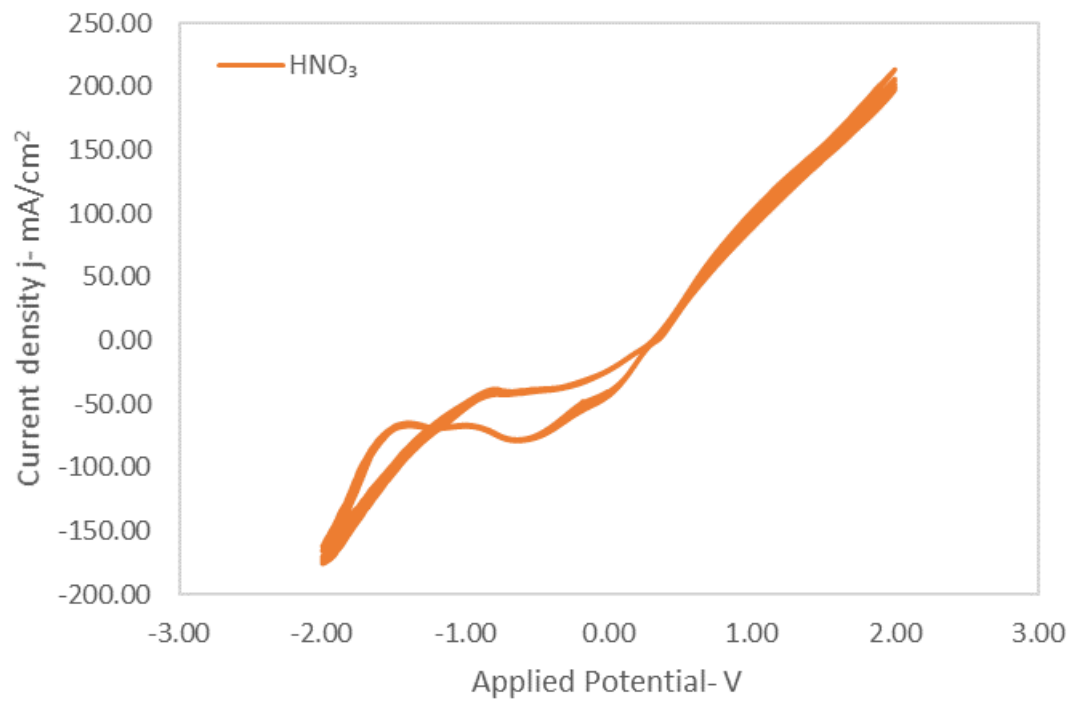
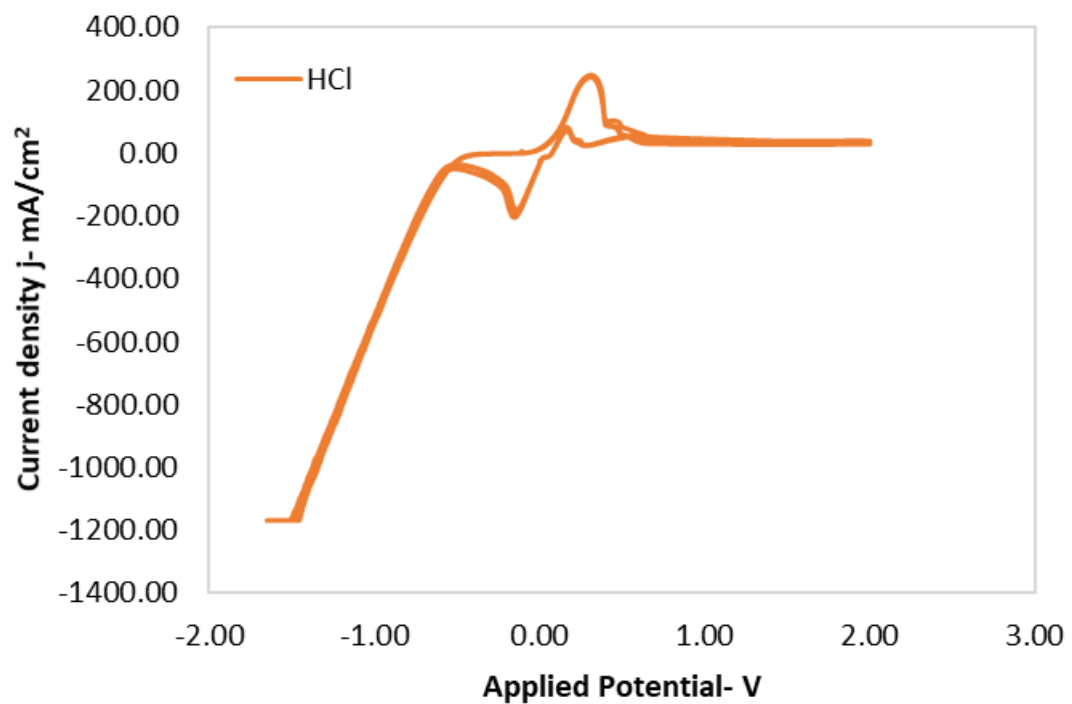


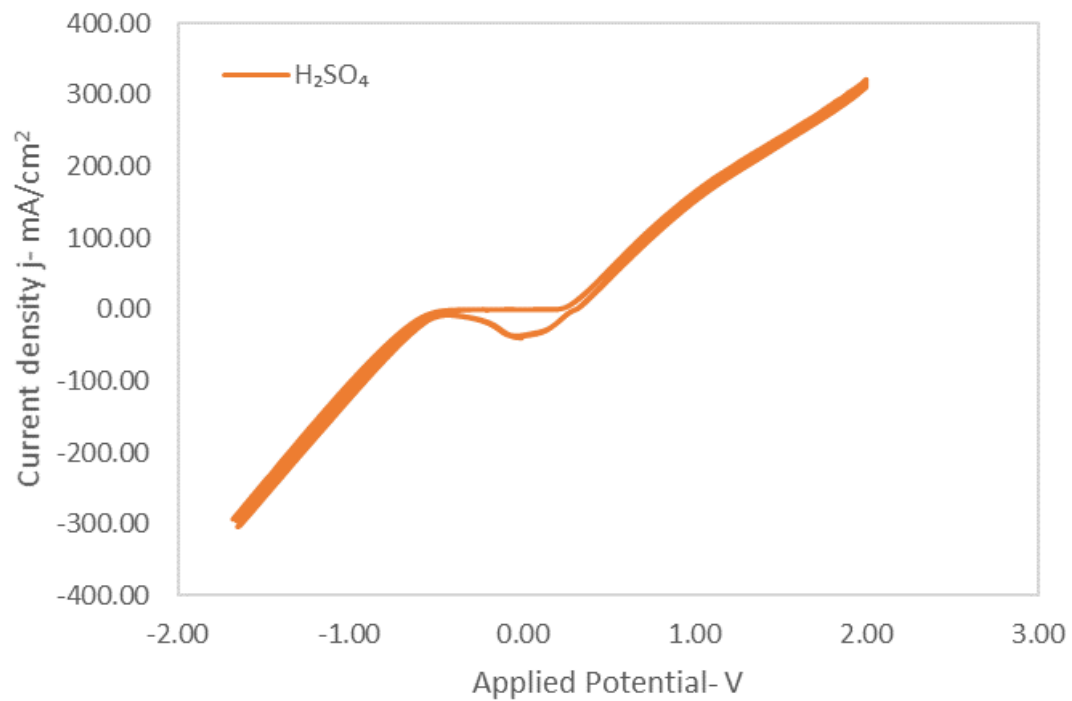
Figure 6 XRF result of copper sheet



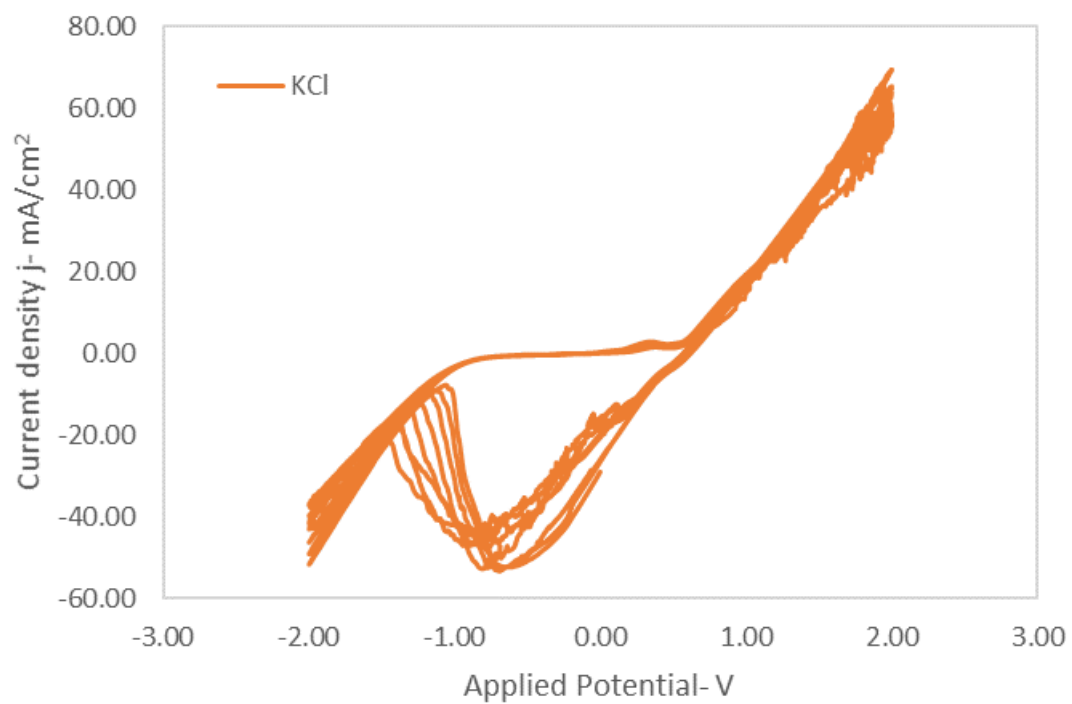
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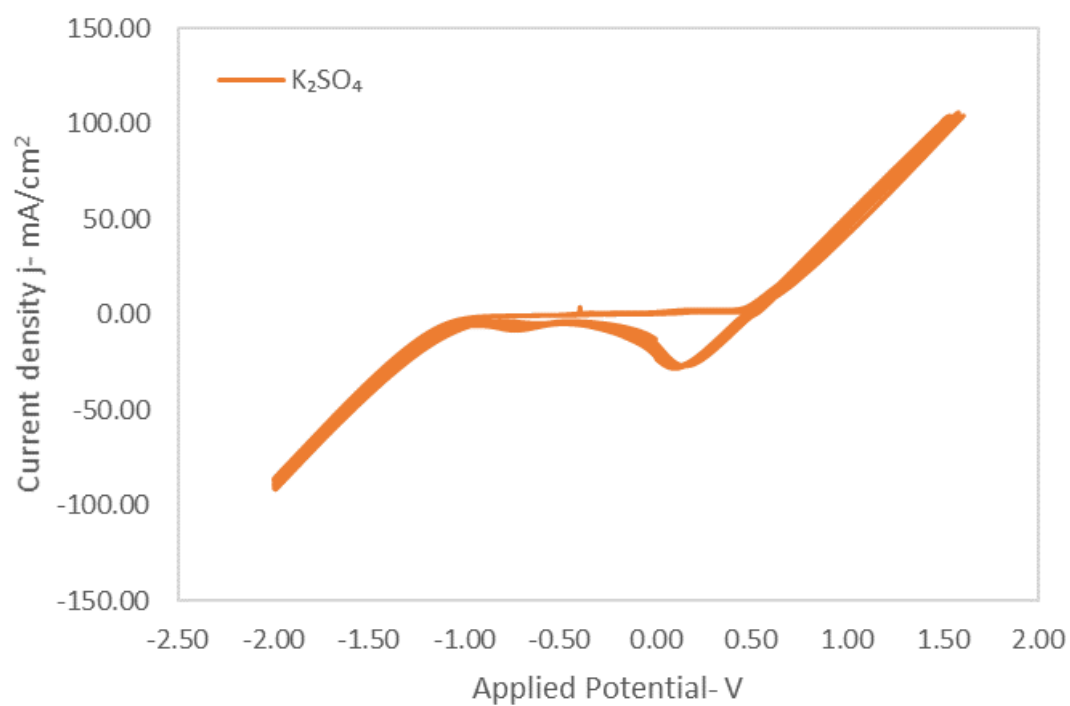
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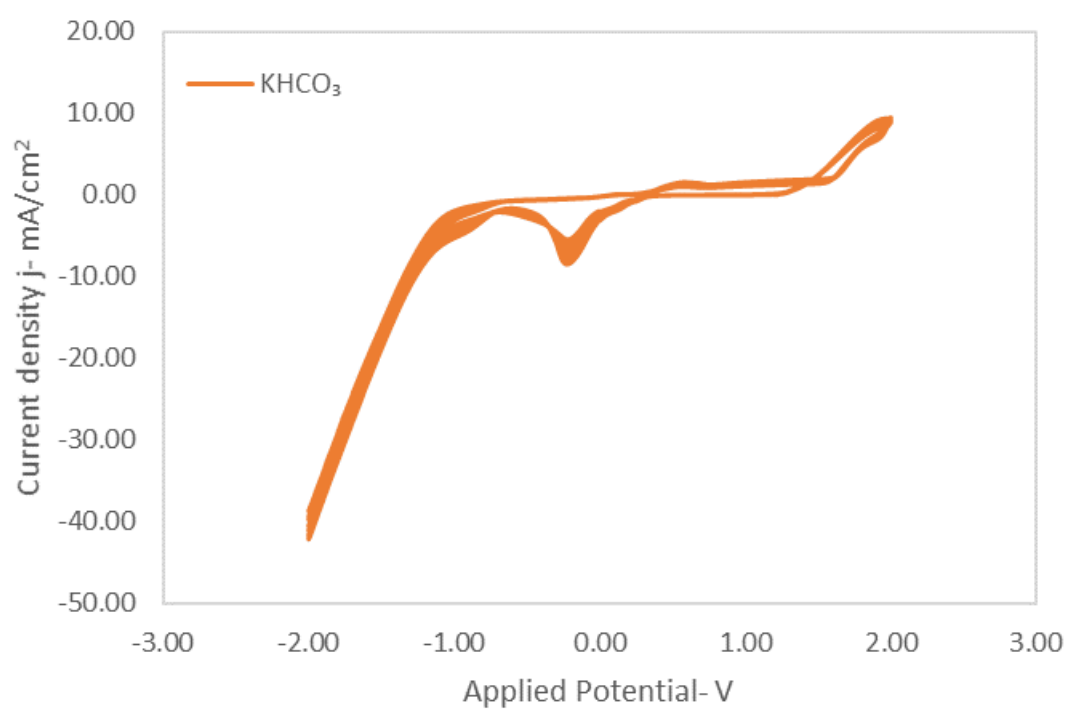
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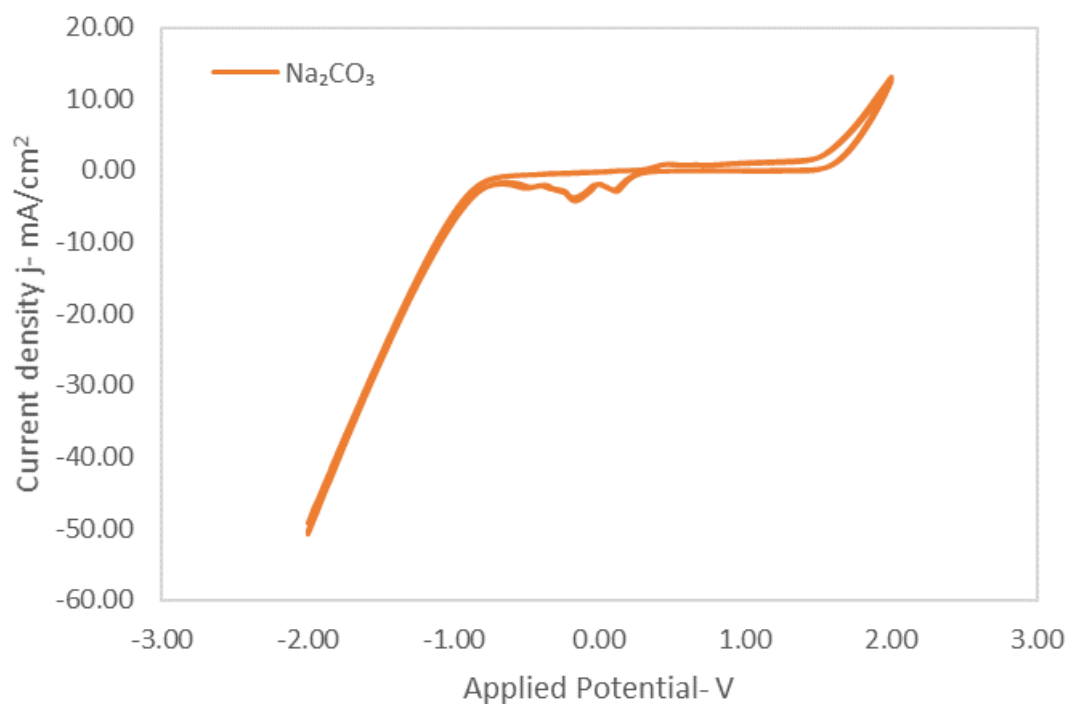
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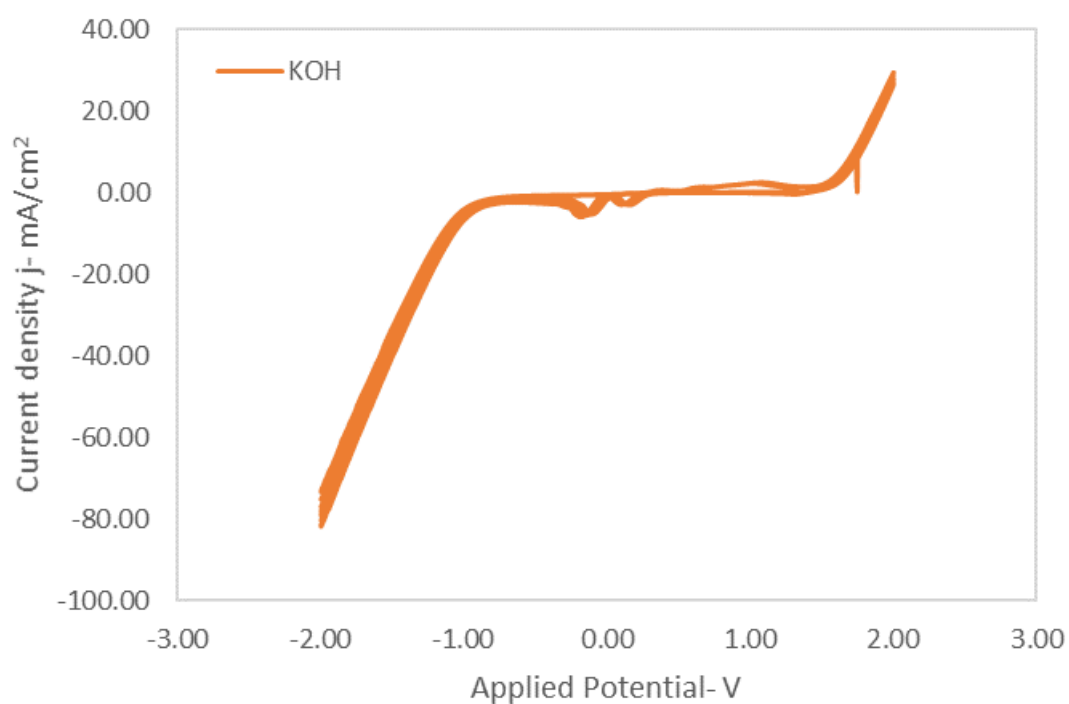
(e)



(f)



(g)



(h)

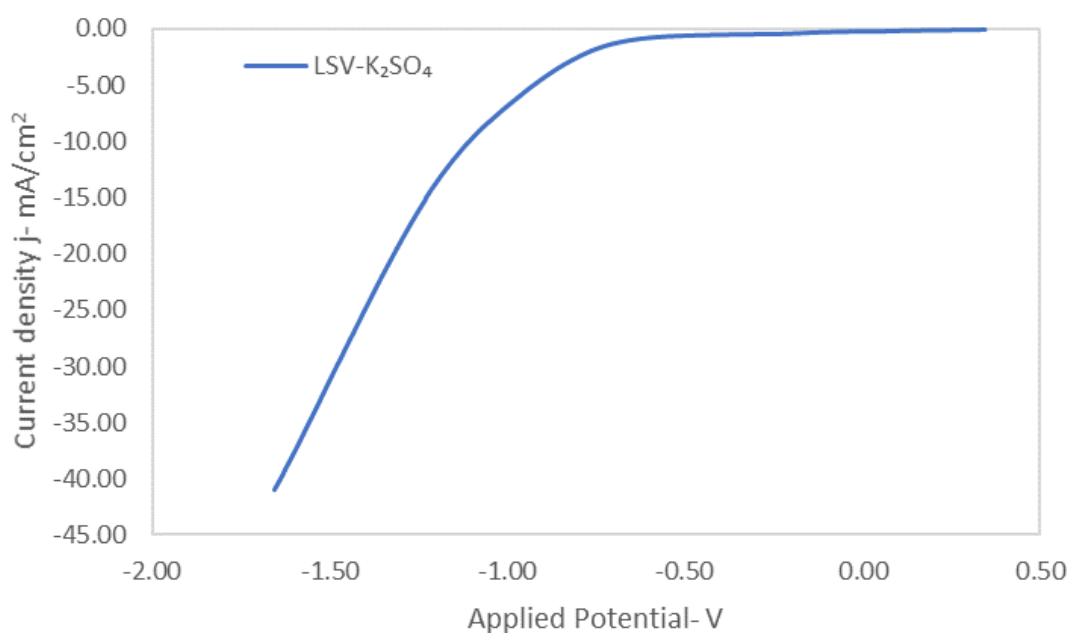
Figure 7 CV curves of copper in various electrolytes with 0.1M concentration (a) H_2SO_4 (b) HNO_3 (c) HCl (d) K_2SO_4 (e) KCl (f) Na_2CO_3 (g) KHCO_3 (h) KOH

As a next step, LSV were carried out in three different media, the results are as in Figure 8. Copper has positive reduction potential against hydrogen, this illustrates that it will not replace hydronium ion in acid solutions. But there is a tendency to react with oxidising ions such NO_3^- ¹. The Gibbs free energy of certain reactions are calculated,

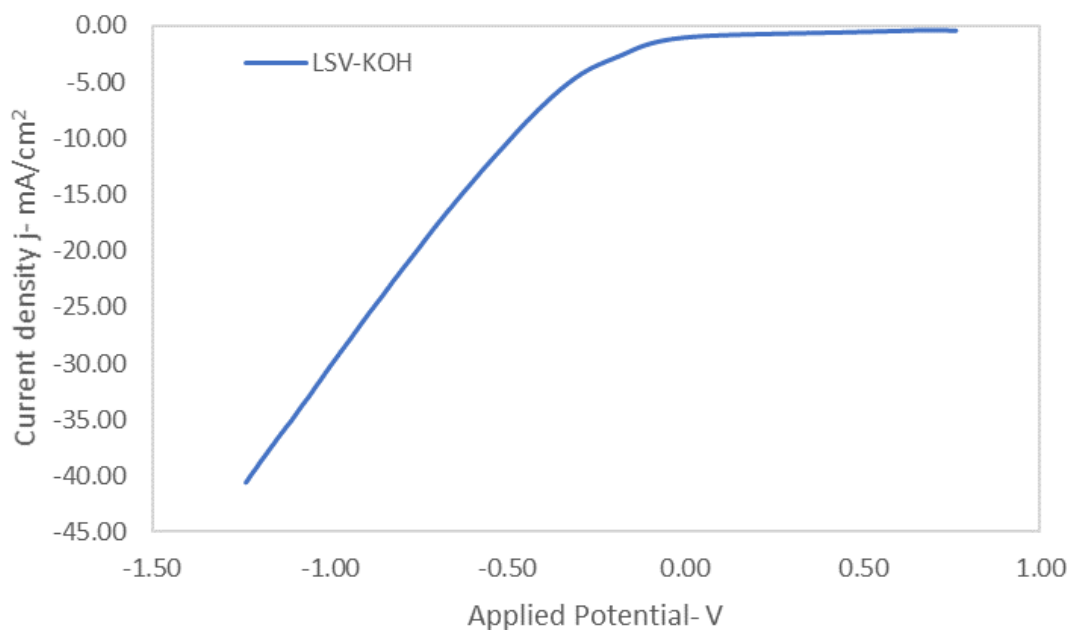


At pH7, $\Delta G = +28\text{kJ/mole}$

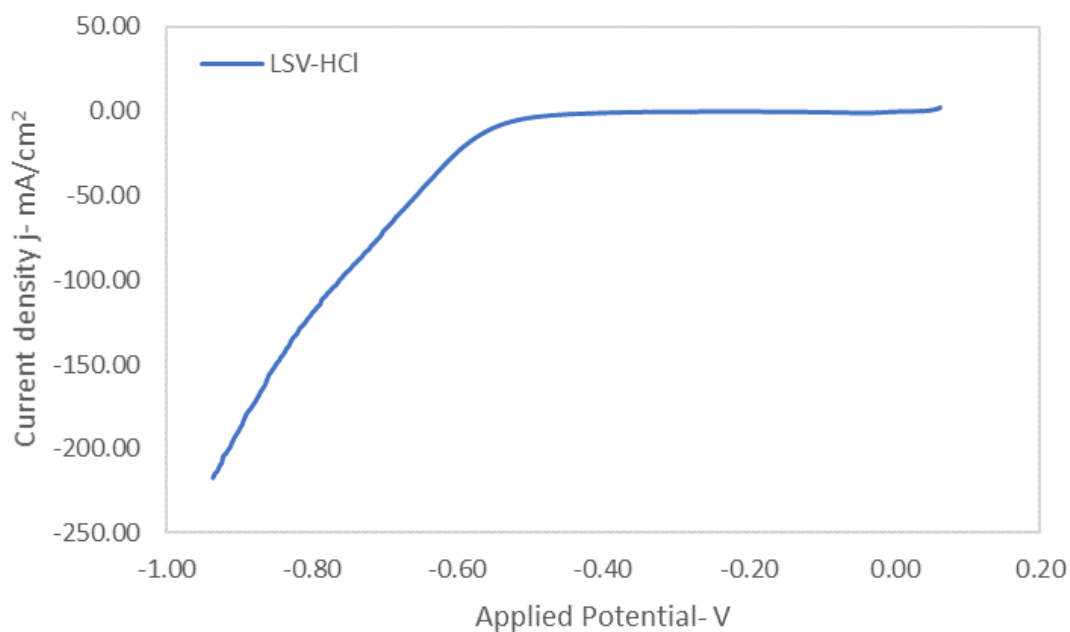
So, it was calculated that the films will be stable in acid and neutral environment. When copper was tested in HCl, it was observed that the solution is turning bluish and thus there was an indication for copper salt formation, for this reason the copper was tested in neutral solution.



(a)



(b)



(c)

Figure 8 LSV curves for Copper in various electrolytes with 0.1M concentration (a) K_2SO_4 (b)KOH (c)HCl

SEM imaging of copper oxide nanowires obtained at various temperature are shown in Figure 9a-d, Only samples at 500°C showed considerable amounts of oxide nanowires thus experiments are carried out at 500 °C for various time intervals and results are shown in Figure

9e-f. The variation in thickness of copper oxide nanowires for sample treated at 500 °C for 4 hour and 30min are Figure 10.

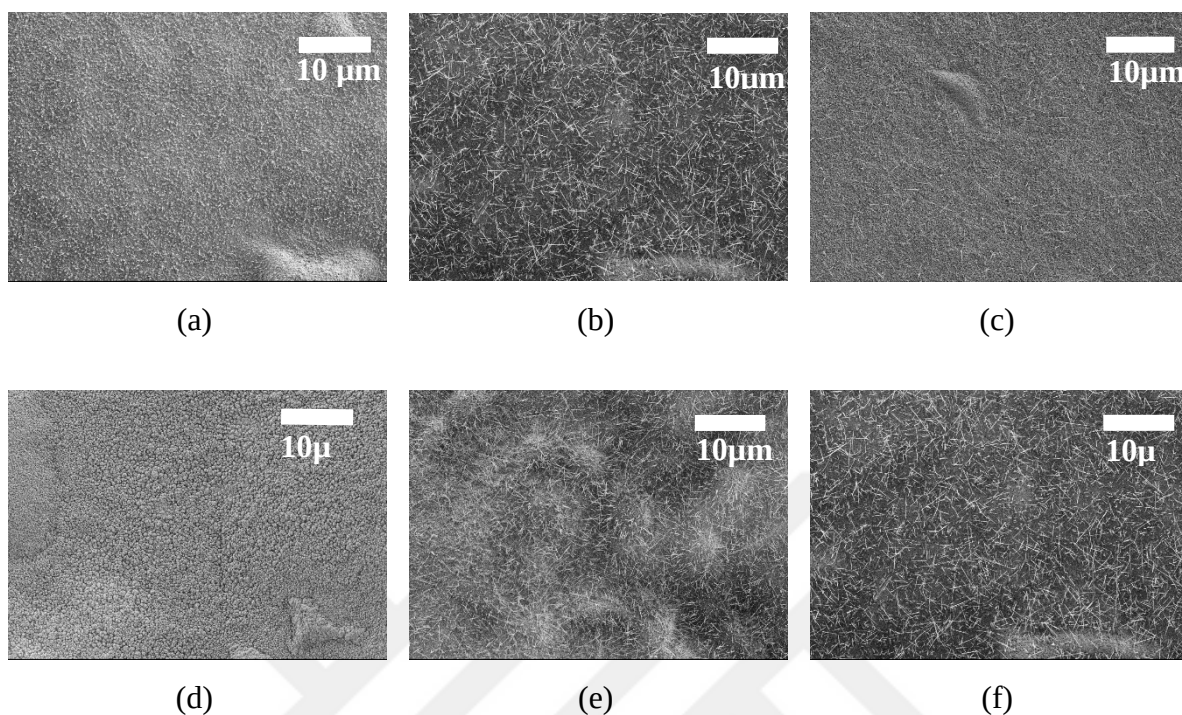


Figure 9- Morphologies of copper samples oxidised at various temperatures a- 600°C for four hours b- 500°C for four hours c- 400°C for four hours d- 300°C for four hours e- 500°C for 30min while d- 500°C for four hours

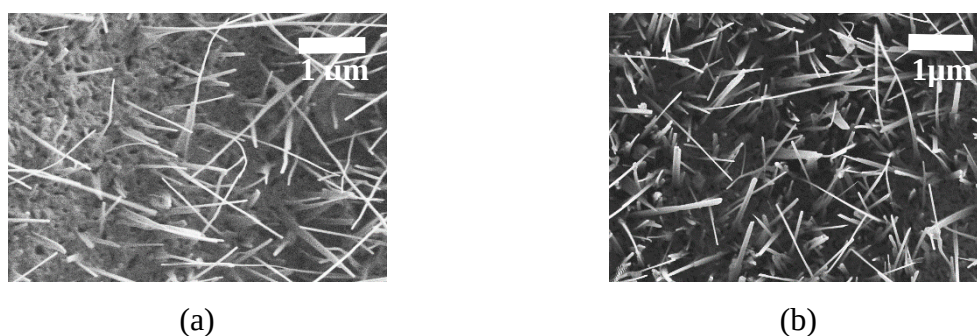


Figure 10- Nanowire morphologies obtained after thermal oxidation of copper sheets at 500°C for 30 and 240 minutes respectively. The diameter in a- 50nm and b- 100nm.

Copper oxide samples oxidised at 400 °C, 500 °C and 600 °C for 4 hours, are reduced under hydrogen plasma and tested for HER. Samples are named Cu400, Cu500 and Cu600.

XRD of thermally synthesized copper oxide and plasma reduced copper oxide is carried out by using Bruker D2 and results are shown in Figure 11, results show that after hydrogen plasma

treatment, oxide content goes down considerably, but since x-ray interaction volume in case of XRD is larger, Copper signals may be coming from copper substrate. For this reason, Raman Spectroscopy is carried out which is surface sensitive.

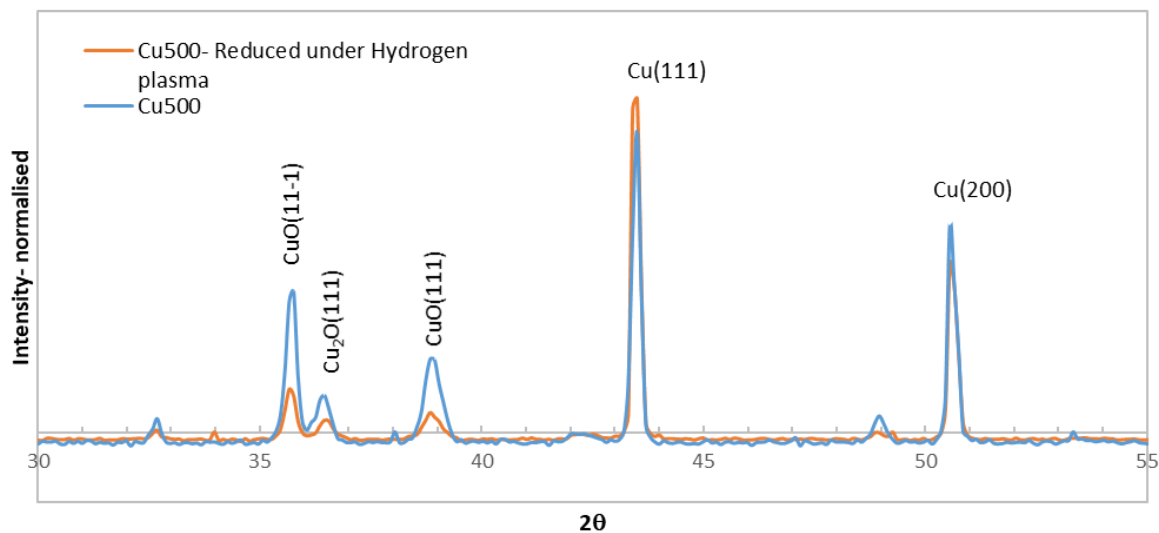
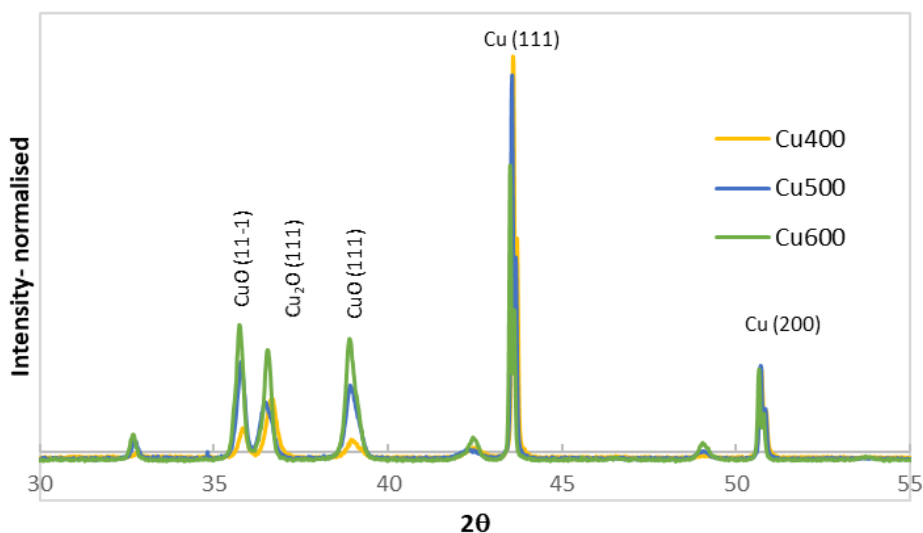
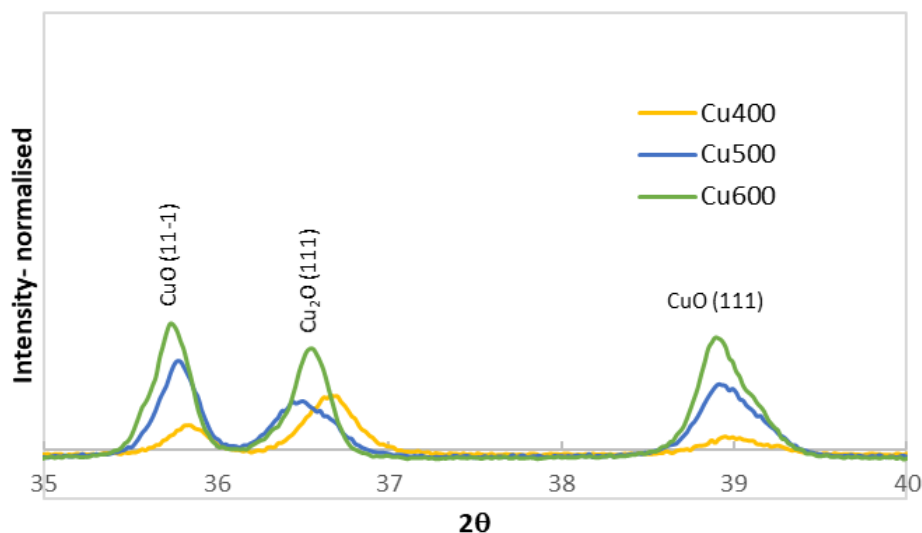


Figure 11- XRD patterns of the thermally oxidised copper at temperature of 500°C, namely - Cu500 and reduced copper oxide under hydrogen plasma.

Furthermore, the XRD of thermally oxidised copper at temperature of 400°C, 500°C and 600°C is carried out to delve into the synthesis mechanism of nanowires. The results are shown in Figure 12.



(a)



(b)

Figure 12- XRD of Cu400, Cu500 and Cu600 a- Complete XRD pattern of oxidised films b- XRD pattern for oxides

XRD of thermally oxidised copper at various temperature indicates that there is a slight shift in d values towards left which corresponds to the relaxation in lattice parameters at higher temperatures. An interesting feature is the shift in Cu_2O at 500°C which reverts at 600°C . This indicates that nanowires formation is related to formation of Cu_2O . At 400°C , the rate of formation of Cu_2O is greater than that of CuO , the rate changes at 500°C and formation rate for CuO exceeds that of Cu_2O but the formation rate of Cu_2O remains the same as it is at 400°C . At 600°C , the formation rate for Cu_2O also changes and competes with CuO . Kinetically speaking, the activity of oxygen and copper to form oxide nanowires is optimum at 500°C .

Raman spectroscopy is carried out to determine the content of copper oxide after hydrogen plasma reduction and the results are shown in, which indicate considerable difference in the area percent of copper oxide that gets reduced.

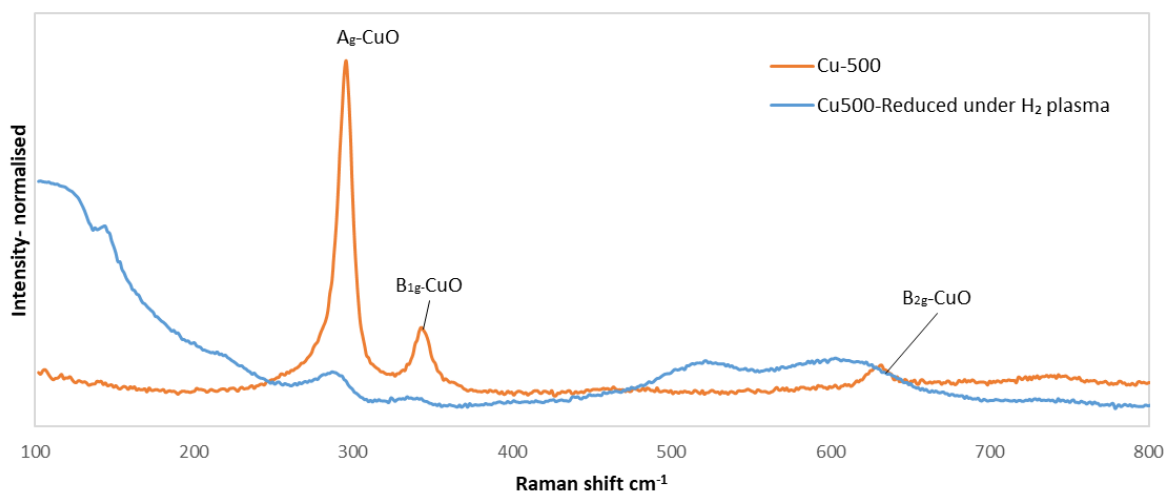


Figure 13- Raman spectra of thermally oxidised copper Cu500 and copper oxide after reduction in hydrogen plasma

The SEM images of nanowires experimented under different conditions is shown in Figure 14.

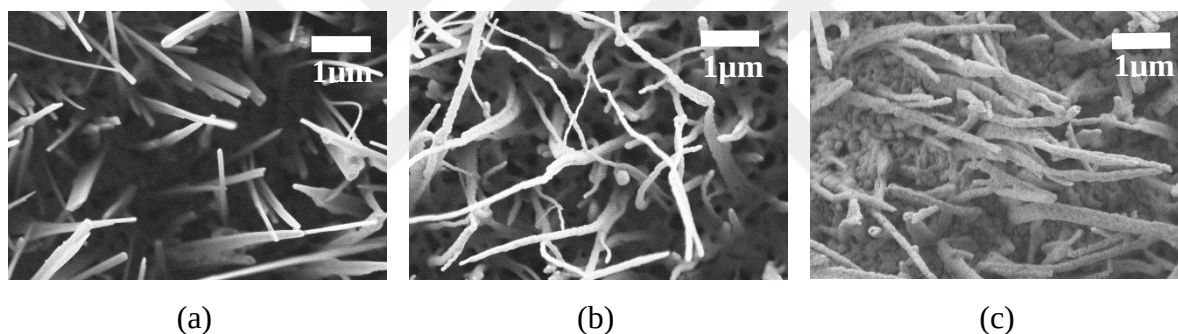


Figure 14- Morphologies of nanowires under different conditions a- Cu500 b- Cu500 after hydrogen plasma reduction c- Cu500-plasma reduced, after electrocatalytic testing

As there is no appreciable change in the morphology of metallic nanowires before and after the HER test, it is an indicator of good stability of the catalyst under neutral environment.

Voltammetry studies are conducted by first calculating and compensating the solution resistance using EIS data. The EIS test is carried out between 10kHz to 10Hz at -0.5V. The solution resistance obtained by EIS was compensated by using the software's IR compensation module. The EIS results obtained are shown in Figure 15.

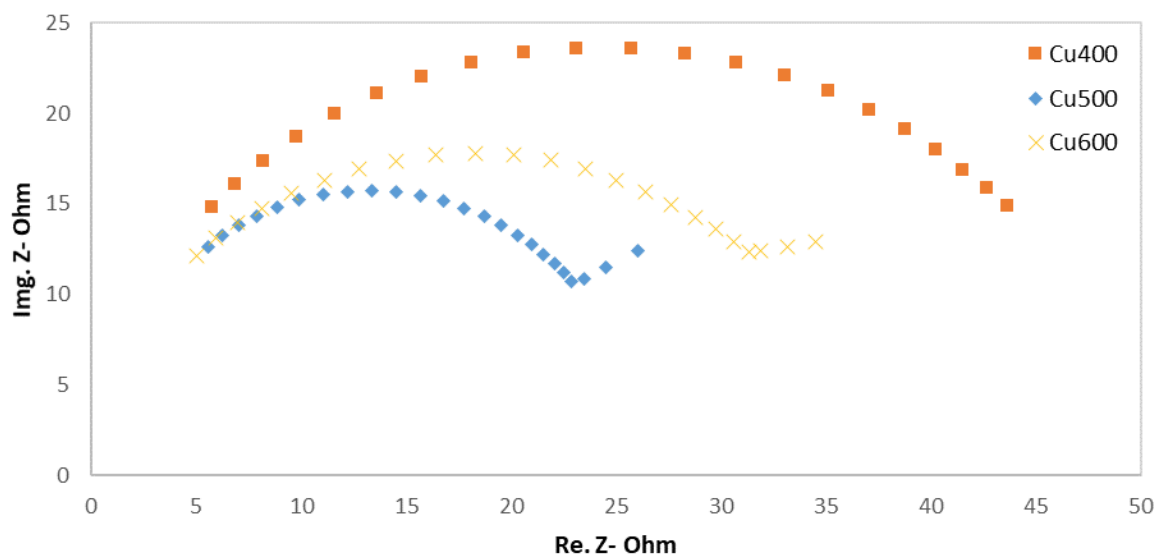
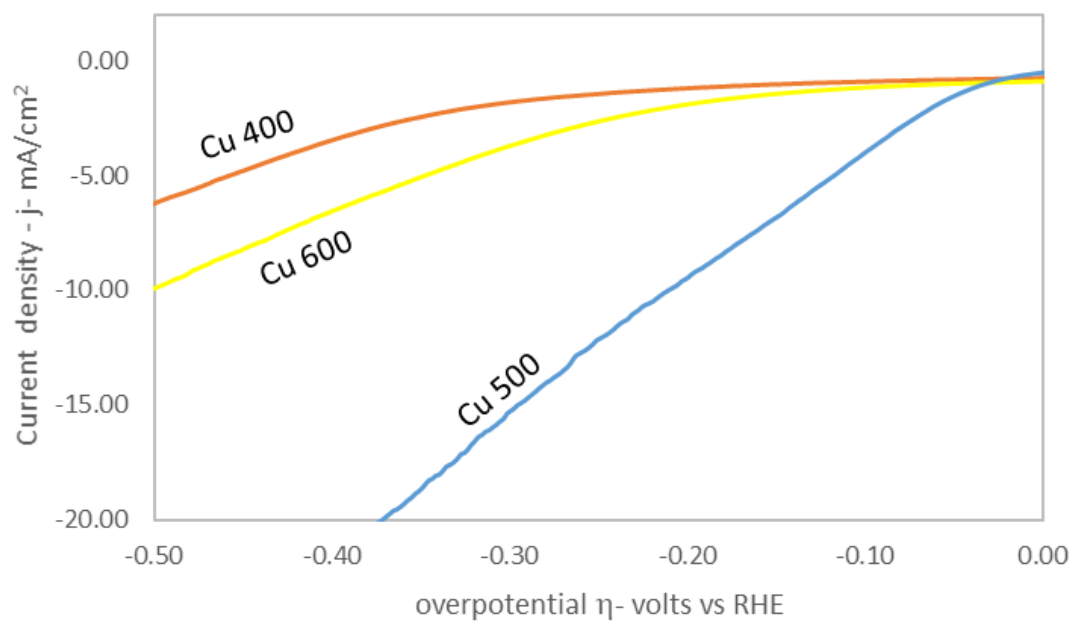


Figure 15- EIS spectra in 0.1M K₂SO₄ from 10kHz to 10Hz at -0.5V. The solution resistance obtained at 10kHz is approximately 5Ohm in each case.

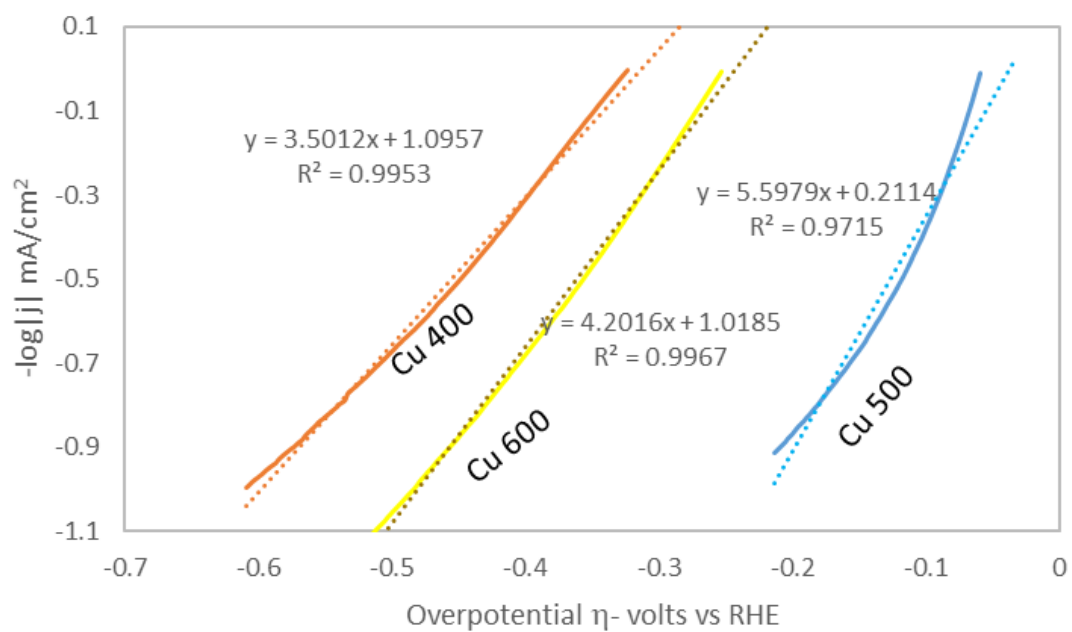
The LSV obtained is converted to polarisation curve and exchange current density along with overpotential to reach a current density of 10mA/cm² which is reported in Figure 16 and

Sample	Tafel slope (b) mV/dec	Exchange current density (i ₀) A/cm ²	Overpotential (η) at 10mA/cm ²
Cu400	285	8exp-5	500
Cu500	178	60exp-5	210
Cu600	238	9.7exp-5	600

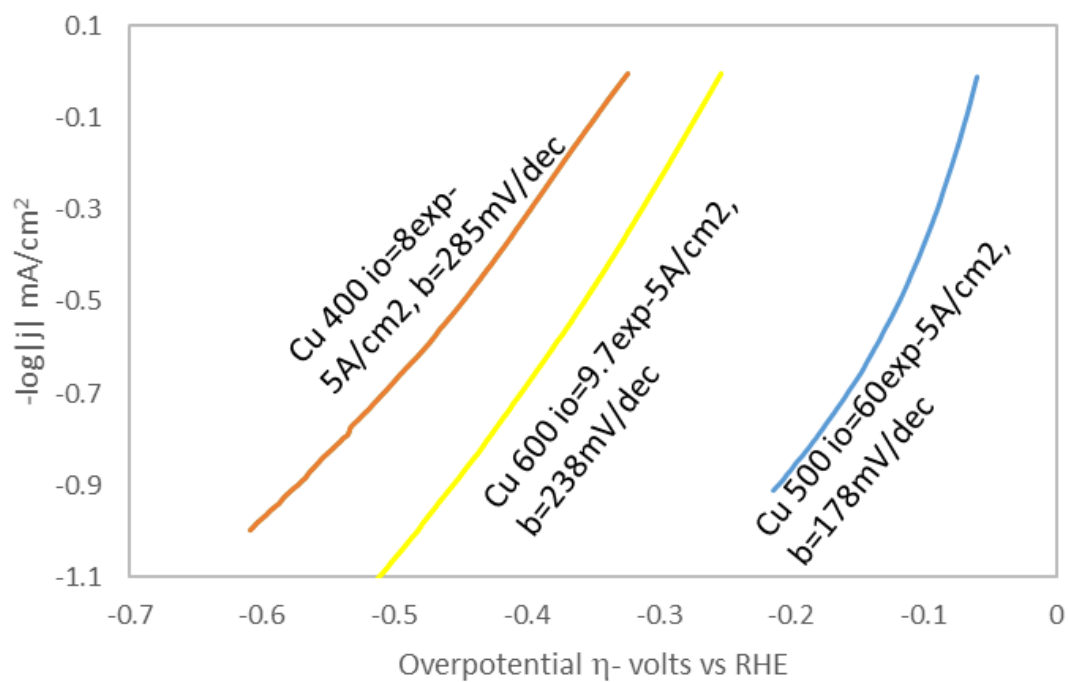
Table 7. It is clear from the polarisation curves that the sample which has metallic nanowires (Cu500) is more efficient than the ones which do not have nanowires (Cu400, Cu600) since the overpotential to reach the specific current density of 10mA/cm² is almost half than the samples without nanowires.



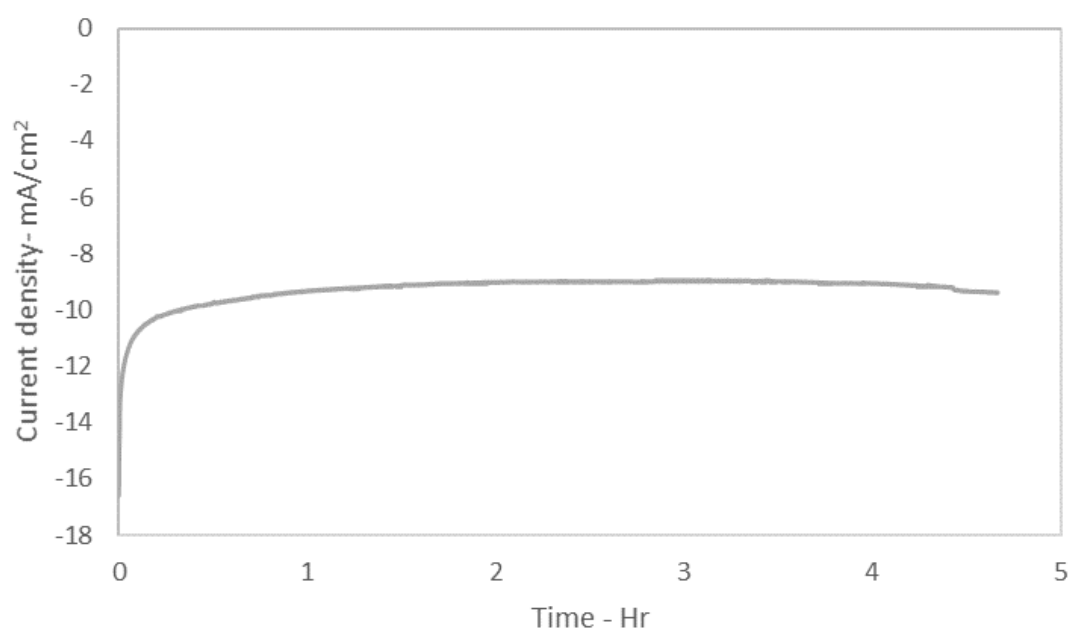
(a)



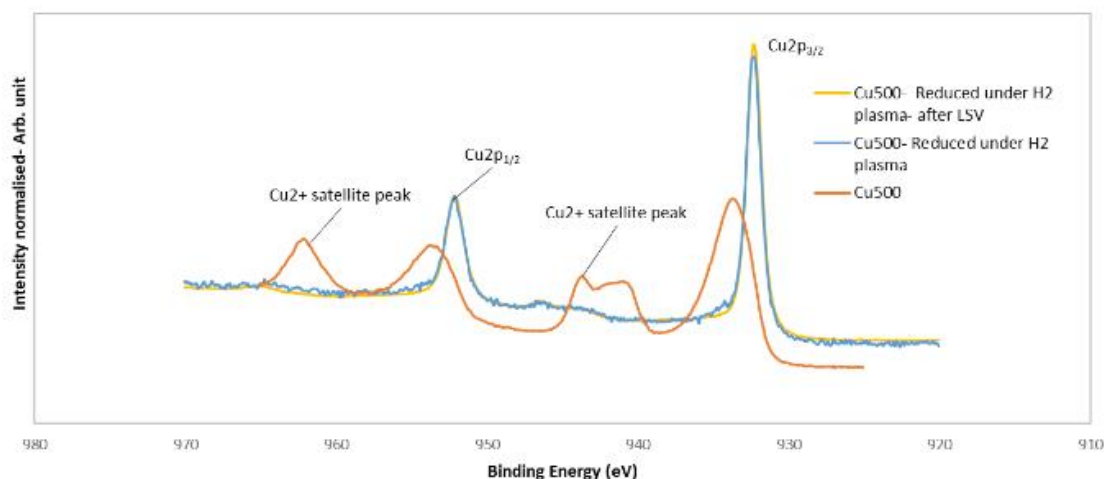
(b)



(c)



(d)



(e)

Figure 16- Electrochemical characterisation of samples, a- Polarisation curve of Cu400, Cu500 and Cu600 in at pH 7 in 0.1M K₂SO₄ solution b- Tafel slope calculations c- Tafel slope and exchange current density values d- time dependent current plot at 0.7V in 0.1M K₂SO₄ (e) XPS Spectra of Cu2p scan for Cu500 under various conditions

Sample	Tafel slope (b) mV/dec	Exchange current density (<i>i</i> ₀) A/cm ²	Overpotential (η) at 10mA/cm ²
Cu400	285	8exp-5	500
Cu500	178	60exp-5	210
Cu600	238	9.7exp-5	600

Table 7- Electrochemical HER performance parameters of the catalyst

To test the stability of the electrode during HER, constant potential test was carried out for five hours and the results are indicated in Figure 16d, which shows that the electrode is fairly stable under these conditions. To further probe the effects of testing conditions on copper morphology before and after the HER test, XPS was carried out and the results are indicated in Figure 16e, which shows that there is no change in chemical makeup of nanowires. To further confirm the findings through Raman spectroscopy, XPS also confirms the difference in chemical make up of nanowires before and after hydrogen plasma treatment, the results are shown in Figure 16e.

2.4 Conclusion

For copper, exchange current density varies from 10^{-7} to 10^{-5} A/cm² in literature^{5,100}, we have achieved an exchange density of 6exp-4A/cm² which is one order of magnitude larger than conventional reports mentioned in literature. The last reported overpotential for 10mA/cm²

current density in year 2019 is around 400mV for flat copper surface¹⁷ for an alkaline environment while in our case it is 210mV for metallic copper nanowires in neutral solution. For platinum, overpotential to reach 10mA/cm² is almost 50mV in basic environment^{36,101,102}, so the goal is to find an inexpensive solution to Pt.

In summary, our work shows that for a single class of material such as copper, the HER catalytic performance varies under different conditions and depends on various factors including morphology of the material under study. This whole study gives a general sense of direction between interaction of surfaces with molecules such as but not limited to water and CO₂. The ultimate goal is to make surfaces which can act in similar way as Pt surface act during catalysis, in this case for hydrogen evolution. The key to understanding this phenomenon is interaction of hydrogen intermediate with surface which solely dependent on binding energy of hydrogen intermediate with surface. Thus, in theory; any material, given suitable morphology and thus intermediate's binding energy with the surface can act like benchmark catalyst for HER, OER and CO₂R reactions.

Chapter 3- Electrochemical CO₂ reduction using metallic Cu nanowires

3.1 Introduction

As the world population will grow, the energy demand will also grow. At present per capita electrical energy consumption is 3200Kw-hr [1], projected energy consumption by the end year 2050 will be 62000Kw-hr [2]. Current energy needs are fulfilled through mainly fossil fuel sources in Figure 17[3].

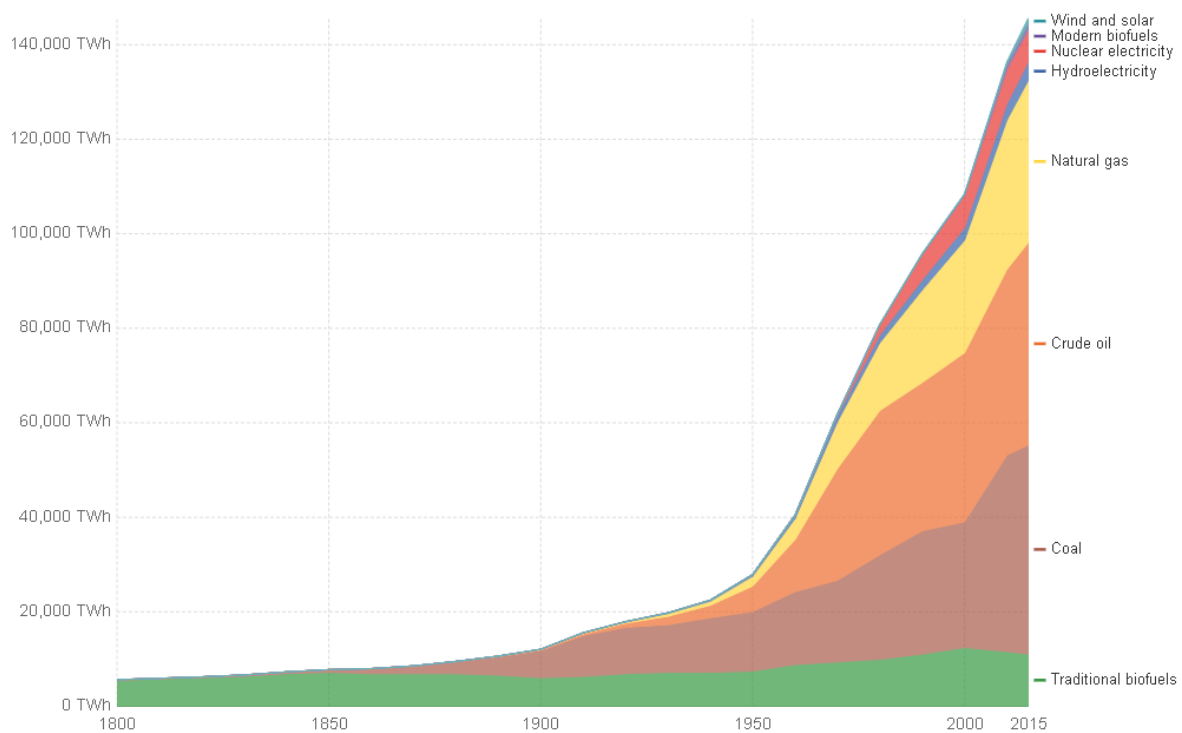


Figure 17 Global energy consumption (year wise) ³

Not only that the energy demand will increase, also the fossil fuel sources will deplete and projections of remaining oil reserves will last until next 70 years at current consumption rate [4]. Fossil fuel causing alarming CO₂ to rise and causing global warming which will continue until the end of fossil fuel sources and after that CO₂ level will fix, at present level; CO₂ is around 400ppm while safe level is 300ppm (Figure 18) [5]. At present, less than 1% of CO₂ globally produced is being utilised in different industrial processes and around 30% is absorbed in plants and oceans and remaining is fixed in atmosphere and is likely the cause of global warming [6].

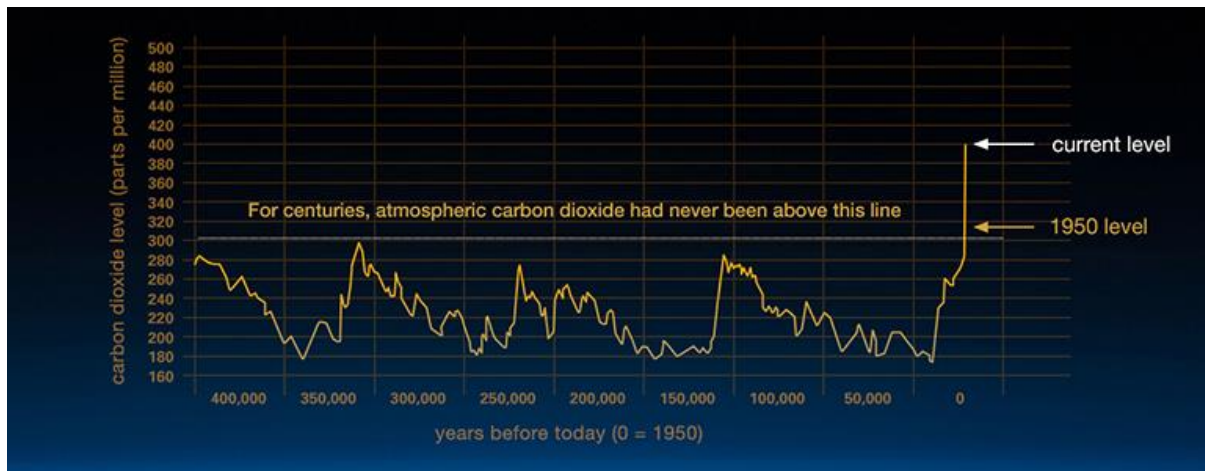


Figure 18 CO₂ level in atmosphere (year wise) ^[5]

The presence of CO₂ has detrimental effect on the environment as the CO₂ level directly corresponds to the earth's average temperature Figure 19^[7], efforts are needed to deal with CO₂.

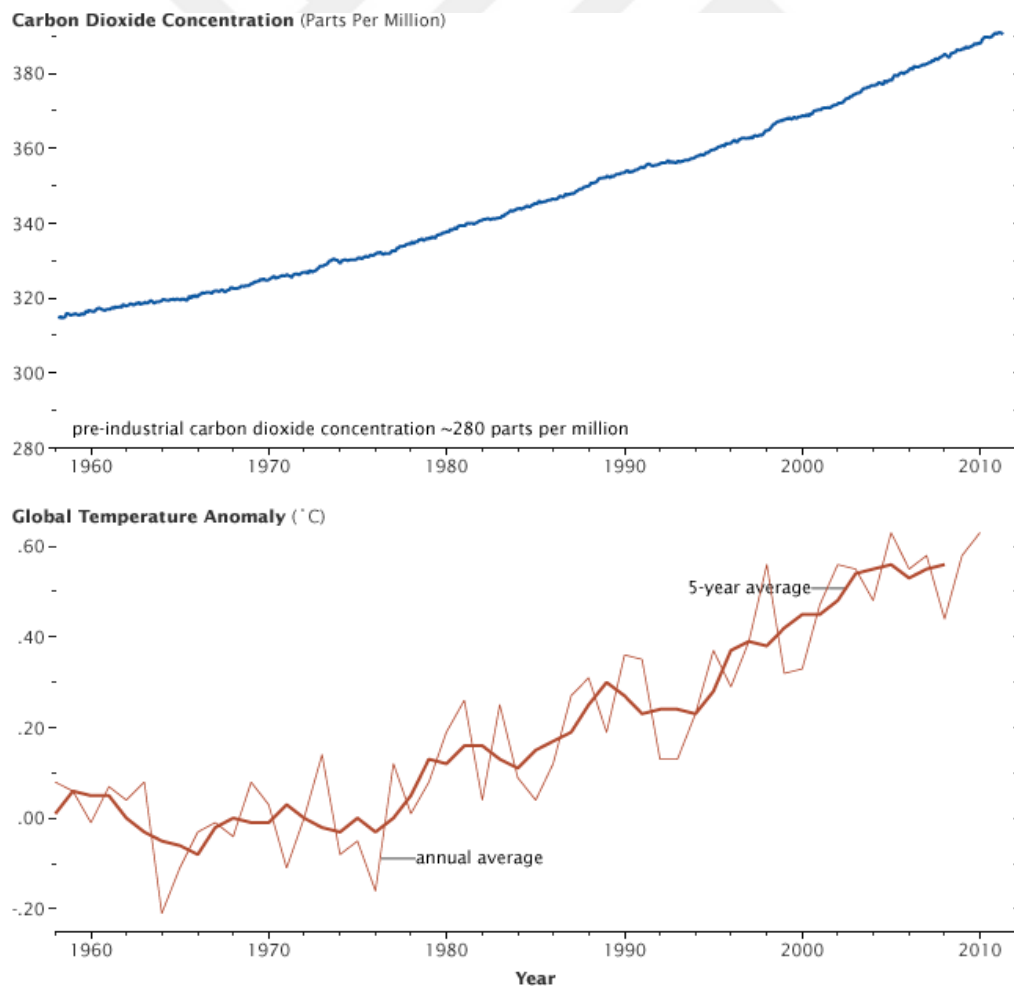


Figure 19 Effect of atmospheric CO₂ level on global average temperature rise ^[7]

The problem with CO₂ can be solved on working with different strategies to mitigate CO₂ evolution, one of which may be utilising CO₂ industrially to form different products such as but not limited to urea, carbonates and others [6]. Efforts are needed to convert CO₂ to fuel sources, in this way a cycle can be established for CO₂ production and its utility and thus by environmental conservations as depicted in Figure 20.



Figure 20 Solution to CO₂ problem

In present study, we have demonstrated the use of metallic copper nanowires synthesised by using DBD plasma technique for the first time.

3.2 Experimental

3.2.1 Synthesis of Metallic Copper nanowires

Copper sheets with a purity of 99.99% are used. First the sheets are polished using grinding and polishing machine and then cleaned with DI water and organic solvents. The samples are then heat treated in oxidising environment at various temperatures to form nanowires as reported in literature ⁹⁹. The samples are then reduced in hydrogen plasma by indigenously made plasma generator which takes an input of 18V, 5%DC, square wave of 0-10Vpp (15watt). The flow rate of hydrogen is set at about 50sccm and the time interval for the plasma reduction is sixty minutes.

3.2.2 Electrochemical evaluation for CO₂R

For CO₂ electroreduction, a two chamber cell separated by proton exchange membrane is used, Figure 21. The cell was gas tight, Hydrogen reference electrode is used and Platinum is used as a counter electrode. In all experiment, KHCO₃ 1M is used as solution. To carry out CO₂ reduction reactions, the cell solution is purged with CO₂ for 15 minutes prior to start of electrochemical measurements.

Before doing any electrochemical measurement, electrochemical impedance spectroscopy is carried out to determine the solutions resistance, which is later used to compensate for the voltage drop in the solution.

To compare the electrode property for CO₂ reduction, experiments were also carried out without bubbling CO₂ in the system, in this case N₂ gas is bubbled through the system and GC indicated absence of any of the CO₂ reduced species.

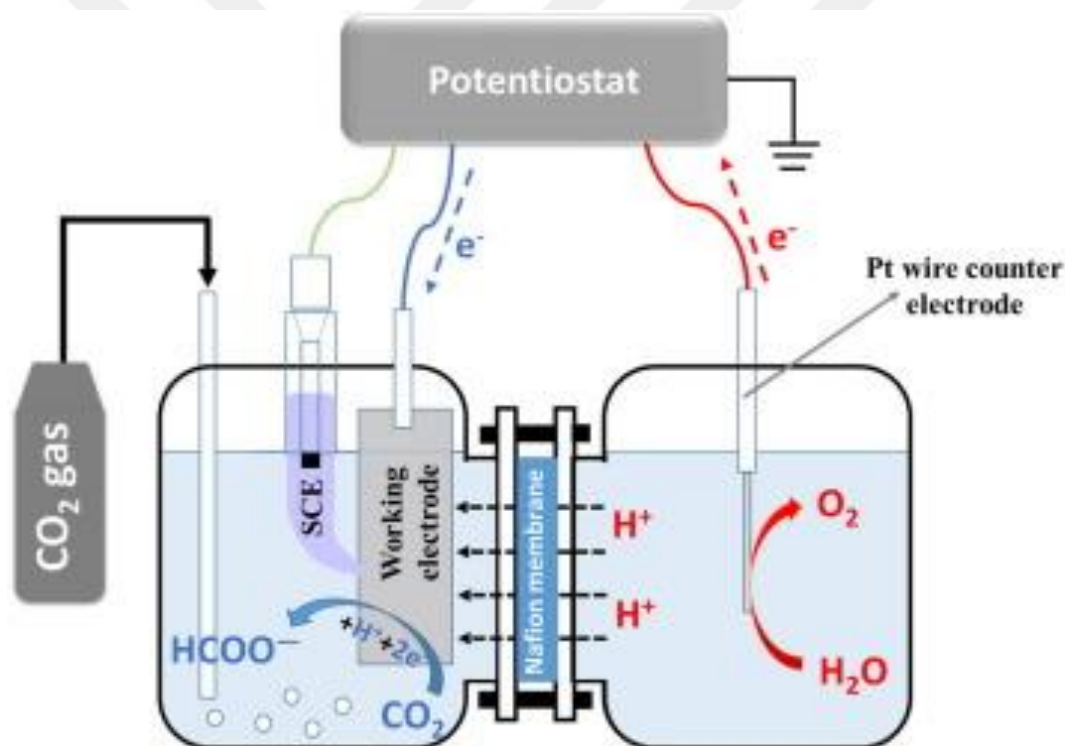
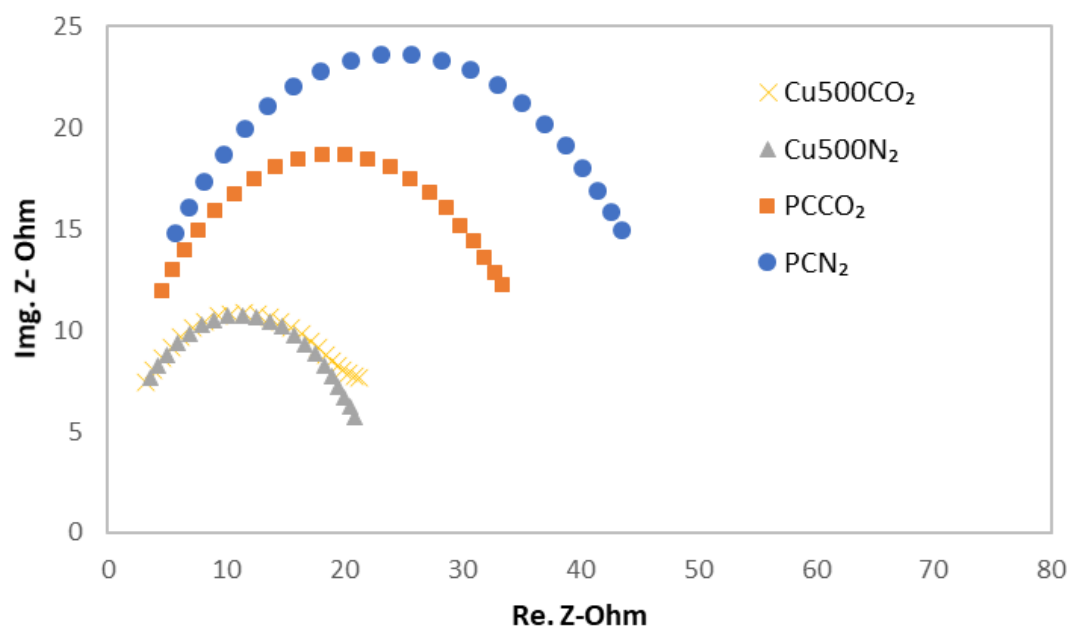


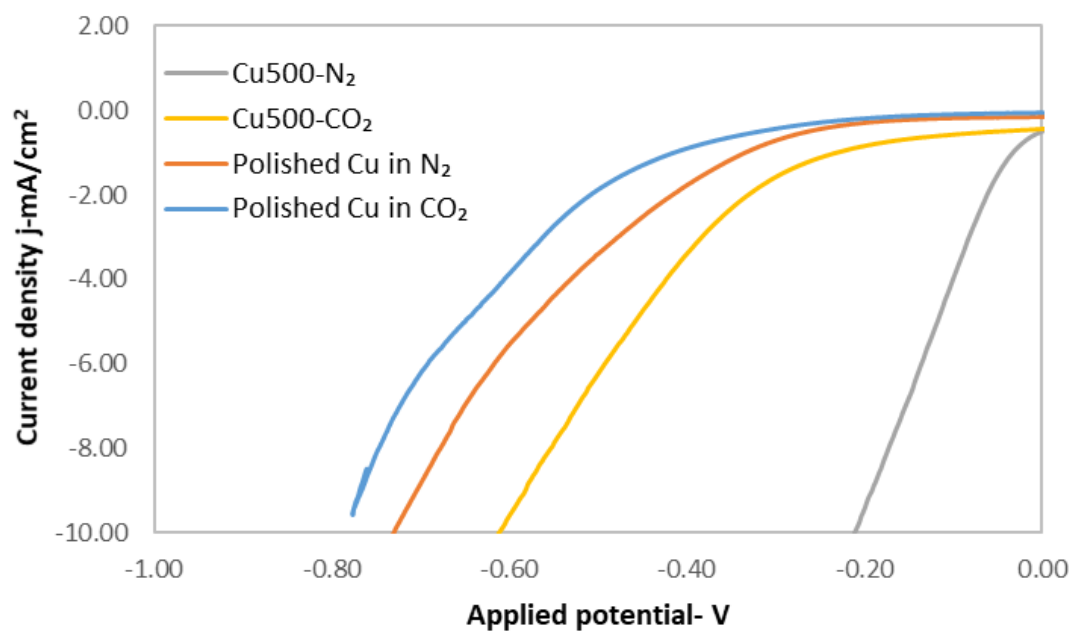
Figure 21 Two compartment cell used for CO₂ electroreduction¹⁰³

3.3 Results and discussions

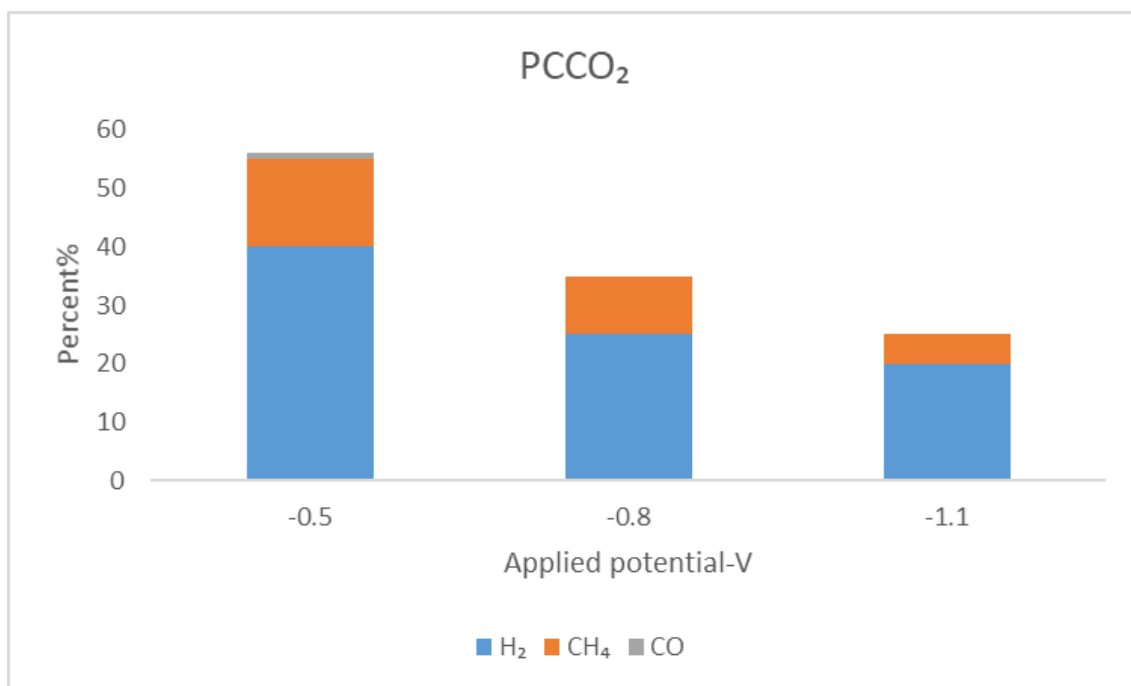
The nanowires synthesized for HER are also tested for CO₂ reduction in electrochemical environment. In a typical experimental procedure, EIS was carried out to determine the solution resistance which was used later to compensate the potential of LSV. The LSV data was used to derive polarization curve. The results are indicated in Figure 22.



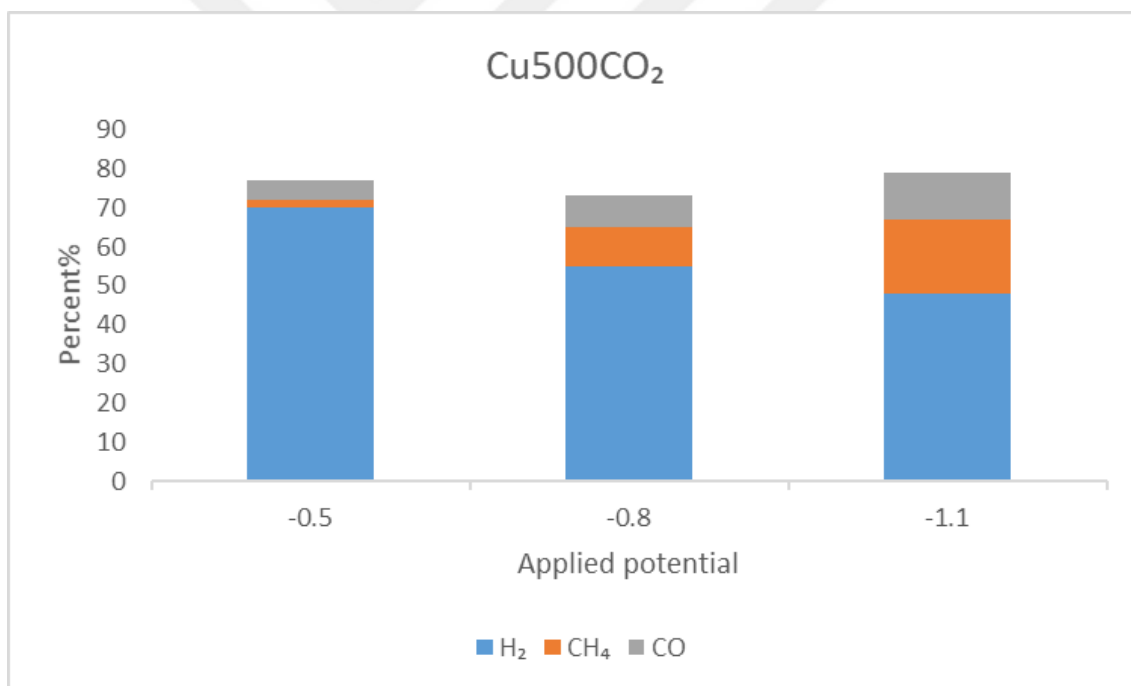
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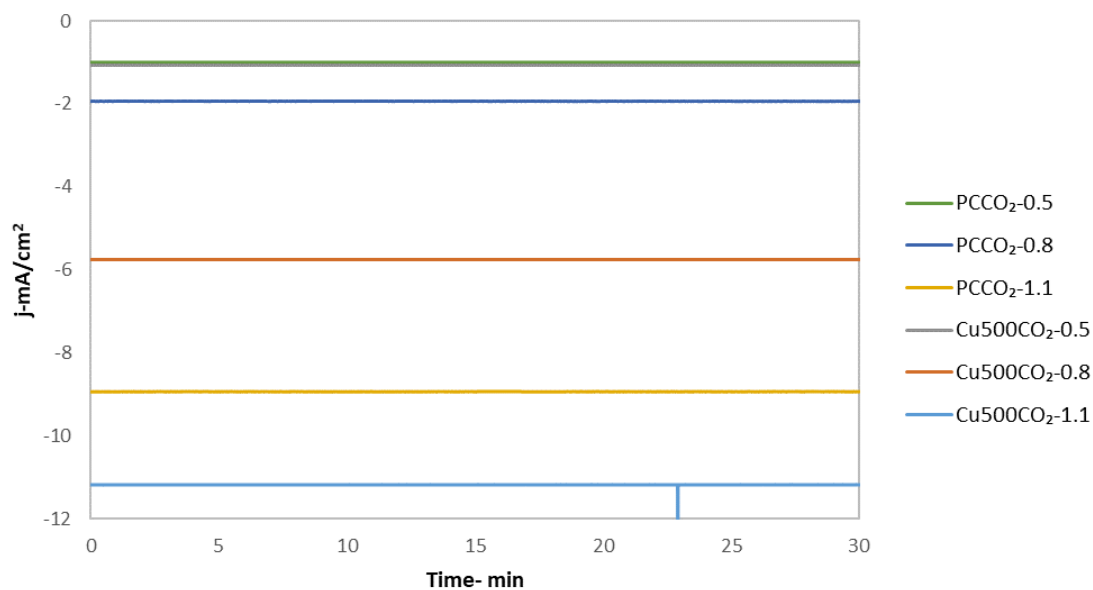
(b)



(c)



(d)



(e)

Figure 22 (a) EIS spectra for various copper samples under CO₂ and N₂ environment (b) Polarisation curves (c) Gaseous product distribution for polished copper sample for CO₂ electroreduction at various applied potentials (d) Gaseous product distribution of Cu500 (e) Fixed potential voltammetry at various potentials for polished copper(pc) and metallic copper nanowires(Cu500).

Time dependent constant potential voltammetry was carried out at various potentials for thirty minutes each and gaseous products were analysed using Shimadzu GC 2014, MS5A, N₂ as carrier gas. The product distribution as a function of faradaic efficiency is listed in Figure 22.

The current time profile are shown in Figure 22. Electrochemical CO₂ reduction performance parameters showed an improvement in CO₂ reduction as compared to bulk copper. The findings are in line with the present state of research. A recent article¹⁰⁴ published on the use of copper nanowires for CO₂ reduction, the paper emphasized on CO reduction using nanowires. Our paper focus on CO₂ reduction. It is established from HER study that the binding energy of intermediate is decreasing due to lowering of overpotential required to reach 10mA/cm², this can be understood from product distribution in CO₂ reduction on nanowire surface, as the nanowires showed great potential for selectivity to gaseous products including Hydrogen.

In making the observation, the very first step was to carry out LSV and to see the difference. EIS was carried out and the solution resistance was compensated. The R_s value was almost same in all cases while the charge transfer resistance changed which is an indication that morphology play a key role in catalysis as redox processes are actually charge transfer

processes. The charge transfer in case of flat surface is higher since the energy barrier of the intermediate in terms of adsorption energy is higher, for this reason the charge transfer resistance is higher while in case of nanowires the decrease in charge transfer indicates that electron are easily transferred to reducing specie in comparison to flat surface (Figure 22). We postulate that decrease in binding energy in case of nanowires can be understood in this way, flat surfaces are constituted by combination of atoms which provide a unique band structure solution for that surface but in case of nanowires, the each nanowire unit has a band structure that acts individually and lowers the intermediate's free energy of adsorption. This is obviously a hypothesis and to prove the point, we shall need to study the band structure of bulk metallic copper and metallic copper nanowires.

LSVs were conducted in KHCO₃ 0.1M solution wrt hydrogen reference electrode. CO₂ gas was bubbled for 15minutes before taking any measurements. To compare the electrode's performance for CO₂ reduction, the results were compared to nitrogen saturated solutions. The key finding is that bicarbonate ion does not generate and carbon-based reduced product during electroreduction. Almost any solution can be used for CO₂ reduction provided that, one it has higher solubility of CO₂ and the constituent of solute other the CO₂ does not interact with electrode; in this case copper electrode.

The key feature in LSVs (Figure 22b) is reduction in overall current performance of electrode during CO₂ reduction process as compare to HER or in other words exchange current density of the surface increases in CO₂ environment which is an indication that overall binding energy has increased as compare to only hydrogen intermediate. This can be due to the presence three kind of binding species present in solution i.e. carbon, oxygen and hydrogen while in case of HER only hydrogen and oxygen were present.

The gaseous product distribution was analysed by using Shimadzu GC2014 with an MS5A column and N₂ as carrier gas (Figure 22). Main observation is overall gaseous products selectivity is different in case of polished copper surface and copper nanowires. The total gaseous product detected at -0.5V is about 60% in case of polished copper surface while total gaseous products detected for copper nanowires is about 80% at -0.5V which remains the same up to -1.1V. In case of flat copper surface, total gaseous products reduced with respect to increase in voltage which is an indication that product selectivity is also a function of applied potential. We postulate that since at higher voltages the overall sum of gaseous product is getting reduced which means that liquid products are increasing in quantity. Liquid products

are usually heavier and bulky than gaseous products that are detected in gaseous state through GC which indicates the reaction kinetics are faster at higher voltage and surface is making more bulky products as compared to products at lower voltages.

One of the marked differences in reduced product is an increased amount of hydrogen in case of nanowires. At every potential, the hydrogen amount is almost doubled in case of nanowires as compared to flat copper surface and at lower voltages the amount is almost tripled. The methane content in case of nanowires is gradually increasing as compared to flat surface where there is a gradual decrease in methane content with applied potential increment. Same goes for CO which is almost non-existent in case of flat copper surface but gradually increases in case of nanowires with an increasing potential function. It can be concluded that nanowires are selective to gaseous products and have good electrochemical character for CO₂ reduction than flat copper surface. The gaseous product distribution is studied using constant potential voltammetry for thirty minutes each. The results are indicated in Figure 22e.

3.4 Conclusion

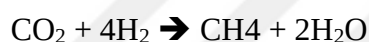
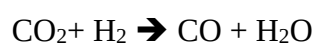
Metallic copper nanowires synthesized by DBD plasma reduction are successfully tested for electrochemical CO₂ reduction. In comparison to HER, for ECO₂R; the overpotential to reach specific current density of 10mA/cm² is increased by 400mV. Overall, gaseous product distribution increased to 80% from a mere 50% in case of bulk copper surface at -0.5V. Metallic copper nanowires showed excellent selectivity towards gaseous products during electrochemical CO₂ reduction such as hydrogen, CO, and CH₄. In ECO₂R, metallic nanowires showed increased selectivity towards methane at higher applied potential values, while in case of bulk copper surface; the selectivity towards methane was decreasing as potential was increased towards more negative values.

Chapter 4- Plasma CO₂ reduction using CuO and NiO loaded Al₂O₃ and SiO₂

4.1 Introduction

CO₂ reduction is under intense research focus in recent years due to the fact that green house gases are increasing global average temperature at a very fast rate, so the idea that green house gaseous such CO₂ can be used as energy storage medium, is fascinating. Chemically recycling CO₂ will open up a sustainable route in which carbon burnt will again be used as a carbon fuel production source.

Thermodynamically for co₂, following reduction reactions are possible,



There are other reactions as well, but the above are core reactions.

CO₂ reduction reaction takes place on ceramic supports on specific atomic sites of Cu, Ni, Au, Ag etc. The problem arises due to the adsorption of water on catalytic sites which deactivates the catalyst performance efficiency which can be dealt with by increasing temperatures up to 300°C. But the negative aspect is at these temperatures carbon deposits on the catalyst sites as graphite which causes further deactivation.

The methanation of CO₂ is an spontaneous reaction at room temperatures, as the temperature is increased to 500°C, the reaction becomes non-spontaneous, for this reason conversion should take place at around 300°C. Ni supported catalyst are extensively used for CO₂ conversion with an efficiency of 80% and 100% selectivity towards methane. CO₂ methanation happens through two different mechanisms, in one CO* and other involves COOH* radical formation as an intermediate. In recent years, much focus is shifted from RWGS to plasma CO reduction using H₂ in DBD. In this technique, rather than raising global vessel temperatures using a furnace, a plasma is using with local temperatures at reaction site upto 5000°C. The recorded CO conversion is upto 50% on Ni-Al₂O₃ catalyst at temperature of upto 300°C.

In most studies, oxides supports are utilised with a loading of transition metal oxides and usually plasma with high power inputs are used, We have presented here work with least power inputs (15watt) with Cu and Ni oxide loaded on alumina and silica. For plasma generation we

have utilised DBD technique and an indigenous system for plasma generation which takes an input of 15watt, 1500Hz, 0-10Vpp.

4.2 Experimental

Porous supports of Al₂O₃ and SiO₂ are used. Cu(NO₃)₂ and Ni(NO₃)₂ salts were used to load the metal oxide content on the supports. In a typical preparation procedure, 5mg of Cu(NO₃)₂ salt is added to 1g Al₂O₃ to prepare 5%wt. mixture of Cu(NO₃)₂ on Al₂O₃. In the same way, 5%Ni(NO₃)₂/Al₂O₃, 10%Cu(NO₃)₂/Al₂O₃ and 10%Ni(NO₃)₂/SiO₂ are prepared and grounded in petry dish using small amount of acetone. The powder is ground until homogenous slurry is obtained which is then dried in air for two hours and further dried in oven at 80°C overnight. In the next step, the powders are heat treated at various temperatures from 200°C to 400°C for nitrate salt to oxide conversion. Various samples are heat treated and then XRD is carried out for full conversion to oxides; either NiO or CuO. SEM is carried out to see the morphology of the ceramic powders.

Once the powders are characterised for their physical and morphological makeup, Plasma CO₂ reduction (PCO₂R) studies are carried out using an indigenously developed plasma reactor. The plasma reactor takes an input of 15watt, 0-10Vpp and 1500Hz. In a typical experiment, glass vessel with a volume of 1ml is filled with catalyst powder and the tube is then placed in a gas-tight reactor with an inlet for reacting gas (CO₂+H₂) and an outlet to GC (Agilent MicroGC450). A typical experimental setup is shown in the following figure.

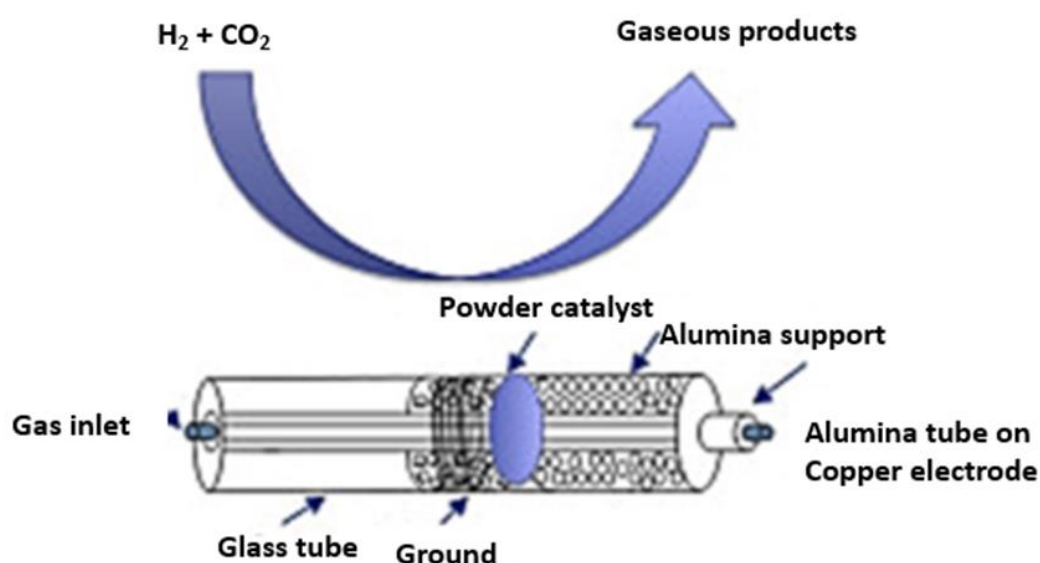


Figure – Plasma CO₂ reduction setup

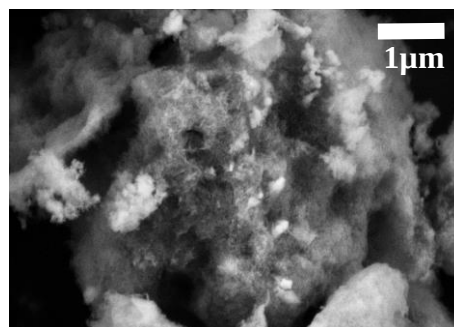
4.3 Results and discussions

In total 18 different samples were analysed, which are indicated in Table 8.

Table 8 Various catalyst used in this study, followed by treatment and BET surface area.

	Catalyst	Treatment	BET Surface area (m ² /g)
1	Al ₂ O ₃	-	200
2	SiO ₂	-	200-600
3	5CuNO ₃ -Al ₂ O ₃	200°C 6hr, 400°C 6hr, 700°C 6hr	
4	10CuNO ₃ -Al ₂ O ₃	200°C 6hr, 400°C 6hr	
5	5CuO-Al ₂ O ₃	Hydrogen plasma reduction- 2hr	230
6	10CuO-Al ₂ O ₃	Hydrogen plasma reduction- 2hr	220
7	5NiNO ₃ -Al ₂ O ₃	300°C 6hr, 400°C 6hr, 700°C 6hr	
8	10NiNO ₃ -Al ₂ O ₃	300°C 6hr, 400°C 6hr	
9	5NiO-Al ₂ O ₃	Hydrogen plasma reduction- 2hr	200
10	10NiO-Al ₂ O ₃	Hydrogen plasma reduction- 2hr	215
11	5CuNO ₃ -SiO ₂	400°C 6hr	
12	10CuNO ₃ -SiO ₂	400°C 6hr	
13	5CuO-SiO ₂	Hydrogen plasma reduction- 2hr	220
14	10CuO- SiO ₂	Hydrogen plasma reduction- 2hr	230
15	5NiNO ₃ - SiO ₂	400°C 6hr	
16	10NiNO ₃ - SiO ₂	400°C 6hr	
17	5NiO- SiO ₂	Hydrogen plasma reduction- 2hr	200
18	10NiO-SiO ₂	Hydrogen plasma reduction- 2hr	190

SEM images of the powders were taken to observe the morphology. The images are shown in Figure 23.



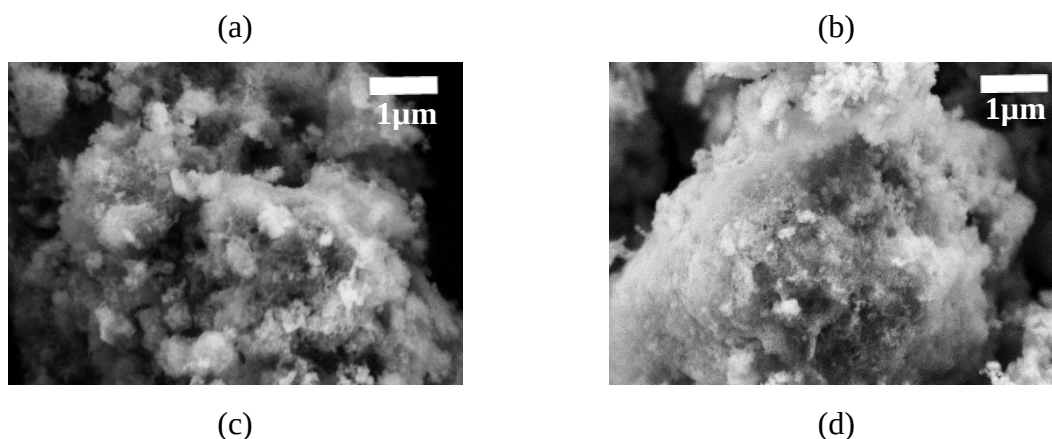


Figure 23 (a) Al₂O₃ (b) 5CuO/Al₂O₃ (c) 5Cu-CuO/Al₂O₃ (d) 5NiO-Al₂O₃

The purpose of SEM was to investigate the morphological changes accompanied by plasma reduction. There was no considerable substance to argue from SEM imaging about distribution of metallic particles. In-lens SEM imaging was carried out to see if particle distribution can be observed from other technique but nothing found. The images are shown in Figure 24.

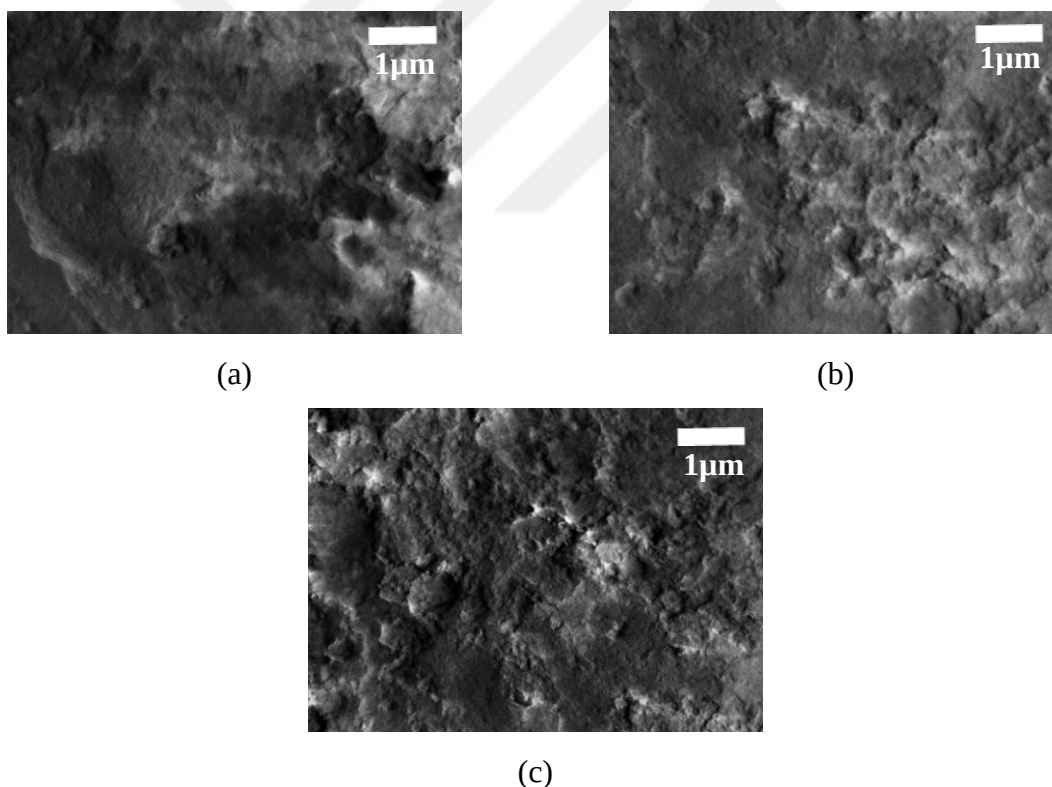
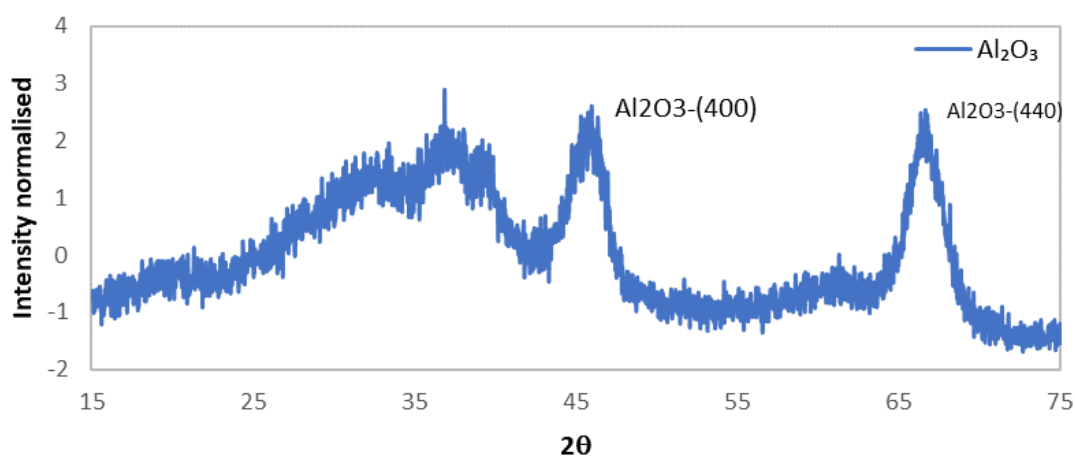


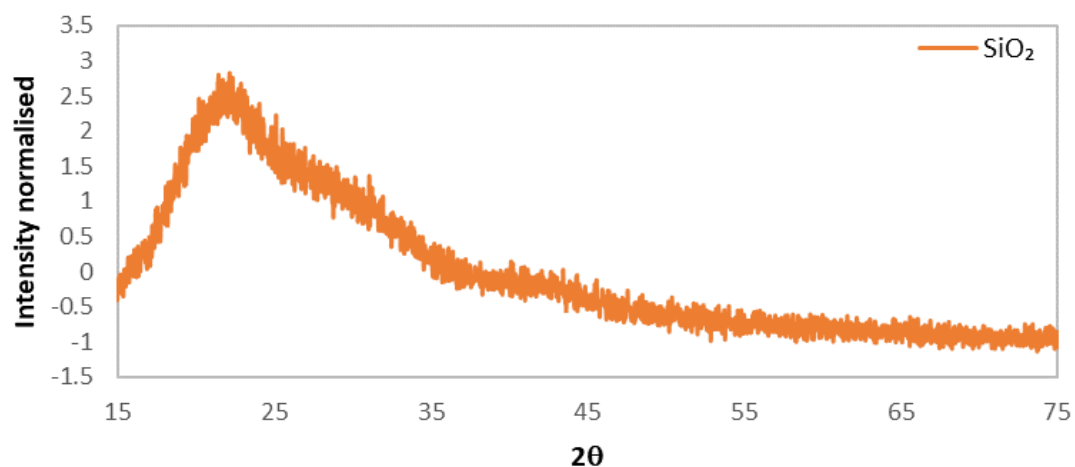
Figure 24 (a) Al₂O₃ (b) 5CuO/Al₂O₃ (c) Cu-CuO/Al₂O₃

XRD of the powders was carried out using D2 Bruker and one sample was analysed using D8. The results are as shown in Figure 25. XRD of Al₂O₃ and SiO₂ supports are indicated in Figure 25a-b. The presence of peak positions in both cases matches with the characteristics peak positions of Al₂O₃ and SiO₂. In Figure 25c-d, copper nitrates loaded on Al₂O₃ and SiO₂ are

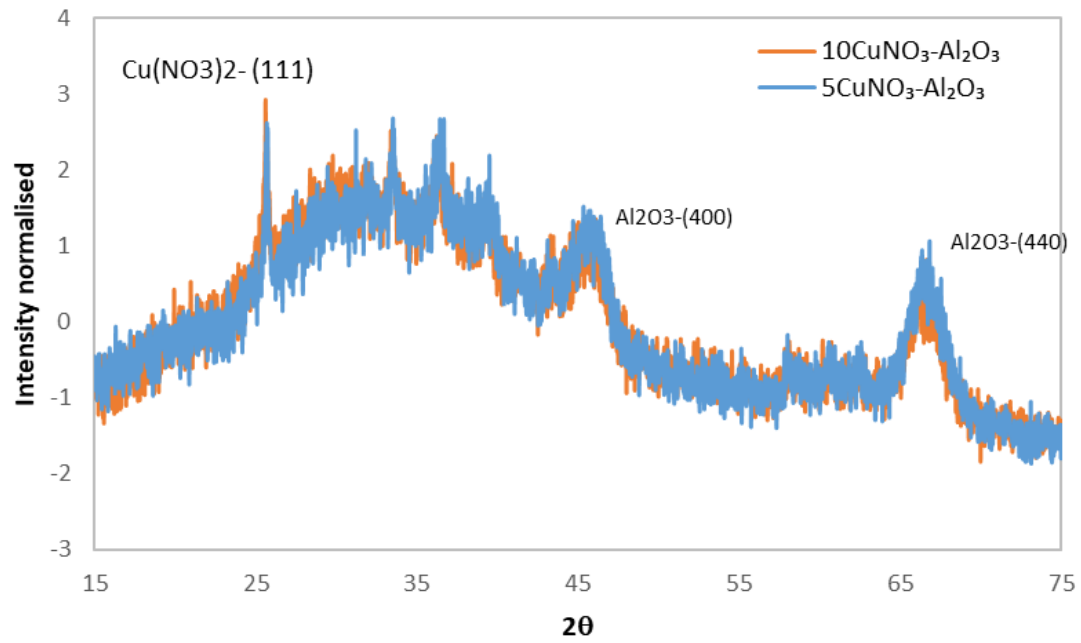
indicated with two different compositions of copper nitrate salts. The appearance of characteristics peak positions in both patterns with support in the back ground is evident. Figure 25e-f indicates the presence of nickel nitrates on supports, again the presence of characteristics peaks is evident for nitrate salts with background of XRD patterns of supports. Figure 35g-j shows the XRD patterns for heat treated samples of the same, it is clear that in case of 10% by weight loaded samples, the conversion of nitrates to oxides is quite clear but in 5% samples, the conversion is missing, this indicates the formation of copper and nickel aluminates. But no such peaks are missing in case of SiO₂ support which confirms that no silicate is formed or atleast nitrates are converted to oxides. Figure 26a-u indicates the characteristics peaks of compounds for reference of Figure 25.



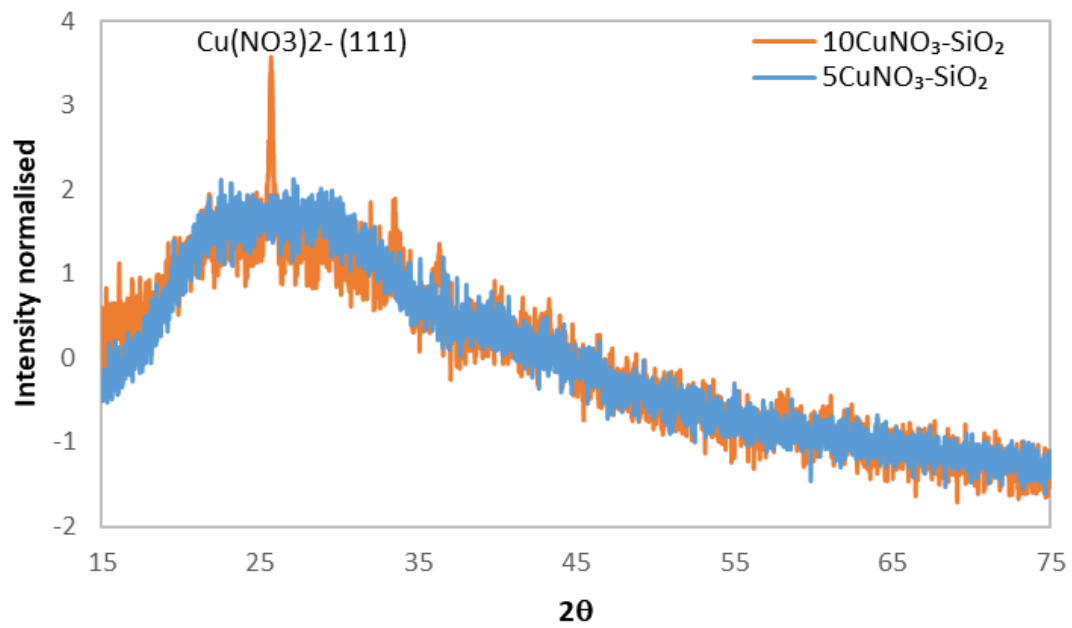
(a)



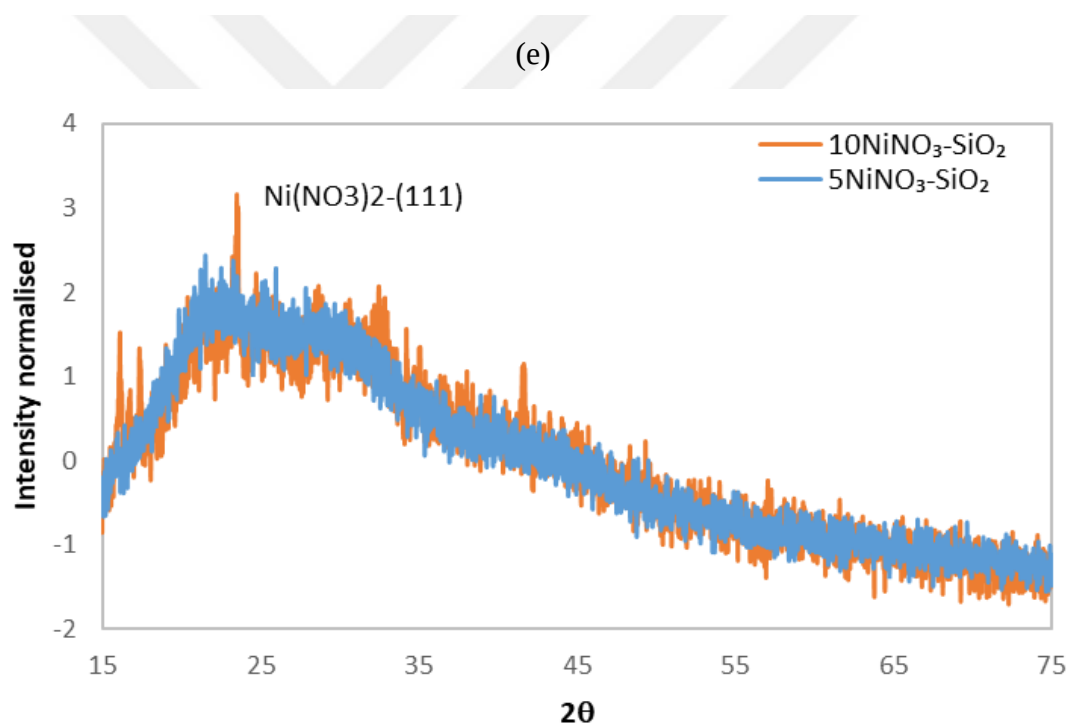
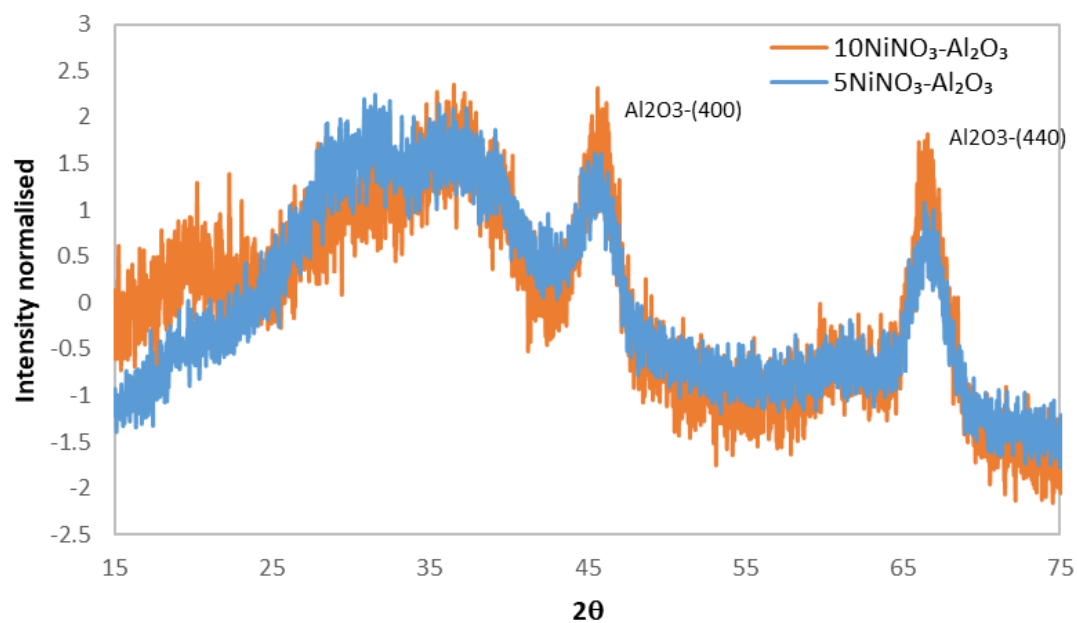
(b)



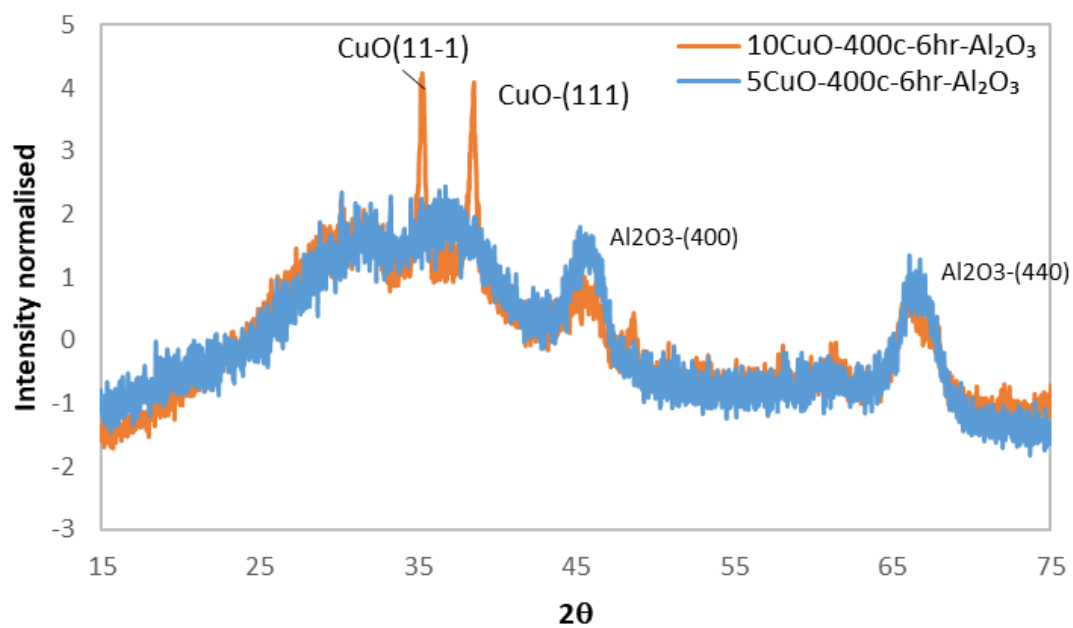
(c)



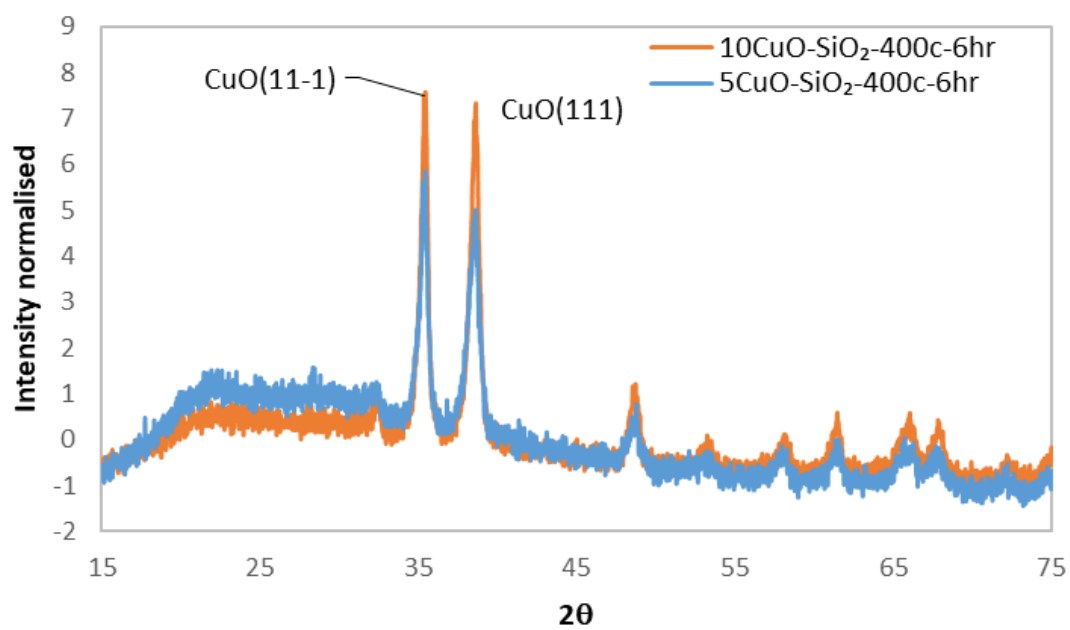
(d)



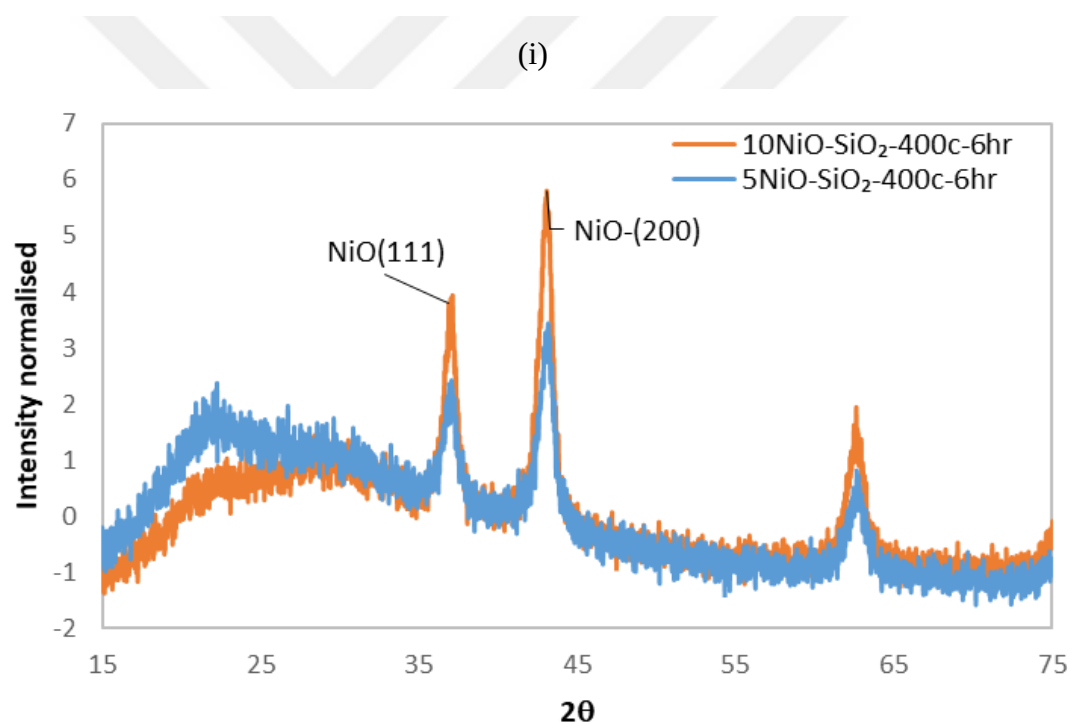
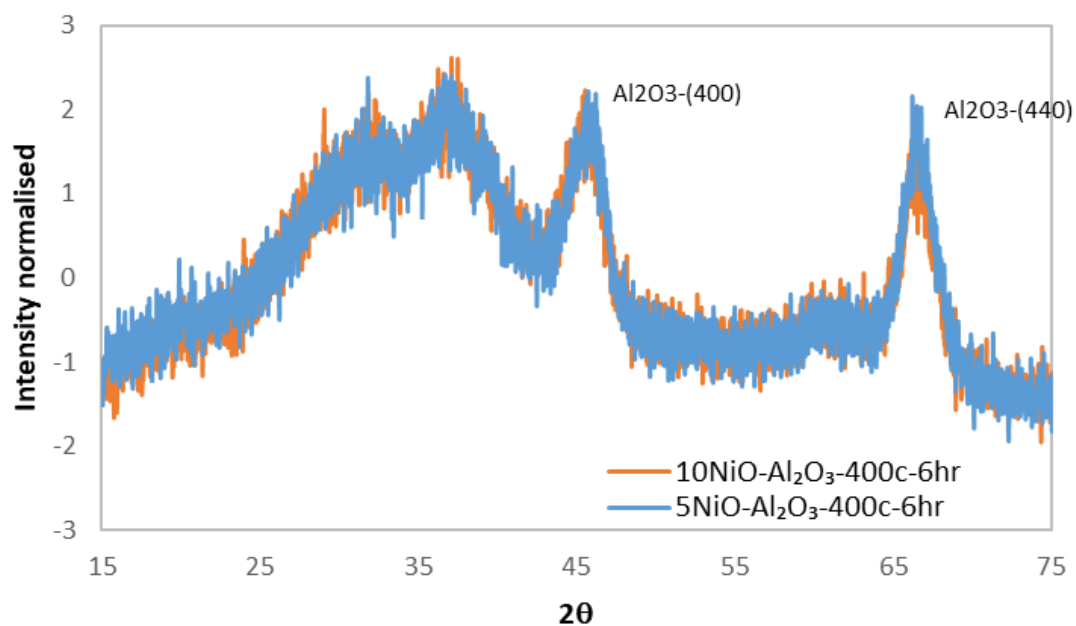
(f)



(g)

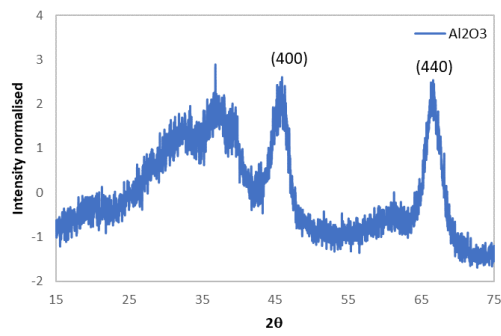


(h)

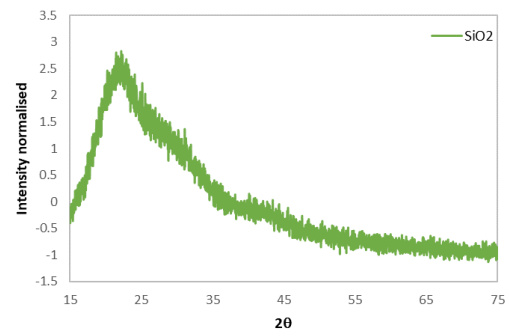


(j)

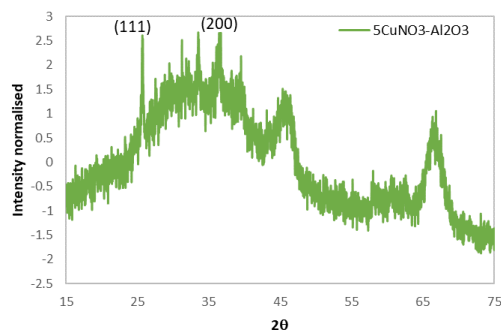
Figure 25 XRD patterns and comparisons for various catalysts a,c,d,g,h on catalyst with alumina support while rest with silica support.



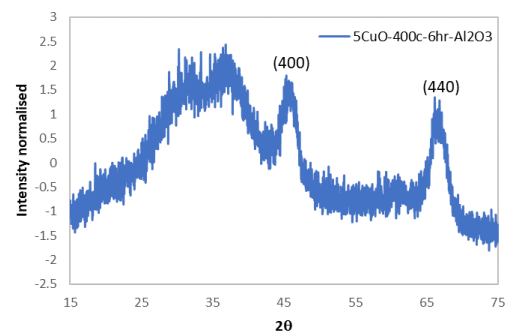
(a)



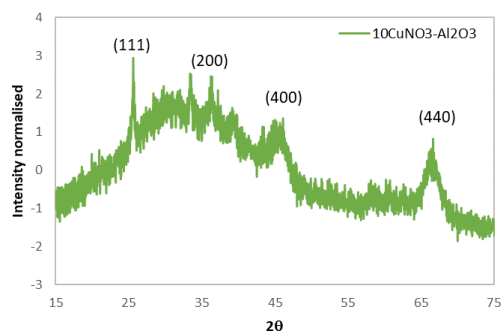
(b)



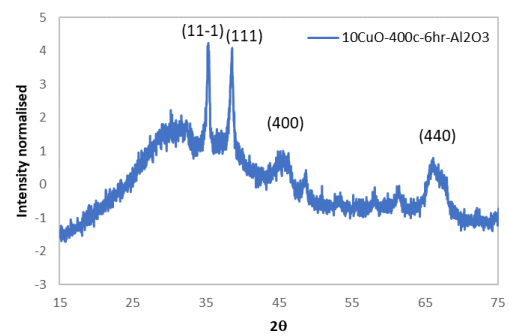
(c)



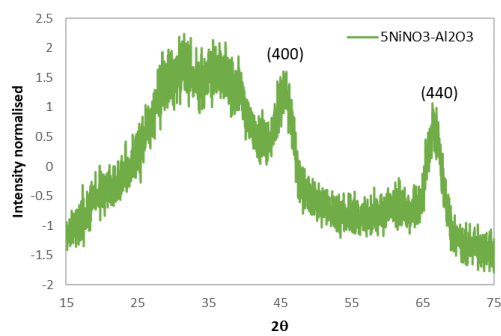
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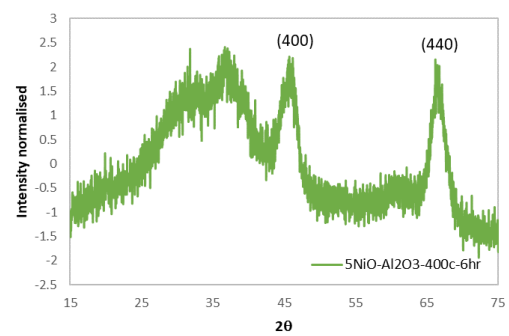
(e)



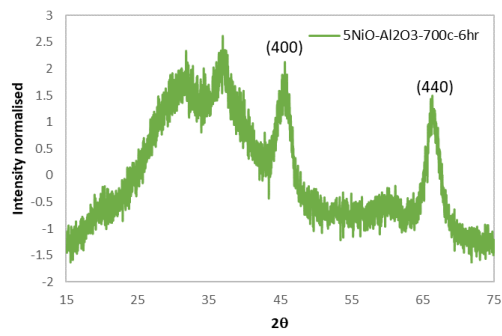
(f)



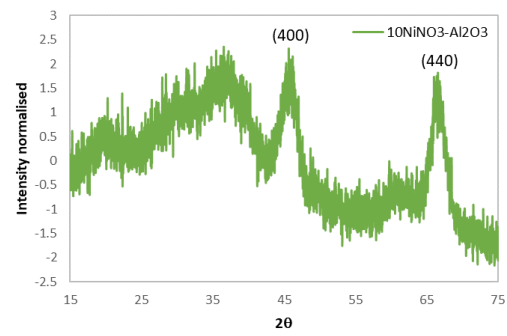
(g)



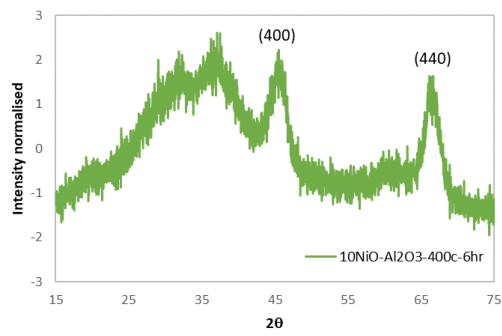
(h)



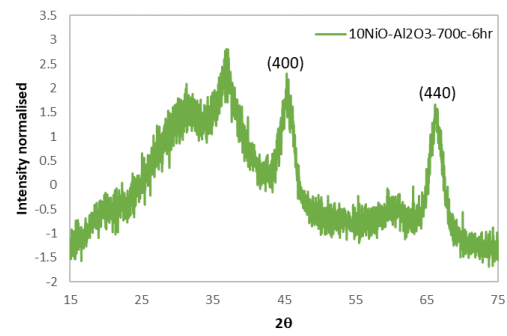
(i)



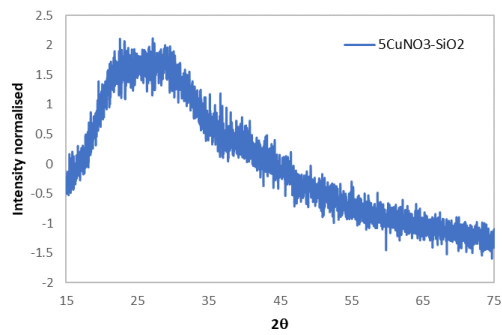
(j)



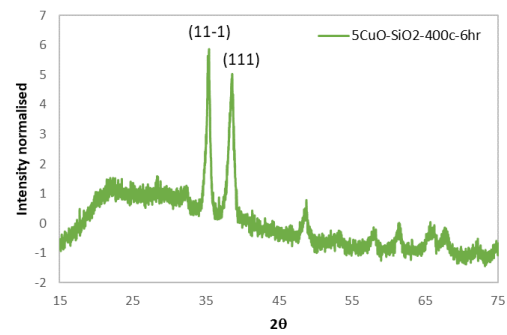
(k)



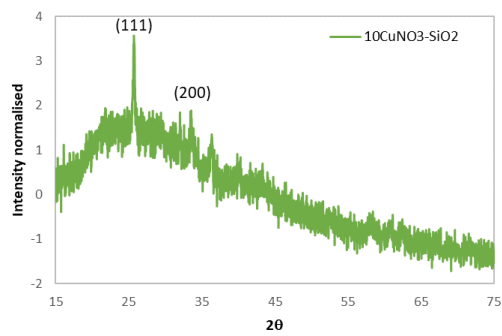
(l)



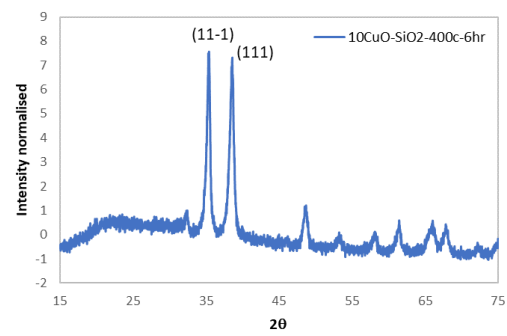
(m)



(n)



(o)



(p)

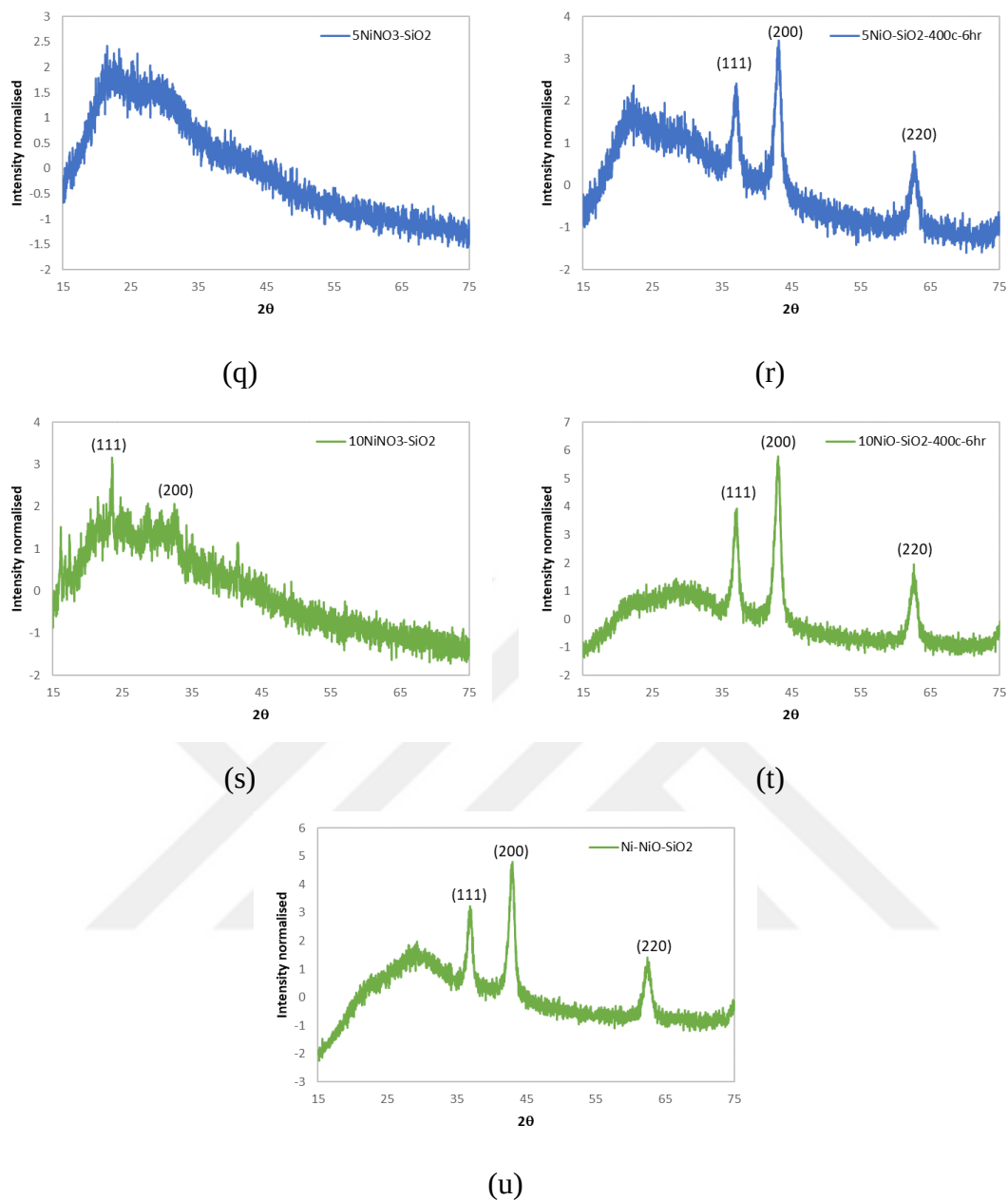


Figure 26 XRD patterns for various catalysts with plane indices

The samples with 5wt% copper oxide and nickel oxide on alumina and silica were reduced under hydrogen plasma. The XRD patterns are as shown in Figure 27,

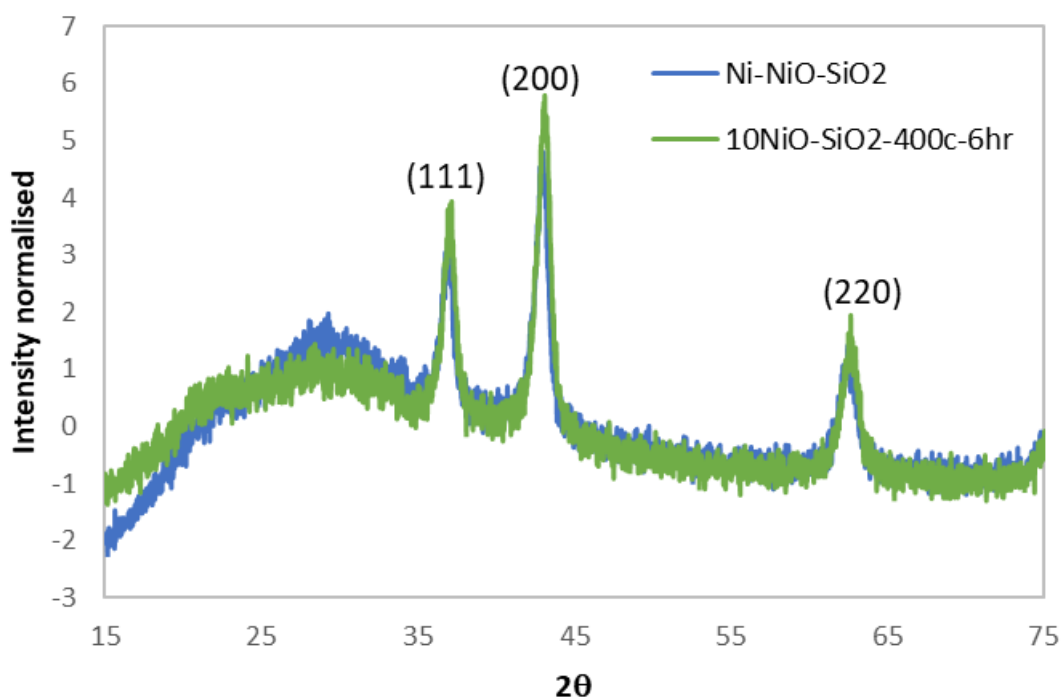
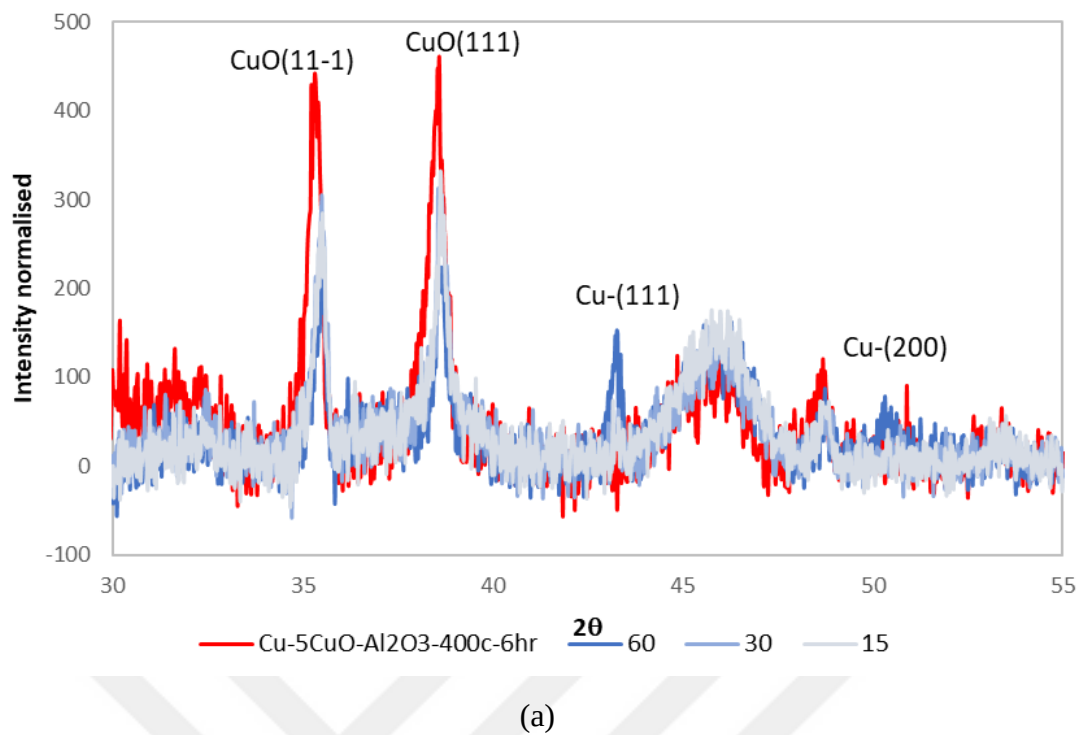
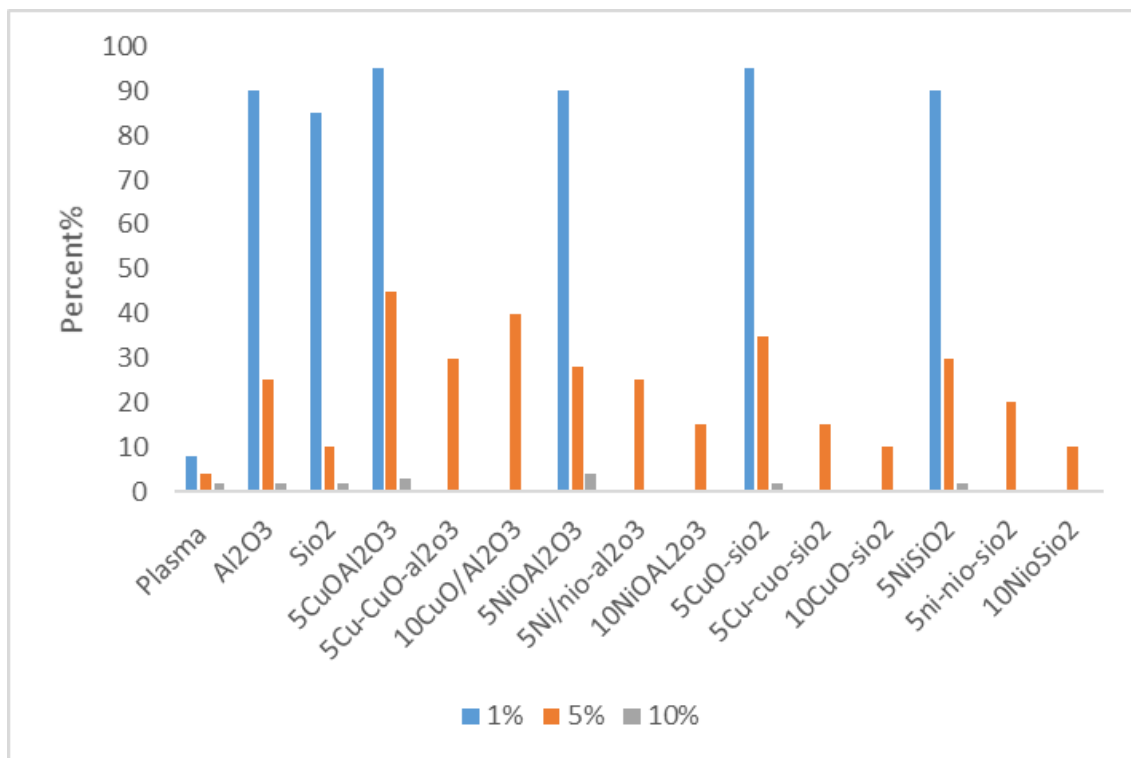
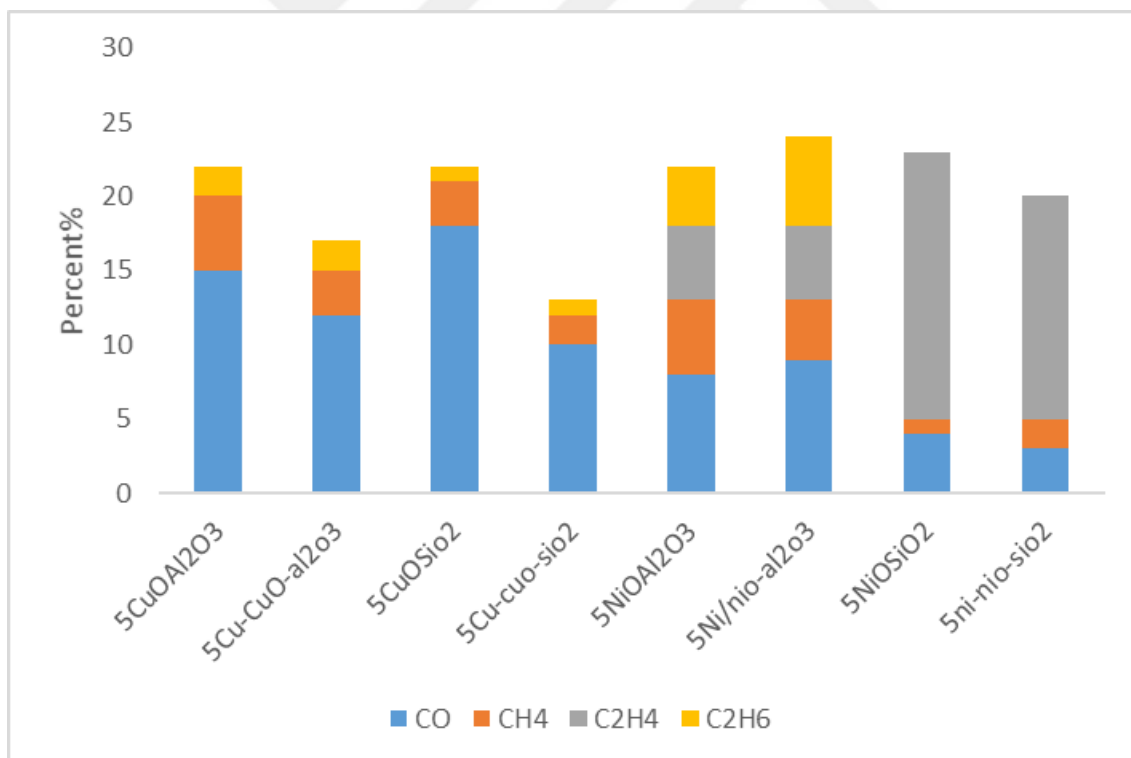


Figure 27 Hydrogen plasma reduction of catalyst powder

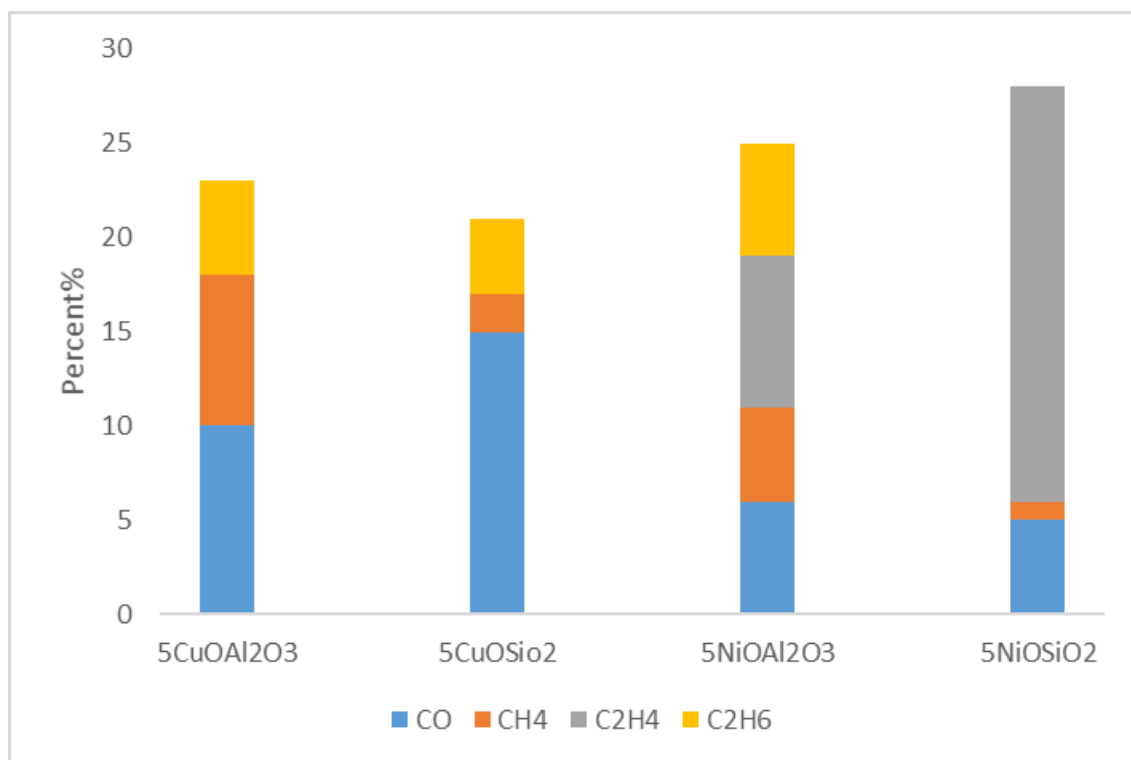
GC analysis was carried out to see the CO₂ reduced product distribution. The results are shown in Figure 28.



(a)



(b)



(c)

Figure 28 GC results of CO₂ reduction using plasma catalysis

To develop an understanding on the mechanistic aspects of the reduction reactions, BET analyses was carried out on the powder. Results are as follows indicated in Table 8.

The first observation is that loading metal oxides on supports results in an increased CO₂ reduction percentage as compare to bare support. The next observation was made on the difference of support; metal oxides loaded on alumina showed an increased percentage conversion as compare to silica. Overall, copper oxide loaded samples showed much greater conversion capacity then nickel oxide loaded samples. One interesting observation was about product selectivity, nickel oxide loaded samples showed development of C₂ species, but no such species were detected in case of copper oxide loaded samples. In case of copper oxide loaded samples, the major product was CO while in case of nickel oxide loaded samples, the major product was C₂.

The catalysts are made by using wet impregnation technique. In short, the load(metal salts such metal nitrate) and support are mixed in specific ratios so as to obtain a specific loading of metal oxide on support, ethanol is used to mix the solution and solvent to obtain a homogenous solid which is dried and then heated at temperatures of up to 400°C to obtain metal oxide of support such as alumina or silica.

This work focuses on alumina and silica and the purpose is to reduce CO₂ molecule under hydrogen plasma. As a first step, only hydrogen plasma's capability is tested for CO₂ reduction which rests at 5% on an optimal CO₂ flow rate. The composition of flow rate affects the hydrogen plasma capacity to reduce CO₂ molecule. At lower amounts of CO₂ in flow composition, almost 10% CO₂ reduction is observed while at higher composition ratios, the CO₂ reduction value dropped to less than 2%. In next experiments, supports such as alumina and silica are used and their capacity to reduce CO₂ molecule under hydrogen plasma is evaluated. Alumina showed reduction of CO₂ more than 20% while silica showed a reduction of up to 10%. Although the surface area of both the powders was almost 200m²/g.

On loading the metal oxides on supports, overall CO₂ reduction capacity of catalyst increased. Loading CuO on alumina increased the CO₂ reduction value up to 50%, increasing the amount of loading caused a slight decrease in CO₂ reduction output i.e. 40%. When the same support is loaded by nickel oxide, overall CO₂ reduction improved in comparison to bare alumina but it was lesser than the catalysts loaded with copper oxide. The reason being the difference in adsorption energy values for Ni²⁺ and Cu²⁺ since Al³⁺ site remains the same in both catalysts. Also, when the amount of loading in case of NiO is increased, same result obtained i.e. overall CO₂ reduction output got reduced. When the support is changes to silica, copper oxide loaded catalyst's CO₂ reduction performance dropped by almost 15% in comparison with copper oxide loaded on alumina. Same result obtained in nickel oxide loaded silica.

To understand the role of these surfaces in CO₂ reduction accompanied with hydrogen plasma, we need to look at the gaseous product distribution. The key difference is presence of ethene in case of nickel oxide loaded supports. Nickel oxide loaded samples on both alumina and silica has ethene in product gases while ethene was not present in case of CuO in alumina or silica, so we can say that Ni²⁺ is playing some role in the synthesis of ethene. In general, CuO loaded samples reduced CO₂ to co predominantly while Cu²⁺ samples reduced CO₂ to C₂ species predominantly. There was another peculiar observation, all the samples that contained Al₂O₃ favoured the formation of ethane, but ethane was absent in case of CuO/silica and NiO on silica. The amount of methane remained the same in almost all samples except NiO/silica where the amount decreased, which indicate the role of alumina and CuO in synthesis of methane. To verify if the catalyst chamber length and amount has anything to do with selectivity of gaseous products, experiments were carried out in 1ml volume, the results are indicated in Figure 28, which shows that there is not considerable difference in product distribution and thus length of

catalyst chamber or in other words the amount of catalyst has nothing to do with product distribution.

To further develop understanding the mechanistic aspects of product distribution, XRD studies were carried out to understand the catalyst chemical structure. Figure 26a,b shows the XRD patterns of silica and alumina supports. Alumina shows typical spinel structure while silica shows amorphous character. The support then loaded with copper nitrate and nickel nitrate salts. The characteristics peaks of nitrate salts are evident from Figure 25, important observation can be made from XRD patterns of nitrate loaded supports, 5CuNO₃ and 5NiNO₃ loaded on Al₂O₃ and silica did not show any characteristics peak in XRD while 10%loaded samples showed characteristic peaks as evident by Figure 25.

There is an interesting feature in the XRD patterns when the salt loaded support were heated up to 400°C, 5 and 10% Ni(NO₃)₂ should have reduced to NiO on Al₂O₃ but there was no NiO peak after heat treatment, same goes for 5CuNO₃ on Al₂O₃, no CuO peak was observed after heat treatment. But 10CuNO₃ on Al₂O₃ showed CuO peaks after heat treatment. Literature suggest that NiO forms a compound with Al₂O₃ i.e. NiAl₂O₄ which has a spinel structure, in simpler words, NiO got dissolved in Al₂O₃ and formed the compound which has a spinel structure which can be seen from XRD. Same goes for CuO on Al₂O₃ which also forms a compound but the solubility of CuO in Al₂O₃ is limited and for this reason we saw CuO peaks in case 10Cu(NO₃)₂/Al₂O₃.

As far as silica support is concerned, no such compound formation took place, both CuO and NiO characteristic peaks were visible in XRD pattern with support pattern in background as shown in Figure 25.

In the next step, the 5%CuO/Al₂O₃ and 5%NiO/SiO₂ are reduced using hydrogen plasma and XRD patterns were observed to see the formation of metal particle, 5%CuO/Al₂O₃ showed small amount of Cu metal formation from XRD while no such nickel metal peaks were observed in case of 5%NiO/SiO₂.

Surface areas of the powdered were measured through BET analyses and almost all powder showed surface areas between 180-220m²/g.

4.4 Conclusion

Various surfaces are created and tested for CO₂ reduction using hydrogen plasma. The materials focused to understand the reduction process were, alumina and silica supports along with copper and nickel oxides as loadings. The copper and nickel oxide were also reduced to their metallic forms on support using hydrogen plasma reduction. The change in the loading of support alters the selectivity of CO₂ reduced products. Nickel oxide showed selectivity to C₂ species in comparison to copper oxide while copper oxide loaded samples showed higher CO₂ reduction percentage as compare to nickel oxide loaded samples. In PCO₂R, both alumina and silica showed greater CO₂ conversion as compared to reduction by using plasma only- Plasma-5%, Silica-10%, Alumina-25% at 5%CO₂ in H₂. In PCO₂R, CuO favoured the formation of CO upto 10% while if CuO was absent the CO content was suppressed to less then 5% with a total CO₂ conversion upto 45%. NiO loaded supports showed the formation of unsaturated C₂ species upto 20% with a total CO₂ conversion of upto 30%. Alumina loaded catalysts showed the formation of CH₄ upto 5% while the same in Silica loaded sample was suppressed to less then 5% with a total CO₂ conversion range from 45%-30%. Saturated C₂ were absent in case of NiO/SiO₂, which indicates that CuO and Al₂O₃ favours the formation of saturated C₂ while NiO and SiO₂ favours the formation unsaturated C₂.

Chapter 5- Electrochemical HER using CuS and NiS

5.1 Introduction

Energy conversion and storage are the global issues at present which are intensely studied. Hydrogen has a high energy density when it comes to fuels¹⁰⁵ for transportation and domestic use. Electrochemical hydrogen production research is a hotspot, since it is predicted that all global leaders are working on cutting CO₂ emissions; to maintain the growth rate of global economy, alternatives of carbon based fuel will be required; the solution is hydrogen economy.

To produce hydrogen, there are many ways. Industrially, hydrogen is produced using steam reforming or steam-methane reforming, only 4% of total hydrogen production is produced electrochemically¹⁰⁶. In recent years, much work is done to improve the efficiency of electrochemical Hydrogen production. It is well known fact that platinum is most efficient catalyst for hydrogen production since it requires very small overpotential to split water, but due to its high cost, it makes the process non-economical. The alternative of platinum is found i.e. MoS. In present study, we have worked on developing sulphides, which are of earth abundant origins such as Ni and Cu sulphides. We have modified the surface of the sulphides using DBD plasma technique.

To confirm the effect, that plasma changes the morphology of the surface, and will eventually affect HER performance. We decided to test CuS and NiS. Both Cu and Ni are earth abundant and can be easily converted to the sulphide forms. The plasma treated samples are compared with non plasma treated for HER applications.

5.2 Experimental

Nickel sulphide (NiS) and Copper sulphide (CuS) are made by electrochemical deposition and thermal methods respectively. In a typical method for NiS, 0.1M thio urea is mixed with 0.1M NiCl₂ solution in 1:1 by molar ratio. Clean copper sheet is used as substrate for deposition of NiS. The deposition was carried out by scanning the voltage of cell between -1.0-+1.5V for at least 15cycles at 5mV/sec. Black coating appeared on copper which is NiS. For CuS synthesis, Copper is heated with excess sulphur at temperature of 150°C for 2hours, black CuS coating is obtained at the end of the experiment. To determine the compositions of metal sulphides, XRD, Raman spectroscopy and XPS is carried out. To observe the morphology SEM is carried out. At the end electromechanical evaluations are made for HER. The samples were also treated with plasma and tested for HER. Before conducting the HER experiments, EIS is carried out

to determine the solution resistance which is later used to compensate for voltage drop during HER. For EIS, the frequency is scanned through 10kHz-10Hz, with an amplitude of 5mV and DC potential of -0.5V.

5.3 Results and discussions

Typical electrodeposition profiles for NiS are shown in Figure 29. For CuS experiments are carried out on various temperatures i.e. 100, 150, 200°C for two hours each.

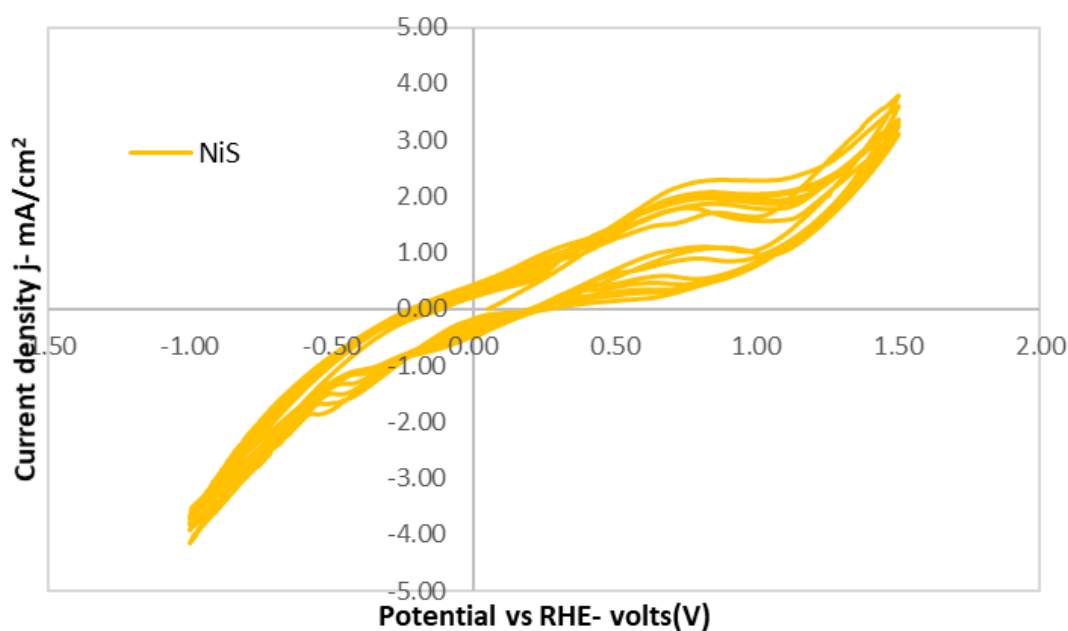
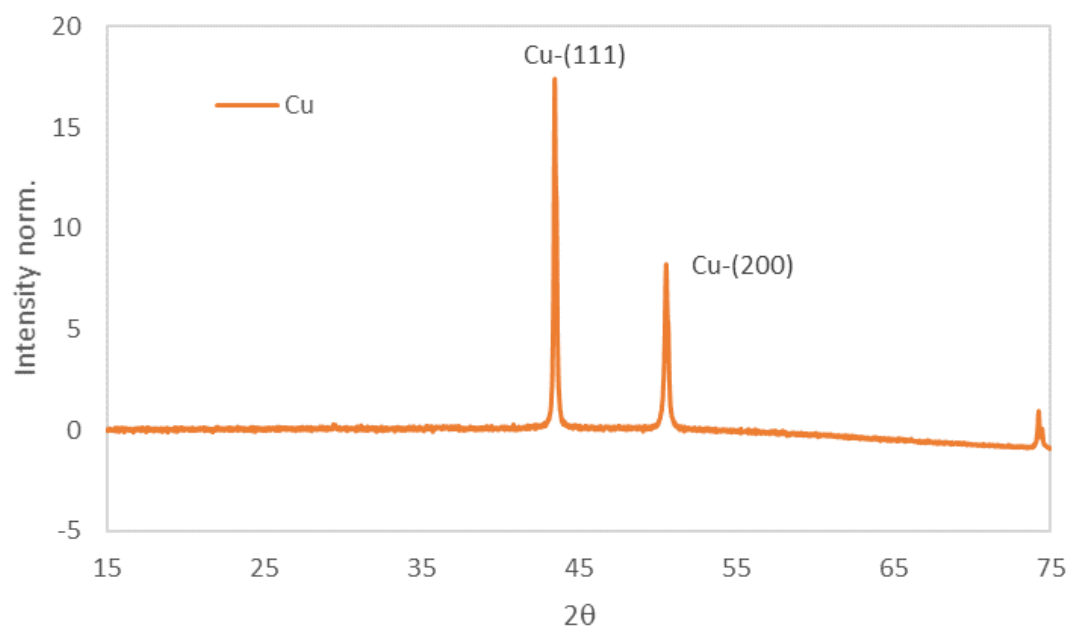
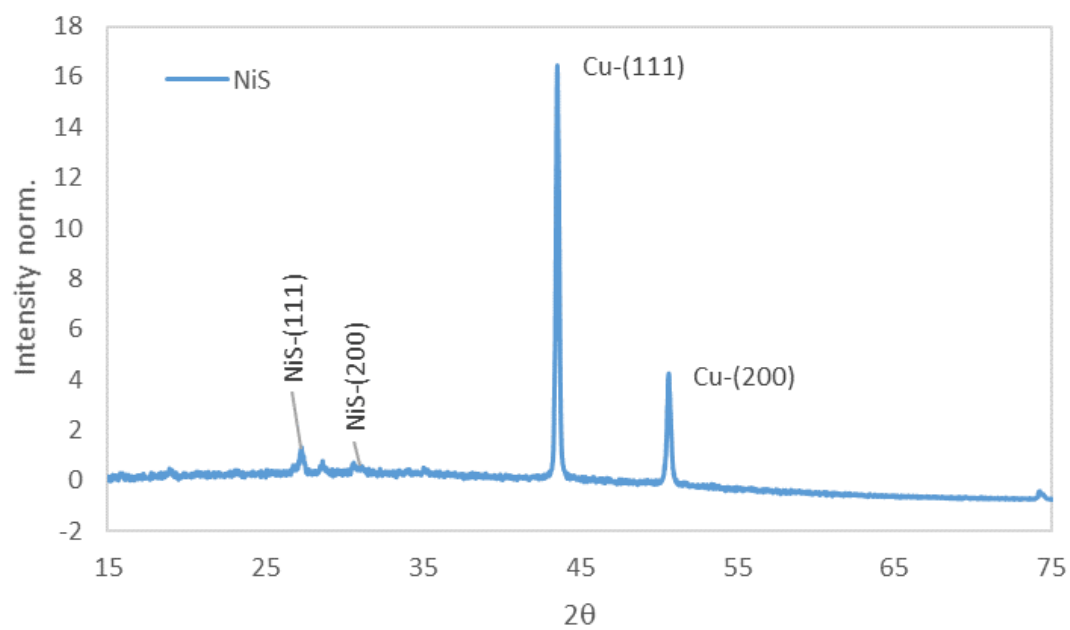


Figure 29 Electrodeposition of NiS- CV profiles

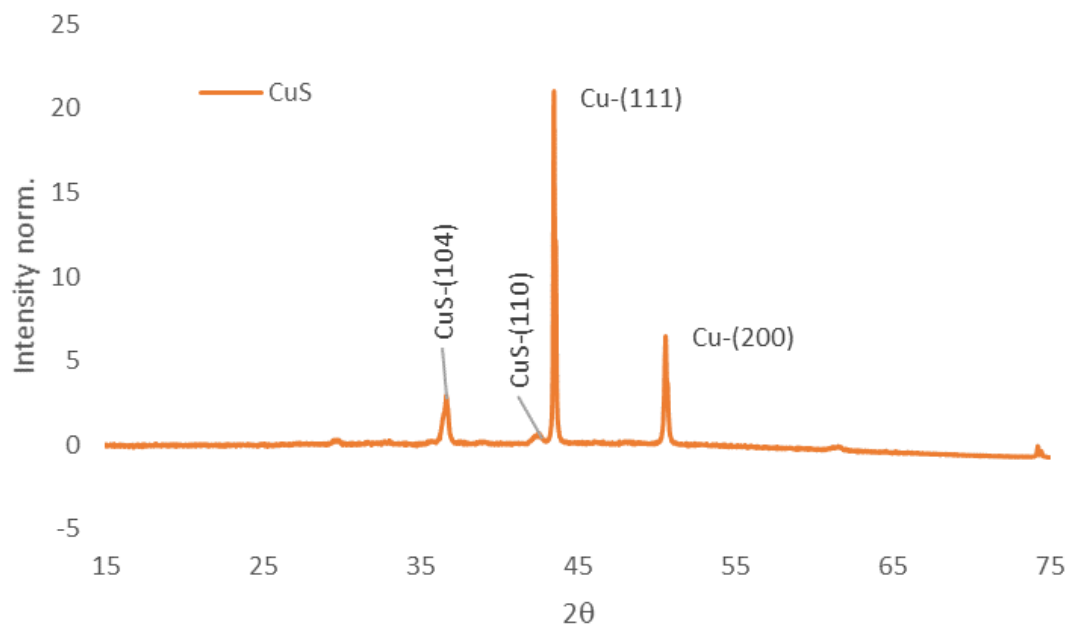
XRD analysis was carried out on the films and the results are shown in Figure 30. Due to small film thickness, XRD peaks for metal sulphides are quite small but difference is evident in the initial portion of XRD scan. For NiS, the peaks between 25-35° corresponds to (101) and (300) while for CuS the peaks between 35-44° corresponds to (104) and (110). Figure 30a shows the XRD pattern of bare copper surface. Figure 30b shows the XRD pattern of NiS deposited on copper, the appearance of peaks in the initial formation confirms the formation of NiS but since the thickness of the films is small, the peak intensities are also small. Similar observation is made for CuS in Figure 30c.



(a)



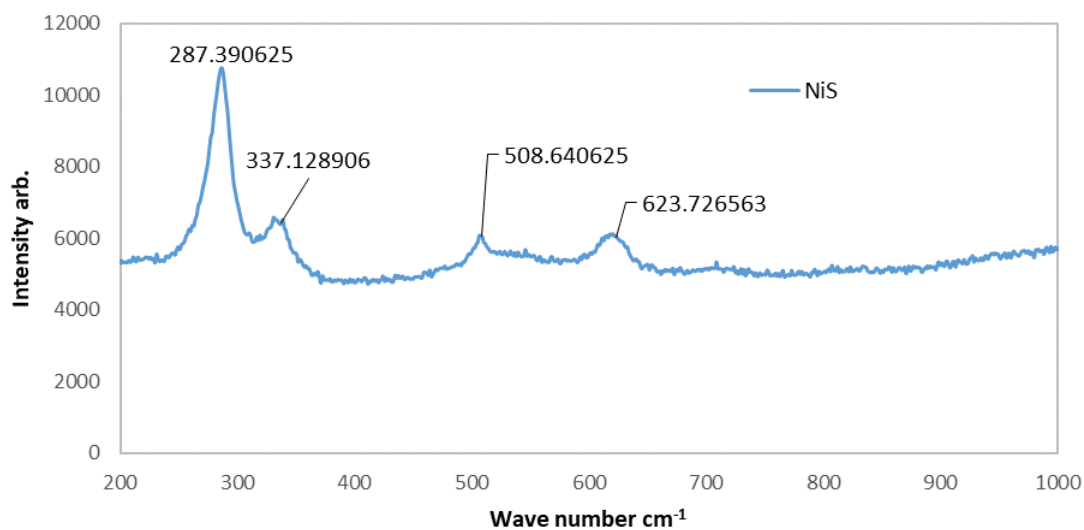
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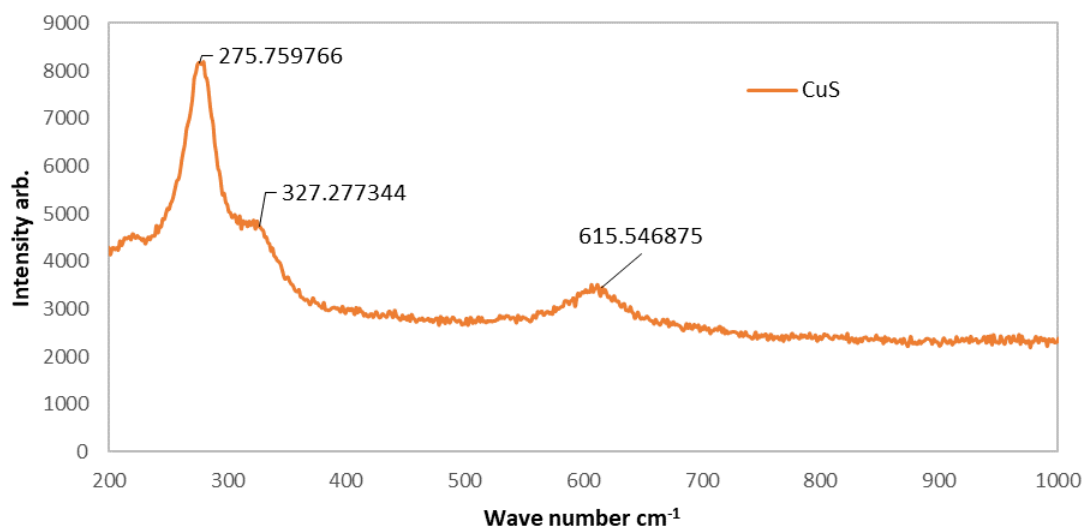
(c)

Figure 30 XRD patterns (a) Copper substrate (b) NiS on Cu substrate (c) CuS on Cu substrate

Raman spectroscopy was carried out to further confirm the evidence for the synthesis of films, Figure 31.



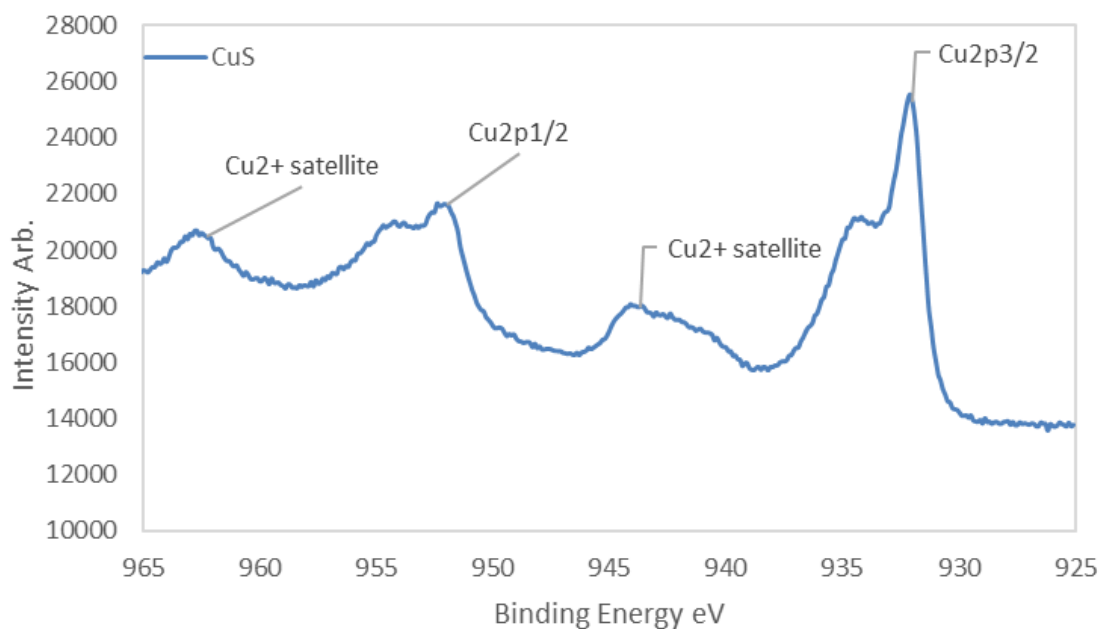
(a)



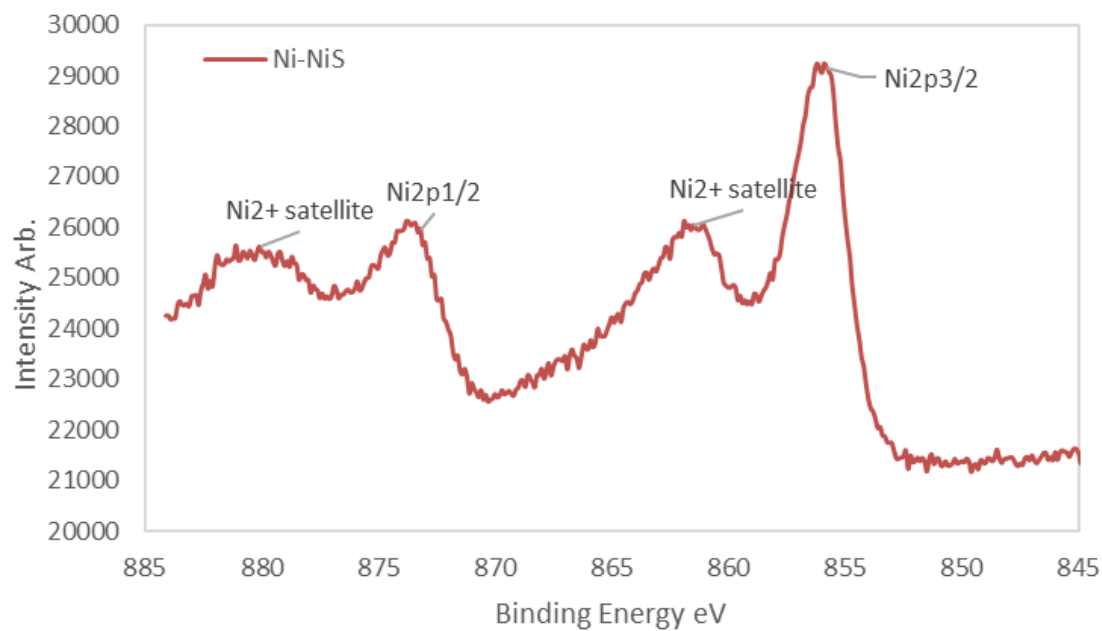
(b)

Figure 31 Ramans spectra 530nm laser (a) NiS (b) CuS

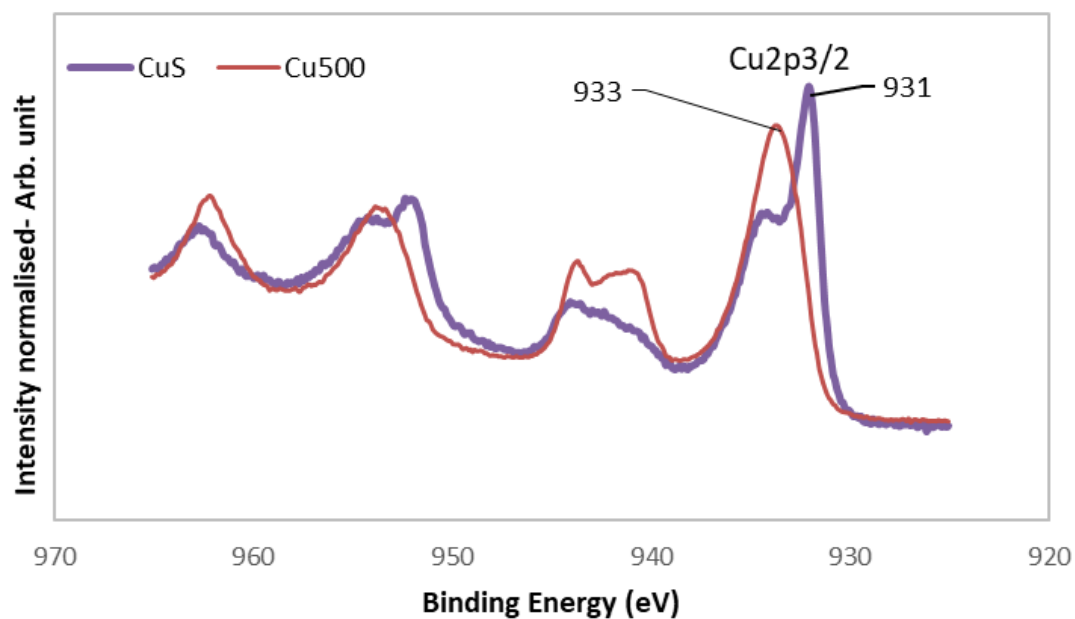
XPS is carried out to strengthen the case of sulphides. Following (Figure 32) are the XPS spectrum of Ni and Cu in the sulphide films. In Figure 32c, comparison of Cu2p_{3/2} peaks is shown which indicates the shift in the peak by 2eV, when the configuration of atoms is changed from oxygen to sulphur.



(a)



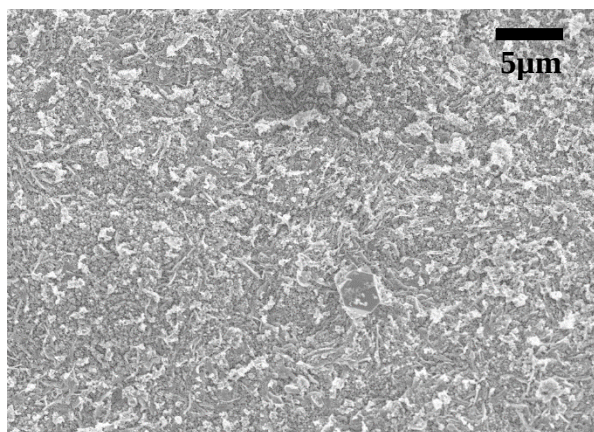
(b)



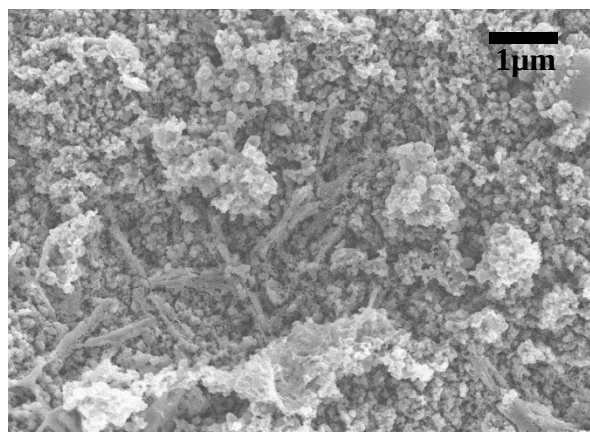
(c)

Figure 32 XPS spectra (a) Cu region in CuS (b) Ni region in NiS (c) comparison of XPS pattern Cu region for CuO(Cu500) and CuS

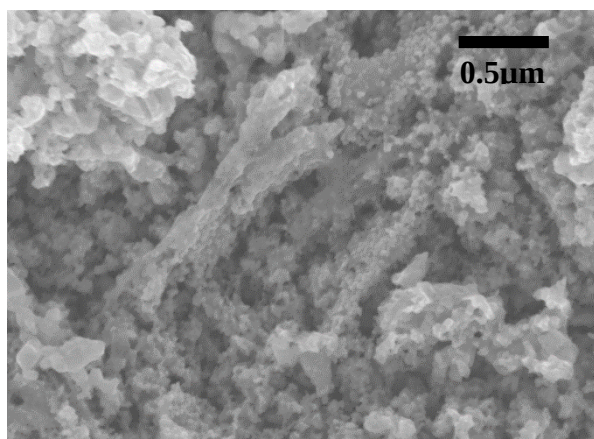
SEM imaging is carried out to observe surface morphology and the images are in Figure 33.



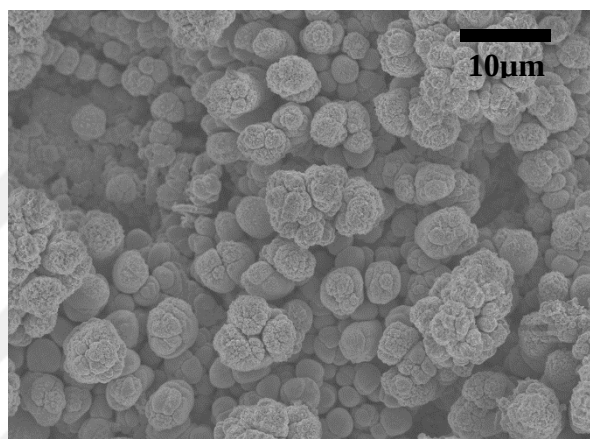
(a)



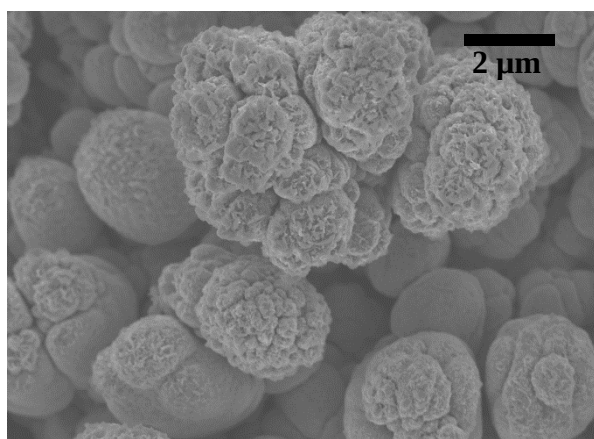
(b)



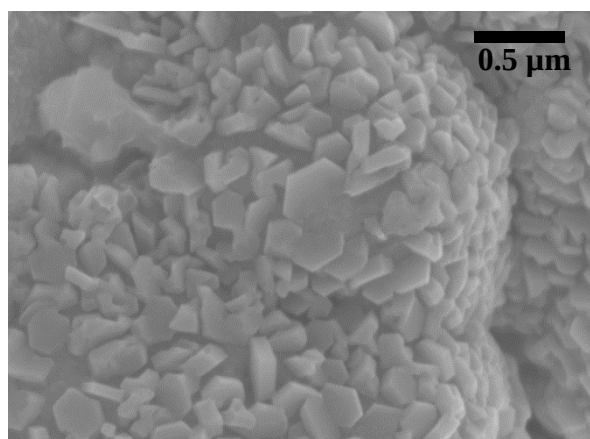
(c)



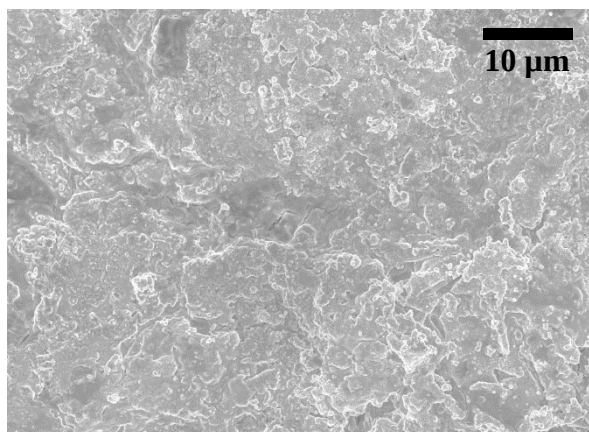
(d)



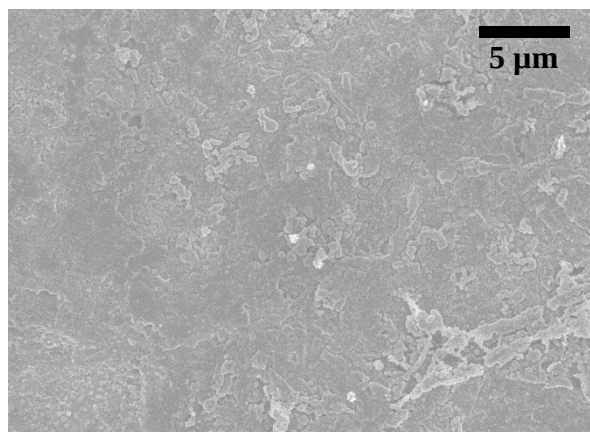
(e)



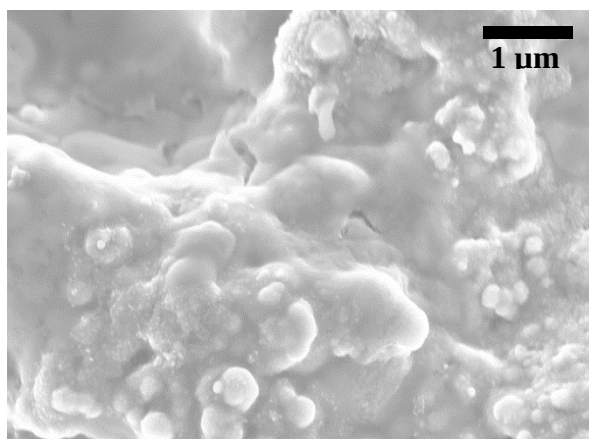
(f)



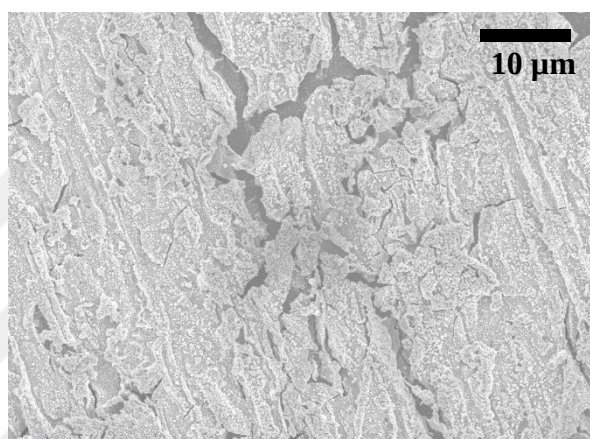
(g)



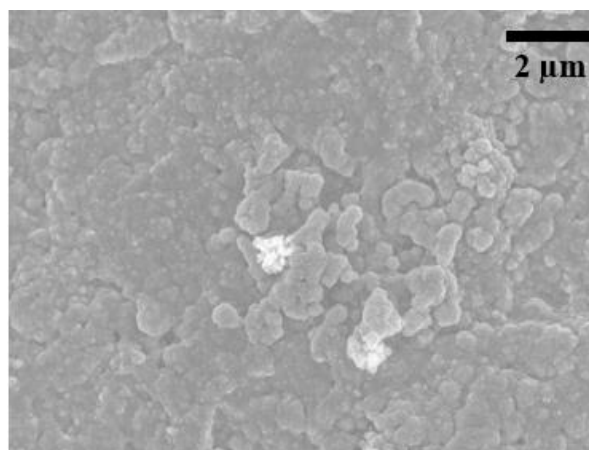
(h)



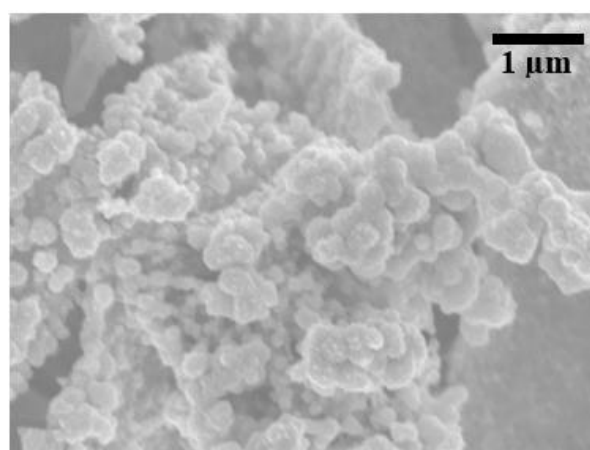
(i)



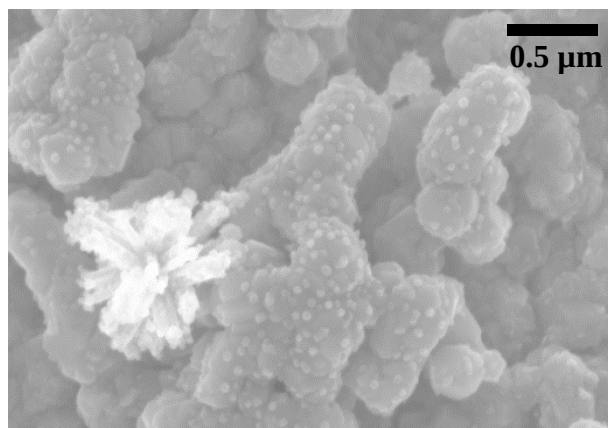
(j)



(k)



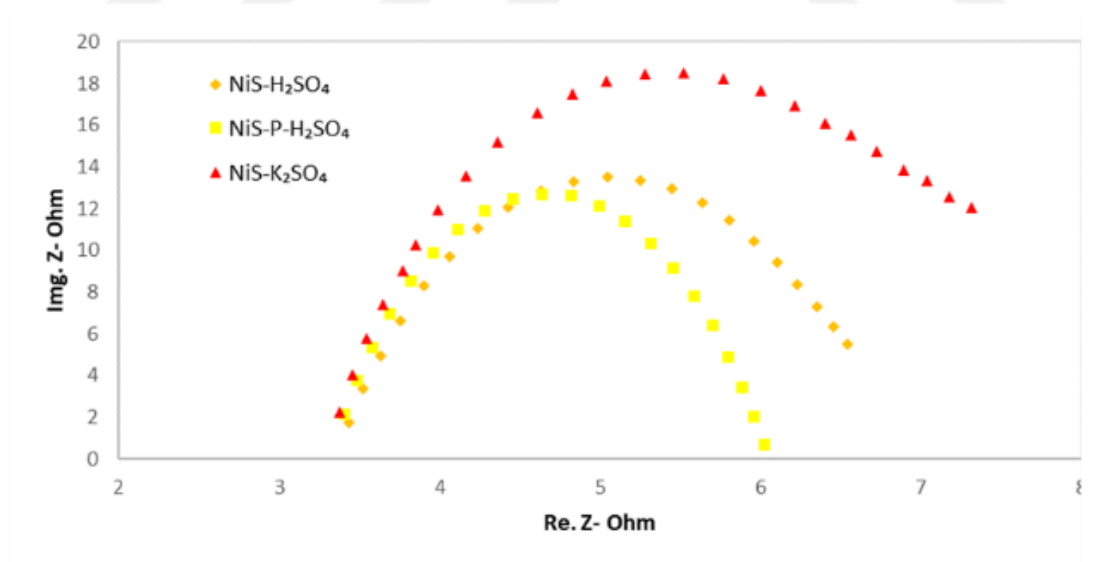
(l)



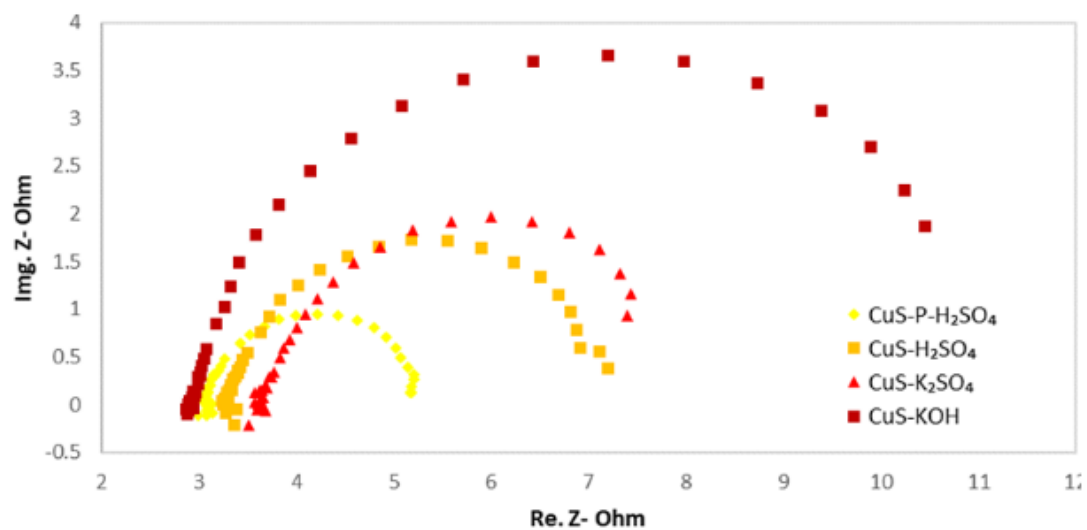
(m)

Figure 33 SEM images of (a-c) CuS (d-f) Plasma treated CuS (g-i) NiS (j-m) plasma treated NiS

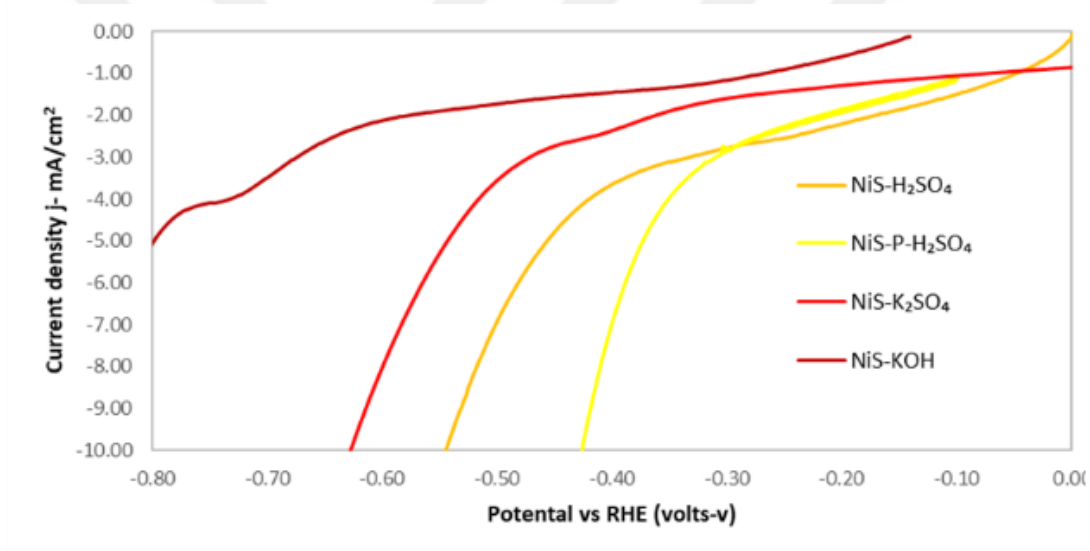
For electrochemical HER, the films were tested in three different solutions of H_2SO_4 , K_2SO_4 and KOH with a concentration of 0.5M. As a first step, EIS is carried out with in HER range and solution resistance is determined for the setup which is used later to compensate the excess voltage drop with in electrodes and solution interface. Results of HER analysis is indicated in Figure 34.



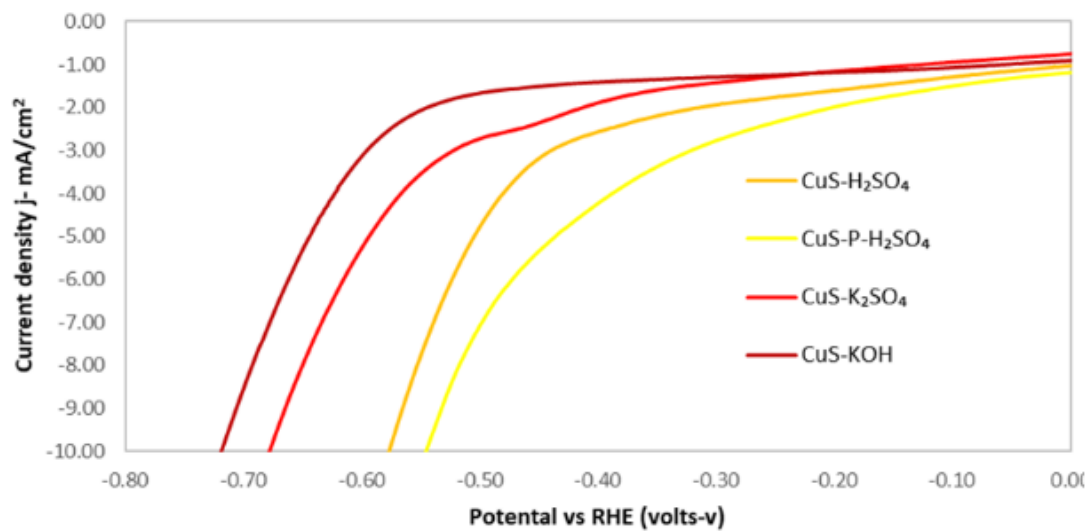
(a)



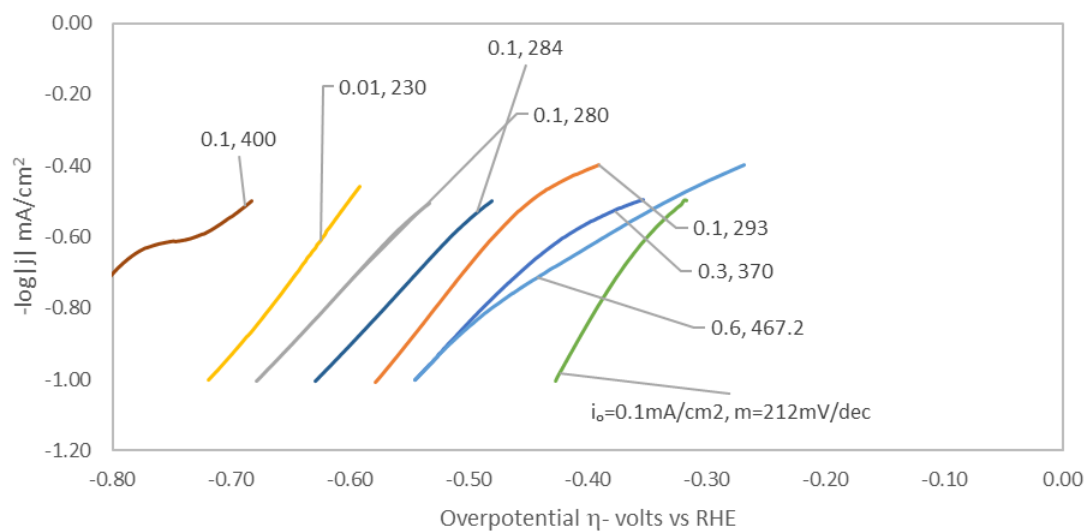
(b)



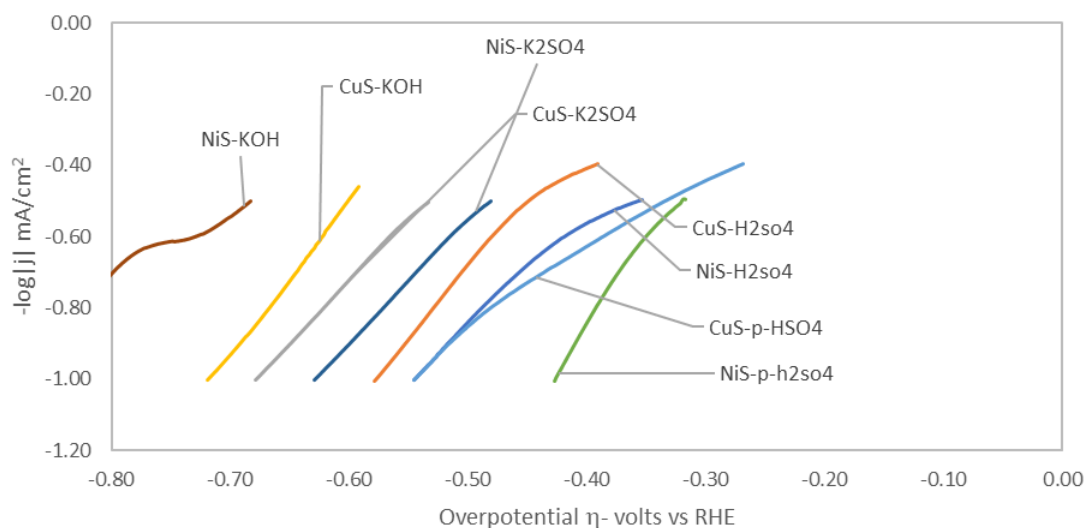
(c)



(d)



(e)



(f)

Figure 34(a-b) EIS spectra of various samples in different media (c-d) Polarisation curves (e-f) Tafel sloped for various samples

Table 9 HER performance parameters for CuS and NiS

Sample	Medium	Tafel slope (b) mV/dec	Exchange current density (i_0) A/cm ²	Overpotential (η) at 10mA/cm ²
CuS	H ₂ SO ₄	293	0.001	600
CuS-p	H ₂ SO ₄	467	0.006	550
CuS	K ₂ SO ₄	280	0.001	680
CuS	KOH	230	0.0001	720
NiS	H ₂ SO ₄	370	0.003	550
NiS-p	H ₂ SO ₄	212	0.001	435
NiS	K ₂ SO ₄	284	0.001	630
NiS	KOH	400	0.001	>1000

As a first attempt, both Ni and Cu sulphides were tried to be synthesised through thermal methods. CuS synthesis was successful but NiS was not synthesised. For NiS, electrochemical way was opted as indicated in various research papers^{107–109}. CuS was attempted to make through electrochemical way but thio-urea forms complex with copper ion and thus a similar method which worked for NiS; did not work for CuS.

After the samples are prepared, they were characterised for their chemical and morphological makeup and eventually tested for HER application. XRD results indicated in Figure 30, the peak intensities are quite low in both cases, since the film deposited in case of NiS was quite thin. Grazing incidence XRD was carried out to observe the change in peak intensities but it did not work. Raman spectroscopy was carried out and Raman spectra is clearly distinguishable in both cases as indicated in Figure 31. The peak at $280\text{-}290\text{cm}^{-1}$ is attributed to S-S interaction while the peaks ahead are characterised and S-metal interaction. To further affirm, the understanding of chemical makeup, XPS is carried out Figure 32. XPS data clearly indicated the presence of Cu^{2+} and Ni^{2+} species in the sample. Once it is established that films have the composition of CuS and NiS, the films were tested for HER.

As a first step for HER, solution resistance was determined by EIS(Figure 34 a-b). The solution resistance varied from 2-4ohms in each case which is used to adjust the I-V data for later experiments. For each experiment, LSVs are carried out in acidic, neutral and basic media. The LSVs data are converted to polarisation curves (Figure 34 c-d) and Tafel plot (Figure 34 e-f). The values of HER parameters are tabulated in Table 9. It is evident from the data that both CuS and NiS showed similar characteristics for HER. The Tafel slope varied from 230-400mV/dec which indicates that mixed mechanism (Tafel-Volmer-Heyrovsky) is involved for water reduction. The interesting feature is the reduction in overpotential values for both surfaces when treated with hydrogen plasma, reduced by 50-100mV. The values of exchange current densities are lower than metallic copper, which is an indication that the reduction process is sluggish.

Overall, the sulphides are synthesised and tested for HER and plasma treated sample performed better than the ones without plasma treatment.

5.4 Conclusion

In conclusion, both NiS and CuS were synthesised and treated with DBD hydrogen plasma. In HER, both plasma treated samples showed an improvement in overpotential to reach specific current density of $10\text{mA}/\text{cm}^2$ by upto 100mV. Further tests will be carried out for CO_2 reduction for these catalysts in future.

6. Conclusions and future work

Binding energy of intermediate on a surface is not only dependent on the chemical makeup of the material, but also on morphological structure of the materials, which in theory directs us that any material can be used to obtain the benchmark properties of reaction, just by controlling the morphology. We observed that the same materials i.e. copper, when tested for HER with two different morphologies of polished copper surface and metallic copper nanowires showed stark contrast in their efficiencies for the HER process. The overpotential to reach a current density of $10\text{mA}/\text{cm}^2$ became half the value on bulk surface and reach to the magnitude of 210mV from 400mV.

Metallic copper nanowires showed excellent selectivity towards gaseous products during electrochemical CO_2 reduction such as hydrogen, CO, and CH_4 . Since binding energy of intermediate on surface is changing which affects the intermediates interaction with the surface and thus, we observed an overall increase in gaseous products. Overall gaseous product content increase by up to 30% from a total value of 50%. One interesting observation is made during ECO₂R, as the applied potential to the electrode is increased the amount of methane and carbon monoxide is also increased, this behaviour was not present in the ECO₂R on bulk copper surface.

The change in the loading of support alters the selectivity of CO_2 reduced products. Nickel oxide showed selectivity to C_2 species in comparison to copper oxide while copper oxide loaded samples showed higher CO_2 reduction percentage as compare to nickel oxide loaded samples. Both Al_2O_3 and SiO_2 are acidic supports and it is understandable that they will hydrogenate the species; in this case CO_2 . The difference in the formation of saturated and unsaturated species gives us a little sense on the mechanistic aspects of the reactions. The pathway to reduced CO_2 species is such that, first the carbon gets rid of all the oxygen and then gets hydrogenated. If we apply this formulation to our existing catalysts, NiO/SiO_2 desorbs the unsaturated hydrocarbons at a faster rate than $\text{CuO}/\text{Al}_2\text{O}_3$ since the later produces saturated hydrocarbons.

In future, work will be directed on the lines of theoretical understanding of the calculations for binding energy of intermediate on surfaces for various reactions (computational side for H_2O and CO_2). Because if we understand on how we can calculate the binding energy of intermediate on a surface, we shall not need to make random surfaces and observe the products after testing, rather we can predict which material system will be more efficient.

The work can also be extended on developing a sustainable system to generate hydrogen and CO₂ reduced products with applicability to industrial scale, extending the working in photo-electrocatalysis direction and make use of available seawater and sunlight for energy resource. Studies will also be performed on developing a plasma generator using various gases with two key application areas, one in modification of surfaces and two in CO₂ reduction. In future studies, work will be extended on metal sulphides and nitrides for HER and CO₂R.



7. References

- (1) Khezri, B.; Fisher, A. C.; Pumera, M. CO₂ reduction: The Quest for Electrocatalytic Materials. *J. Mater. Chem. A* **2017**, 5 (18), 8230–8246. <https://doi.org/10.1039/c6ta09875d>.
- (2) Nakajima, K.; Takahashi, K.; Tanaka, M.; Kuroki, T.; Okubo, M. CO₂ reduction Using Adsorption Followed by Nonthermal Plasma Treatment. *J. Phys. Conf. Ser.* **2015**, 646 (1). <https://doi.org/10.1088/1742-6596/646/1/012056>.
- (3) Alper, E.; Yuksel Orhan, O. CO₂ Utilization: Developments in Conversion Processes. *Petroleum* **2017**, 3 (1), 109–126. <https://doi.org/10.1016/j.petlm.2016.11.003>.
- (4) Jones, J.-P.; Prakash, G. K. S.; Olah, G. A. Electrochemical CO₂ Reduction: Recent Advances and Current Trends. *Isr. J. Chem.* **2014**, 54 (10), 1451–1466. <https://doi.org/10.1002/ijch.201400081>.
- (5) Qiao, S. Z.; Zheng, Y.; Jiao, Y.; Jaroniec, M.; Qiao, S. Z. Advancing the Electrochemistry of the Hydrogen- Evolution Reaction through Combining Experiment and Theory. **2015**, 52–65. <https://doi.org/10.1002/anie.201407031>.
- (6) Bentley, R. W. Global Oil and Gas Depletion: An Overview. *Energy Policy* **2002**, 30 (3), 189–205. [https://doi.org/10.1016/S0301-4215\(01\)00144-6](https://doi.org/10.1016/S0301-4215(01)00144-6).
- (7) Perkins, C.; Weimer, A. W. Likely Near-Term Solar-Thermal Water Splitting Technologies. *Int. J. Hydrogen Energy* **2004**, 29 (15), 1587–1599. <https://doi.org/10.1016/j.ijhydene.2004.02.019>.
- (8) Bolton, J. R.; Strickler, S. J.; Connolly, J. S. Limiting and Realizable Efficiencies of Solar Photolysis of Water. *Nature* **1985**, 316 (6028), 495–500. <https://doi.org/10.1038/316495a0>.
- (9) Hisatomi, T.; Domen, K. Progress in the Demonstration and Understanding of Water Splitting Using Particulate Photocatalysts. *Curr. Opin. Electrochem.* **2017**, 2 (1), 148–154. <https://doi.org/10.1016/j.coelec.2017.04.005>.
- (10) Mcpherson, E. G.; Simpson, J. R. Through Urban Forestry : Guidelines for Professional and Volunteer Tree Planters Publisher : *United States Dep. Agric.* **1999**, 248.

- (11) Bar-On, Y. M.; Phillips, R.; Milo, R. The Biomass Distribution on Earth. *Proc. Natl. Acad. Sci.* **2018**, *115* (25), 6506 LP – 6511. <https://doi.org/10.1073/pnas.1711842115>.
- (12) Crowther, T. W.; Glick, H. B.; Covey, K. R.; Bettigole, C.; Maynard, D. S.; Thomas, S. M.; Smith, J. R.; Hintler, G.; Duguid, M. C.; Amatulli, G.; et al. Mapping Tree Density at a Global Scale. *Nature* **2015**, *525*, 201.
- (13) Mitchell, L. E.; Lin, J. C.; Bowling, D. R.; Pataki, D. E.; Strong, C.; Schauer, A. J.; Bares, R.; Bush, S. E.; Stephens, B. B.; Mendoza, D.; et al. Long-Term Urban Carbon Dioxide Observations Reveal Spatial and Temporal Dynamics Related to Urban Characteristics and Growth. *Proc. Natl. Acad. Sci.* **2018**, *115* (12), 2912 LP – 2917. <https://doi.org/10.1073/pnas.1702393115>.
- (14) Say, N. P.; Yücel, M. Energy Consumption and CO₂ Emissions in Turkey: Empirical Analysis and Future Projection Based on an Economic Growth. *Energy Policy* **2006**, *34* (18), 3870–3876. <https://doi.org/10.1016/j.enpol.2005.08.024>.
- (15) Saracoglu, N. The Biomass Potential of Turkey for Energy Production: Part I. *Energy Sources, Part B Econ. Planning, Policy* **2010**, *5* (3), 272–278. <https://doi.org/10.1080/15567240802532981>.
- (16) Sharifi-Asl, S.; Macdonald, D. D. Investigation of the Kinetics and Mechanism of the Hydrogen Evolution Reaction on Copper. *J. Electrochem. Soc.* **2013**, *160* (6), H382–H391. <https://doi.org/10.1149/2.143306jes>.
- (17) Farinazzo Bergamo Dias Martins, P.; Papa Lopes, P.; Ticianelli, E. A.; Stamenkovic, V. R.; Markovic, N. M.; Strmcnik, D. Hydrogen Evolution Reaction on Copper: Promoting Water Dissociation by Tuning the Surface Oxophilicity. *Electrochem. commun.* **2019**, *100*, 30–33. <https://doi.org/10.1016/J.ELECOM.2019.01.006>.
- (18) Rodríguez, J.; Campbell, K.; Fogarty, J.; Williams, R. Florida State University Libraries. *Fam Med* **2014**, *46* (2), 100–104.
- (19) Ganesh, I. Conversion of Carbon Dioxide into Methanol - A Potential Liquid Fuel: Fundamental Challenges and Opportunities (a Review). *Renew. Sustain. Energy Rev.* **2014**, *31*, 221–257. <https://doi.org/10.1016/j.rser.2013.11.045>.
- (20) Lu, Q.; Jiao, F. Electrochemical CO₂ Reduction: Electrocatalyst, Reaction Mechanism, and Process Engineering. *Nano Energy* **2016**, *29*, 439–456.

<https://doi.org/10.1016/j.nanoen.2016.04.009>.

- (21) Kehlet, J. Trends in the Exchange Current for Hydrogen Evolution. **2005**, 2–6.
<https://doi.org/10.1149/1.1856988>.
- (22) Lieberman, M. A.; Lichtenberg, A. J. *Principles of Plasma Discharges and Materials Processing*; John Wiley & Sons, 2005.
- (23) Oh, Y.-J.; Park, G.-S.; Chung, C.-H. Planarization of Copper Layer for Damascene Interconnection by Electrochemical Polishing in Alkali-Based Solution. *J. Electrochem. Soc. - J Electrochem SOC* **2006**, 153. <https://doi.org/10.1149/1.2200288>.
- (24) Khor, A.; Leung, P. K.; Mohamed, M. R.; Flox, C.; Xu, Q.; A. Shah, A. *Review of Zinc-Based Hybrid Flow Batteries: From Fundamentals to Applications*; 2018; Vol. 8.
<https://doi.org/10.1016/j.mtener.2017.12.012>.
- (25) Ma, M.; Trzeźniewski, B. J.; Xie, J.; Smith, W. A. Selective and Efficient Reduction of Carbon Dioxide to Carbon Monoxide on Oxide-Derived Nanostructured Silver Electrocatalysts. *Angew. Chemie - Int. Ed.* **2016**, 55 (33), 9748–9752.
<https://doi.org/10.1002/anie.201604654>.
- (26) Lau, G. P. S.; Schreier, M.; Vasilyev, D.; Scopelliti, R.; Grätzel, M.; Dyson, P. J. New Insights into the Role of Imidazolium-Based Promoters for the Electroreduction of CO₂ on a Silver Electrode. *J. Am. Chem. Soc.* **2016**, 138 (25), 7820–7823.
<https://doi.org/10.1021/jacs.6b03366>.
- (27) Kim, C.; Jeon, H. S.; Eom, T.; Jee, M. S.; Kim, H.; Friend, C. M.; Min, B. K.; Hwang, Y. J. Achieving Selective and Efficient Electrocatalytic Activity for CO₂ Reduction Using Immobilized Silver Nanoparticles. *J. Am. Chem. Soc.* **2015**, 137 (43), 13844–13850. <https://doi.org/10.1021/jacs.5b06568>.
- (28) Liu, S.; Tao, H.; Zeng, L.; Liu, Q.; Xu, Z.; Liu, Q.; Luo, J. L. Shape-Dependent Electrocatalytic Reduction of CO₂ to CO on Triangular Silver Nanoplates. *J. Am. Chem. Soc.* **2017**, 139 (6), 2160–2163. <https://doi.org/10.1021/jacs.6b12103>.
- (29) Garza, A.; Bell, A. T.; Head-Gordon, M. On the Mechanism of CO₂ Reduction at Copper Surfaces: Pathways to C₂ Products. *ACS Catal.* **2018**, acscatal.7b03477.
<https://doi.org/10.1021/acscatal.7b03477>.
- (30) Kuhl, K. P.; Cave, E. R.; Abram, D. N.; Jaramillo, T. F. New Insights into the

- Electrochemical Reduction of Carbon Dioxide on Metallic Copper Surfaces. *Energy Environ. Sci.* **2012**, 5 (5), 7050–7059. <https://doi.org/10.1039/c2ee21234j>.
- (31) Hori, Y.; Takahashi, R.; Yoshinami, Y.; Murata, A. Electrochemical Reduction of CO at a Copper Electrode. *J. Phys. Chem. B* **1997**, 101 (36), 7075–7081. <https://doi.org/10.1021/jp970284i>.
- (32) Loiudice, A.; Lobaccaro, P.; Kamali, E. A.; Thao, T.; Huang, B. H.; Ager, J. W.; Buonsanti, R. Tailoring Copper Nanocrystals towards C2 Products in Electrochemical CO2 Reduction. *Angew. Chemie - Int. Ed.* **2016**, 55 (19), 5789–5792. <https://doi.org/10.1002/anie.201601582>.
- (33) Mistry, H.; Varela, A. S.; Bonifacio, C. S.; Zegkinoglou, I.; Sinev, I.; Choi, Y. W.; Kisslinger, K.; Stach, E. A.; Yang, J. C.; Strasser, P.; et al. Highly Selective Plasma-Activated Copper Catalysts for Carbon Dioxide Reduction to Ethylene. *Nat. Commun.* **2016**, 7, 1–8. <https://doi.org/10.1038/ncomms12123>.
- (34) Cheng, T.; Xiao, H.; Goddard, W. A. Reaction Mechanisms for the Electrochemical Reduction of CO2 to CO and Formate on the Cu(100) Surface at 298 K from Quantum Mechanics Free Energy Calculations with Explicit Water. *J. Am. Chem. Soc.* **2016**, 138 (42), 13802–13805. <https://doi.org/10.1021/jacs.6b08534>.
- (35) Ma, M.; Djanashvili, K.; Smith, W. A. Controllable Hydrocarbon Formation from the Electrochemical Reduction of CO2 over Cu Nanowire Arrays. *Angew. Chemie - Int. Ed.* **2016**, 55 (23), 6680–6684. <https://doi.org/10.1002/anie.201601282>.
- (36) Gan, L.; Fang, J.; Zhang, K.; Lai, Y.; Li, J. A Binary Copper-Nickel Hierarchical Structure Templated by Metal-Organic Frameworks for Efficient Hydrogen Evolution Reaction. *Int. J. Hydrogen Energy* **2019**, 44 (5), 2841–2847. <https://doi.org/10.1016/J.IJHYDENE.2018.12.025>.
- (37) Monama, G. R.; Modibane, K. D.; Ramohlola, K. E.; Molapo, K. M.; Hato, M. J.; Makhafole, M. D.; Mashao, G.; Mdluli, S. B.; Iwuoha, E. I. Copper(II) Phthalocyanine/Metal Organic Framework Electrocatalyst for Hydrogen Evolution Reaction Application. *Int. J. Hydrogen Energy* **2019**, 44 (34), 18891–18902. <https://doi.org/10.1016/j.ijhydene.2019.02.052>.
- (38) Döner, A. Hydrogen Evolution on Pd Modified CoCuZn and CoMnZn Cathodes. *Int.*

- J. Hydrogen Energy* **2018**, 43 (51), 22797–22806.
<https://doi.org/10.1016/j.ijhydene.2018.10.160>.
- (39) Sivasakthi, P.; Premalatha, S.; Bapu, G. N. K. R.; Chandrasekaran, M. Pulse Electrodeposited Ni-CeO₂Gd Doped Nanocomposite on Copper Foam as an Electrocatalysts for Hydrogen Evolution Reaction. *Int. J. Hydrogen Energy* **2017**, 42 (8), 4741–4750. <https://doi.org/10.1016/j.ijhydene.2017.01.164>.
- (40) Farsak, M.; Kardaş, G. Effect of Current Change on Iron-Copper-Nickel Coating on Nickel Foam for Hydrogen Production. *Int. J. Hydrogen Energy* **2019**, 44 (27), 14151–14156. <https://doi.org/10.1016/j.ijhydene.2018.07.141>.
- (41) Jin, X.; Li, J.; Cui, Y.; Liu, X.; Wang, K.; Zhou, Y.; Yang, W.; Zhang, X.; Zhang, C.; Jiang, X.; et al. In-Situ Synthesis of Porous Ni₂P Nanosheets for Efficient and Stable Hydrogen Evolution Reaction. *Int. J. Hydrogen Energy* **2019**, 44 (12), 5739–5747. <https://doi.org/10.1016/j.ijhydene.2019.01.042>.
- (42) Lu, Y.; Geng, S.; Wang, S.; Rao, S.; Huang, Y.; Zou, X.; Zhang, Y.; Xu, Q.; Lu, X. Electrodeposition of Ni–Mo–Cu Coatings from Roasted Nickel Matte in Deep Eutectic Solvent for Hydrogen Evolution Reaction. *Int. J. Hydrogen Energy* **2019**, 44 (12), 5704–5716. <https://doi.org/10.1016/j.ijhydene.2019.01.072>.
- (43) Li, Y.; Zhang, X.; Hu, A.; Li, M. Morphological Variation of Electrodeposited Nanostructured Ni-Co Alloy Electrodes and Their Property for Hydrogen Evolution Reaction. *Int. J. Hydrogen Energy* **2018**, 43, 22012–22020. <https://doi.org/10.1016/j.ijhydene.2018.10.038>.
- (44) Ali, Y.; Nguyen, V. T.; Nguyen, N. A.; Shin, S.; Choi, H. S. Transition-Metal-Based NiCoS/C-Dot Nanoflower as a Stable Electrocatalyst for Hydrogen Evolution Reaction. *Int. J. Hydrogen Energy* **2019**, 44 (16), 8214–8222. <https://doi.org/10.1016/j.ijhydene.2019.01.297>.
- (45) Siwek, K. I.; Eugénio, S.; Santos, D. M. F.; Silva, M. T.; Montemor, M. F. 3D Nickel Foams with Controlled Morphologies for Hydrogen Evolution Reaction in Highly Alkaline Media. *Int. J. Hydrogen Energy* **2019**, 44 (3), 1701–1709. <https://doi.org/10.1016/j.ijhydene.2018.11.070>.
- (46) Cho, G.; Kim, H.; Park, Y. S.; Hong, Y. K.; Ha, D. H. Phase Transformation of Iron

- Phosphide Nanoparticles for Hydrogen Evolution Reaction Electrocatalysis. *Int. J. Hydrogen Energy* **2018**, 43 (24), 11326–11334.
<https://doi.org/10.1016/j.ijhydene.2018.02.197>.
- (47) Ma, B.; Yang, Z.; Yuan, Z.; Chen, Y. Effective Surface Roughening of Three-Dimensional Copper Foam via Sulfurization Treatment as a Bifunctional Electrocatalyst for Water Splitting. *Int. J. Hydrogen Energy* **2019**, 44 (3), 1620–1626.
<https://doi.org/10.1016/j.ijhydene.2018.11.115>.
- (48) Liu, Y.; Lu, H.; Kou, X. Electrodeposited Ni-Co-Sn Alloy as a Highly Efficient Electrocatalyst for Water Splitting. *Int. J. Hydrogen Energy* **2019**, 44 (16), 8099–8108.
<https://doi.org/10.1016/j.ijhydene.2019.02.078>.
- (49) Farahbakhsh, N.; Sanjabi, S. Activated Cu/Cu₂O Foam with Ni Nanoparticles for Electrocatalytic Activity Enhancement of Hydrogen Evolution Reaction (HER) in Acidic Media. *J. Ind. Eng. Chem.* **2019**, 70, 211–225.
<https://doi.org/10.1016/j.jiec.2018.10.018>.
- (50) Sun, J.-S.; Wen, Z.; Han, L.-P.; Chen, Z.-W.; Lang, X.-Y.; Jiang, Q. Nonprecious Intermetallic Al₇Cu₄Ni Nanocrystals Seamlessly Integrated in Freestanding Bimodal Nanoporous Copper for Efficient Hydrogen Evolution Catalysis. *Adv. Funct. Mater.* **2018**, 28 (14), 1706127. <https://doi.org/10.1002/adfm.201706127>.
- (51) Ahn, B. W.; Kim, T. Y.; Kim, S. H.; Song, Y. Il; Suh, S. J. Amorphous MoS₂ Nanosheets Grown on Copper@nickel-Phosphorous Dendritic Structures for Hydrogen Evolution Reaction. *Appl. Surf. Sci.* **2018**, 432, 183–189.
<https://doi.org/10.1016/j.apsusc.2017.06.262>.
- (52) Zhang, H.; Ren, W.; Guan, C.; Cheng, C. Pt Decorated 3D Vertical Graphene Nanosheet Arrays for Efficient Methanol Oxidation and Hydrogen Evolution Reactions. *J. Mater. Chem. A* **2017**, 5 (41), 22004–22011.
<https://doi.org/10.1039/c7ta07340b>.
- (53) Kas, R. Electrochemical Carbon Dioxide Reduction on Rough Copper Surfaces. **2016**.
<https://doi.org/10.3990/1.9789036540469>.
- (54) Gao, S.; Lin, Y.; Jiao, X.; Sun, Y.; Luo, Q.; Zhang, W.; Li, D.; Yang, J.; Xie, Y. Partially Oxidized Atomic Cobalt Layers for Carbon Dioxide Electroreduction to

- Liquid Fuel. *Nature* **2016**, 529 (7584), 68–71. <https://doi.org/10.1038/nature16455>.
- (55) Taifan, W.; Boily, J. F.; Baltrusaitis, J. Surface Chemistry of Carbon Dioxide Revisited. *Surf. Sci. Rep.* **2016**, 71 (4), 595–671. <https://doi.org/10.1016/j.surfrep.2016.09.001>.
- (56) Hummadi, K. K.; Luiten-Olieman, M. W. J.; Mul, G.; de Wit, P.; Benes, N. E.; Milbrat, A.; Kas, R.; Kortlever, R.; Koper, M. T. M. Three-Dimensional Porous Hollow Fibre Copper Electrodes for Efficient and High-Rate Electrochemical Carbon Dioxide Reduction. *Nat. Commun.* **2016**, 7 (1), 1–7. <https://doi.org/10.1038/ncomms10748>.
- (57) Kortlever, R.; Peters, I.; Balemans, C.; Kas, R.; Kwon, Y.; Mul, G.; Koper, M. T. M. Palladium-Gold Catalyst for the Electrochemical Reduction of CO₂ to C₁-C₅ hydrocarbons. *Chem. Commun.* **2016**, 52 (67), 10229–10232. <https://doi.org/10.1039/c6cc03717h>.
- (58) Hussain, J.; Jónsson, H.; Skúlason, E. Faraday Efficiency and Mechanism of Electrochemical Surface Reactions: CO₂ Reduction and H₂ Formation on Pt(111). *Faraday Discuss.* **2016**, 195, 619–636. <https://doi.org/10.1039/C6FD00114A>.
- (59) Coskun, H.; Aljabour, A.; De Luna, P.; Farka, D.; Greunz, T.; Stifter, D.; Kus, M.; Zheng, X.; Liu, M.; Hassel, A. W.; et al. Biofunctionalized Conductive Polymers Enable Efficient CO₂ electroreduction. *Sci. Adv.* **2017**, 3 (8), 1–8. <https://doi.org/10.1126/sciadv.1700686>.
- (60) Feaster, J. T.; Shi, C.; Cave, E. R.; Hatsukade, T.; Abram, D. N.; Kuhl, K. P.; Hahn, C.; Nørskov, J. K.; Jaramillo, T. F.; Saito, K.; et al. Understanding Selectivity for the Electrochemical Reduction of Carbon Dioxide to Formic Acid and Carbon Monoxide on Metal Electrodes. *ACS Catal.* **2017**, 7 (7), 4822–4827. <https://doi.org/10.1021/acscatal.7b00687>.
- (61) Cave, E. R.; Montoya, J. H.; Kuhl, K. P.; Abram, D. N.; Hatsukade, T.; Shi, C.; Hahn, C.; Nørskov, J. K.; Jaramillo, T. F. Electrochemical CO₂ reduction on Au Surfaces: Mechanistic Aspects Regarding the Formation of Major and Minor Products. *Phys. Chem. Chem. Phys.* **2017**, 19 (24), 15856–15863. <https://doi.org/10.1039/c7cp02855e>.
- (62) Hatsukade, T.; Kuhl, K. P.; Cave, E. R.; Abram, D. N.; Feaster, J. T.; Jongerius, A. L.;

- Hahn, C.; Jaramillo, T. F. Carbon Dioxide Electroreduction Using a Silver–Zinc Alloy. *Energy Technol.* **2017**, *5* (6), 955–961. <https://doi.org/10.1002/ente.201700087>.
- (63) Ma, M.; Liu, K.; Shen, J.; Kas, R.; Smith, W. A. In Situ Fabrication and Reactivation of Highly Selective and Stable Ag Catalysts for Electrochemical CO₂ Conversion. *ACS Energy Lett.* **2018**, *3* (6), 1301–1306. <https://doi.org/10.1021/acsenenergylett.8b00472>.
- (64) Moreno-García, P.; Schlegel, N.; Zanetti, A.; Cedeno López, A.; Gálvez-Vázquez, M. D. J.; Dutta, A.; Rahaman, M.; Broekmann, P. Selective Electrochemical Reduction of CO₂ to CO on Zn-Based Foams Produced by Cu²⁺ and Template-Assisted Electrodeposition. *ACS Appl. Mater. Interfaces* **2018**, *10* (37), 31355–31365. <https://doi.org/10.1021/acsami.8b09894>.
- (65) Proppe, A. H.; De Luna, P.; Todorović, P.; Shekhah, O.; Baek, S.-W.; Choi, J.; Dinh, C.-T.; Wang, Y.; García de Arquer, F. P.; Tan, C. S.; et al. Metal–Organic Frameworks Mediate Cu Coordination for Selective CO₂ Electroreduction. *J. Am. Chem. Soc.* **2018**, *140* (36), 11378–11386. <https://doi.org/10.1021/jacs.8b06407>.
- (66) Feng, Y.; Li, Z.; Liu, H.; Dong, C.; Wang, J.; Kulinich, S. A.; Du, X.-W. Laser-Prepared CuZn Alloy Catalyst for Selective Electrochemical Reduction of CO₂ to Ethylene. *Langmuir* **2018**, *34*, acs.langmuir.8b02837. <https://doi.org/10.1021/acs.langmuir.8b02837>.
- (67) Yu, L.; Xie, Y.; Zhou, J.; Li, Y.; Yu, Y.; Ren, Z. Robust and Selective Electrochemical Reduction of CO₂: The Case of Integrated 3D TiO₂@MoS₂ Architectures and Ti-S Bonding Effect. *J. Mater. Chem. A* **2018**, 4706–4713. <https://doi.org/10.1039/C7TA11376E>.
- (68) Wang, R.; Sun, X.; Ould-Chikh, S.; Osadchii, D.; Bai, F.; Kapteijn, F.; Gascon, J. Metal–Organic–Framework–Mediated Nitrogen-Doped Carbon for CO₂ Electrochemical Reduction. *ACS Appl. Mater. Interfaces* **2018**, *10* (17), 14751–14758. <https://doi.org/10.1021/acsami.8b02226>.
- (69) Zhang, X.-D.; Wu, J.-X.; Xu, M.; Yang, H.-F.; Hou, S.-Z.; Cao, P.-S.; Gu, Z.-Y. Cathodized Copper Porphyrin Metal–Organic Framework Nanosheets for Selective Formate and Acetate Production from CO₂ Electroreduction. *Chem. Sci.* **2018**, 2199–2205. <https://doi.org/10.1039/c8sc04344b>.

- (70) Nizio, M.; Albarazi, A.; Cavadias, S.; Galvez, M. E.; Costa, P. Da; Nizio, M.; Albarazi, A.; Cavadias, S.; Amouroux, J.; Galvez, M. E. Hybrid Plasma-Catalytic Methanation of CO₂ at Low Temperature over Ceria Zirconia Supported Ni Catalysts To Cite This Version : HAL Id : Hal-01289154 Hybrid Plasma-Catalytic Methanation of CO₂ at Low Temperature over Ceria Zirconia Supported Ni Catalysts. **2016**.
- (71) Benrabbah, R.; Cavaniol, C.; Liu, H.; Ognier, S.; Cavadias, S.; Gálvez, M. E.; Da Costa, P. Plasma DBD Activated Ceria-Zirconia-Promoted Ni-Catalysts for Plasma Catalytic CO₂ Hydrogenation at Low Temperature. *Catal. Commun.* **2017**, *89*, 73–76. <https://doi.org/10.1016/j.catcom.2016.10.028>.
- (72) Xu, Y.; Chen, Y.; Li, J.; Zhou, J.; Song, M.; Zhang, X.; Yin, Y. Improved Low-Temperature Activity of Ni–Ce/ γ -Al₂O₃ Catalyst with Layer Structural Precursor Prepared by Cold Plasma for CO₂ Methanation. *Int. J. Hydrogen Energy* **2017**, *42* (18), 13085–13091. <https://doi.org/10.1016/j.ijhydene.2017.04.019>.
- (73) Azzolina-Jury, F.; Bento, D.; Henriques, C.; Thibault-Starzyk, F. Chemical Engineering Aspects of Plasma-Assisted CO₂ Hydrogenation over Nickel Zeolites under Partial Vacuum. *J. CO₂ Util.* **2017**, *22*, 97–109. <https://doi.org/10.1016/j.jcou.2017.09.017>.
- (74) Azzolina-Jury, F.; Thibault-Starzyk, F. Mechanism of Low Pressure Plasma-Assisted CO₂ Hydrogenation Over Ni-USY by Microsecond Time-Resolved FTIR Spectroscopy. *Top. Catal.* **2017**, *60* (19–20), 1709–1721. <https://doi.org/10.1007/s11244-017-0849-2>.
- (75) Mei, D. H.; Liu, S. Y.; Tu, X. CO₂ Reforming with Methane for Syngas Production Using a Dielectric Barrier Discharge Plasma Coupled with Ni/ γ -Al₂O₃ Catalysts: Process Optimization through Response Surface Methodology. *J. CO₂ Util.* **2017**, *21*, 314–326. <https://doi.org/10.1016/j.jcou.2017.06.020>.
- (76) Zhu, F.; Zhang, H.; Yan, X.; Yan, J.; Ni, M.; Li, X.; Tu, X. Plasma-Catalytic Reforming of CO₂-Rich Biogas over Ni/ γ -Al₂O₃ Catalysts in a Rotating Gliding Arc Reactor. *Fuel* **2017**, *199*, 430–437. <https://doi.org/10.1016/j.fuel.2017.02.082>.
- (77) Zhou, A.; Chen, D.; Ma, C.; Yu, F.; Dai, B. DBD Plasma-ZrO₂ Catalytic Decomposition of CO₂ at Low Temperatures. *Catalysts* **2018**, *8* (7), 256. <https://doi.org/10.3390/catal8070256>.

- (78) Azzolina-Jury, F. Novel Boehmite Transformation into γ -Alumina and Preparation of Efficient Nickel Base Alumina Porous Extrudates for Plasma-Assisted CO₂ Methanation. *J. Ind. Eng. Chem.* **2019**, *71*, 410–424. <https://doi.org/10.1016/j.jiec.2018.11.053>.
- (79) Ma, X.; Li, S.; Ronda-Lloret, M.; Chaudhary, R.; Lin, L.; van Rooij, G.; Gallucci, F.; Rothenberg, G.; Raveendran Shiju, N.; Hessel, V. Plasma Assisted Catalytic Conversion of CO₂ and H₂O Over Ni/Al₂O₃ in a DBD Reactor. *Plasma Chem. Plasma Process.* **2019**, *39* (1), 109–124. <https://doi.org/10.1007/s11090-018-9931-1>.
- (80) Snoeckx, R.; Bogaerts, A. Plasma Technology-a Novel Solution for CO₂ Conversion? *Chem. Soc. Rev.* **2017**, *46* (19), 5805–5863. <https://doi.org/10.1039/c6cs00066e>.
- (81) Guo, F.; Chu, W.; Xu, J.; Zhong, L. Glow Discharge Plasma-Assisted Preparation of Nickel-Based Catalyst for Carbon Dioxide Reforming of Methane. *Chinese J. Chem. Phys.* **2008**, *21* (5), 481–486. <https://doi.org/10.1088/1674-0068/21/05/481-486>.
- (82) Cheng, D.; Zhu, X.; Ben, Y.; He, F.; Cui, L.; Liu, C. Carbon Dioxide Reforming of Methane over Ni/Al₂O₃ Treated with Glow Discharge Plasma. *Catal. Today* **2006**, *115* (1–4), 205–210. <https://doi.org/10.1016/j.cattod.2006.02.063>.
- (83) Greeley, J.; Jaramillo, T. F.; Bonde, J.; Chorkendorff, I.; Nørskov, J. K. Computational High-Throughput Screening of Electrocatalytic Materials for Hydrogen Evolution. *Nat. Mater.* **2006**, *5* (11), 909–913. <https://doi.org/10.1038/nmat1752>.
- (84) Nørskov, J. K.; Bligaard, T.; Rossmeisl, J.; Christensen, C. H. Towards the Computational Design of Solid Catalysts. *Nat. Chem.* **2009**, *1* (1), 37–46. <https://doi.org/10.1038/nchem.121>.
- (85) Zheng, Y.; Jiao, Y.; Li, L. H.; Xing, T.; Chen, Y.; Jaroniec, M.; Zhang Qiao, S. Toward Design of Synergistically Active Carbon-Based Catalysts for Electrocatalytic Hydrogen Evolution. **2014**. <https://doi.org/10.1021/nn501434a>.
- (86) Jiao, Y.; Zheng, Y.; Davey, K.; Qiao, S.-Z. Activity Origin and Catalyst Design Principles for Electrocatalytic Hydrogen Evolution on Heteroatom-Doped Graphene. *Nat. energy* **2016**. <https://doi.org/10.1038/NENERGY.2016.130>.
- (87) Schmickler, W.; Trasatti, S. Comment on “Trends in the Exchange Current for Hydrogen Evolution” [J. Electrochem. Soc., 152, J23 (2005)]. *J. Electrochem. Soc.*

- 2006**, 153 (12), L31. <https://doi.org/10.1149/1.2358294>.
- (88) Wei, X.; Li, N.; Zhang, X. Cu@C Nanoporous Composites Containing Little Copper Oxides Derived from Dimethyl Imidazole Modified MOF199 as Electrocatalysts for Hydrogen Evolution Reaction. *Appl. Surf. Sci.* **2017**, 425, 663–673. <https://doi.org/10.1016/J.APSUSC.2017.07.067>.
- (89) Chien, M.-H.; Vazquez-Miranda, S.; Sharif, R.; Hingerl, K.; Cobet, C. In Situ Optical Quantification of Adsorbates and Surface Charges on Copper Crystals and Their Impact on the Hydrogen Evolution Reaction in Hydrochloric Electrolytes. **2018**. <https://doi.org/10.1021/acs.jpcc.8b01149>.
- (90) Wu, H.; Chen, W. Copper Nitride Nanocubes: Size-Controlled Synthesis and Application as Cathode Catalyst in Alkaline Fuel Cells. *J. Am. Chem. Soc.* **2011**, 133 (39), 15236–15239. <https://doi.org/10.1021/ja204748u>.
- (91) Du, J.; Chen, Z.; Ye, S.; Wiley, B. J.; Meyer, T. J. Copper as a Robust and Transparent Electrocatalyst for Water Oxidation. *Angew. Chemie - Int. Ed.* **2015**, 54 (7), 2073–2080. <https://doi.org/10.1002/anie.201408854>.
- (92) Sun, Q.; Dong, Y.; Wang, Z.; Yin, S.; Zhao, C. Synergistic Nanotubular Copper-Doped Nickel Catalysts for Hydrogen Evolution Reactions. *Small* **2018**, 14 (14), 1704137. <https://doi.org/10.1002/sml.201704137>.
- (93) Yu, F.; Li, F.; Zhang, B.; Li, H.; Sun, L.; Light, H. V.; Kim, H. G.; Borse, P. H.; Jang, J. S.; Ahn, W.; et al. Efficient Electrocatalytic Water Oxidation by a Copper Oxide Thin Film in Borate Buffer. *ACS Catal.* **2015**, 5 (2), 627–630. <https://doi.org/10.1021/cs501510e>.
- (94) Zhang, W.; Fu, D.; Bai, Y.; Yuan, C. In-Situ Anion Exchange Synthesis of Copper Selenide Electrode as Electrocatalyst for Hydrogen Evolution Reaction. *Int. J. Hydrogen Energy* **2017**, 42 (16), 10925–10930. <https://doi.org/10.1016/J.IJHYDENE.2017.02.126>.
- (95) Wasalathanthri, R. N.; Jeffrey, S.; Awni, R. A.; Sun, K.; Giolando, D. M. Electrodeposited Copper–Cobalt–Phosphide: A Stable Bifunctional Catalyst for Both Hydrogen and Oxygen Evolution Reactions. *ACS Sustain. Chem. Eng.* **2019**, 7 (3), 3092–3100. <https://doi.org/10.1021/acssuschemeng.8b04807>.

- (96) Chiang, C.-Y.; Shin, Y.; Ehrman, S. Dopant Effects on Copper Oxide Photoelectrochemical Cell Water Splitting. *Energy Procedia* **2014**, *61*, 1799–1802. <https://doi.org/10.1016/j.egypro.2014.12.216>.
- (97) Sakthivel, T.; Ramachandran, R.; Kirubakaran, K. Photocatalytic Properties of Copper-Two Dimensional Graphitic Carbon Nitride Hybrid Film Synthesized by Pyrolysis Method. *J. Environ. Chem. Eng.* **2018**, *6* (2), 2636–2642. <https://doi.org/10.1016/j.jece.2018.04.009>.
- (98) Liu, X.; Cui, S.; Sun, Z.; Ren, Y.; Zhang, X.; Du, P. Self-Supported Copper Oxide Electrocatalyst for Water Oxidation at Low Overpotential and Confirmation of Its Robustness by Cu K-Edge X-Ray Absorption Spectroscopy. *J. Phys. Chem. C* **2016**, *120* (2), 831–840. <https://doi.org/10.1021/acs.jpcc.5b09818>.
- (99) Jiang, X.; Herricks, T.; Xia, Y. CuO Nanowires Can Be Synthesized by Heating Copper Substrates in Air. *Nano Lett.* **2002**, *2* (12), 1333–1338. <https://doi.org/10.1021/nl0257519>.
- (100) Abd Elhamid, M. H.; Ateya, B. G.; Weil, K. G.; Pickering, H. W. Calculation of the Hydrogen Surface Coverage and Rate Constants of the Hydrogen Evolution Reaction from Polarization Data. *J. Electrochem. Soc.* **2002**, *147* (6), 2148. <https://doi.org/10.1149/1.1393500>.
- (101) Muthukumar, P.; Kumar, V. V.; Reddy, G. R. K.; Kumar, P. S.; Anthony, S. P. Fabrication of Strong Bifunctional Electrocatalytically Active Hybrid Cu-Cu₂O Nanoparticles in a Carbon Matrix. *Catal. Sci. Technol.* **2018**, *8* (5), 1414–1422. <https://doi.org/10.1039/c7cy02048a>.
- (102) Pi, M.; Yang, T.; Wang, S.; Chen, S. One-Pot Synthesis of in Situ Carbon-Decorated Cu₃P Particles with Enhanced Electrocatalytic Hydrogen Evolution Performance. *J. Mater. Res.* **2018**, *33* (5), 546–555. <https://doi.org/10.1557/jmr.2017.401>.
- (103) Zhao, C.; Wang, J. Electrochemical Reduction of CO₂ to Formate in Aqueous Solution Using Electro-Deposited Sn Catalysts. *Chem. Eng. J.* **2016**, *293*, 161–170. <https://doi.org/10.1016/j.cej.2016.02.084>.
- (104) Zhang, H.; Zhang, Y.; Li, Y.; Ahn, S.; Palmore, G. T. R.; Fu, J.; Peterson, A. A.; Sun, S. Cu Nanowire-Catalyzed Electrochemical Reduction of CO or CO₂. *Nanoscale*

- 2019**, 11 (25), 12075–12079. <https://doi.org/10.1039/C9NR03170G>.
- (105) Edwards, P. P.; Kuznetsov, V. L.; David, W. I. F.; Brandon, N. P. Hydrogen and Fuel Cells: Towards a Sustainable Energy Future. *Energy Policy* **2008**, 36 (12), 4356–4362. <https://doi.org/10.1016/j.enpol.2008.09.036>.
- (106) ARAT, H. T.; SÜRER, M. G. State of Art of Hydrogen Usage as a Fuel on Aviation. *Eur. Mech. Sci.* **2017**, 2 (1), 20–30. <https://doi.org/10.26701/ems.364286>.
- (107) Sun, H.; Qin, D.; Huang, S.; Guo, X.; Li, D.; Luo, Y.; Meng, Q. Dye-Sensitized Solar Cells with NiS Counter Electrodes Electrodeposited by a Potential Reversal Technique. *Energy Environ. Sci.* **2011**, 4 (8), 2630. <https://doi.org/10.1039/c0ee00791a>.
- (108) Shang, X.; Qin, J. F.; Lin, J. H.; Dong, B.; Chi, J. Q.; Liu, Z. Z.; Wang, L.; Chai, Y. M.; Liu, C. G. Tuning the Morphology and Fe/Ni Ratio of a Bimetallic Fe-Ni-S Film Supported on Nickel Foam for Optimized Electrolytic Water Splitting. *J. Colloid Interface Sci.* **2018**, 523, 121–132. <https://doi.org/10.1016/j.jcis.2018.03.083>.
- (109) Zhang, C.; Cai, X.; Qian, Y.; Jiang, H.; Zhou, L.; Li, B.; Lai, L.; Shen, Z.; Huang, W. Electrochemically Synthesis of Nickel Cobalt Sulfide for High-Performance Flexible Asymmetric Supercapacitors. *Adv. Sci.* **2018**, 5 (2). <https://doi.org/10.1002/advs.201700375>.