Electrochemical studies of Schiff-base derived mononuclear copper complex in the presence of acid

A

Dissertation

Submitted in partial fulfilment of the requirement for the

Degree of

Masters of Science

In

Chemistry

By

JEMINI

(Registration No.:301702016)

Under the Supervision of

Dr. Davinder Kumar

(Assistant Professor)

School of Chemistry & Biochemistry
Thapar Institute of Engineering & Technology
Patiala-147004, India

CERTIFICATE

This is to certify that the dissertation entitled, **"Electrochemical studies of Schiff-base derived mononuclear copper complex in the presence of acid"**, being submitted by **Ms. Jemini** in partial fulfilment of requirement for the award of the degree of **Masters of Science** in **Chemistry** and being submitted to the School of Chemistry and Biochemistry, Thapar Institute of Engineering and Technology, Patiala is a bonafide work carried out by her under my supervision. The work has reached the standard necessary for submission, and the contents of this dissertation have not been submitted to any other university or institute for the award of any degree or diploma.

Davinder Kumar

Jemini

(Dr. Davinder Kumar)

Assistant Professor

School of Chemistry and Biochemistry

Thapar Institute of Engineering and Technology, Patiala - 147004

CANDIDATE'S DECALARATION

I, hereby, declare that the work being presented in the dissertation entitled **"Electrochemical studies of Schiff-base derived mononuclear copper complex in the presence of acid"** in partial fulfilment of the requirement for the award of the degree of **Masters of Science** in Chemistry and being submitted to School of Chemistry and Biochemistry, Thapar Institute of Engineering and Technology, Patiala is my own research work carried out during the period of January to July 2019 under the supervision of **Dr. Davinder Kumar**. I have not submitted the contents embodied in this dissertation for the award of any degree elsewhere.

Jemini

Jemini

Date: 11 – 10 – 2019

It is certified that the above statement made by the student is correct to the best of my knowledge and belief.

Davinder Kumar

Dr. Davinder Kumar
Assistant Professor
School of Chemistry and Biochemistry
Thapar Institute of Engineering and Technology, Patiala – 147004

CERTIFICATE

This is to certify that the dissertation entitled, **"Electrochemical studies of Schiff-base derived mononuclear copper complex in the presence of acid"**, being submitted by **Ms. Jemini** in partial fulfilment of requirement for the award of the degree of **Masters of Science** in **Chemistry** and being submitted to the School of Chemistry and Biochemistry, Thapar Institute of Engineering and Technology, Patiala is a bonafide work carried out by her under my supervision. The work has reached the standard necessary for submission, and the contents of this dissertation have not been submitted to any other university or institute for the award of any degree or diploma.

Davinder Kumar

Jemini

(Dr. Davinder Kumar)
Assistant Professor
School of Chemistry and Biochemistry
Thapar Institute of Engineering and Technology, Patiala - 147004

ACKNOWLEDGEMENT

Today, when I look back into my life, it feels that no road is too tough to be walked on. With the guidance and encouragement of elders, and hard work; impossible can also be turned into possible. It was nearly impossible to accomplish my project without the help and inspiration extended by these personalities and I would not forget to thank them.

Although it is difficult to translate the feelings of regards into reality, yet it is detectable when I execute my sense of profound respect to my supervisor **Dr. Davinder Kumar**, School of Chemistry and Biochemistry, for his guidance, thoughtful planning, knowledge and motivation during the course of my project. I respect him for inspiring me in many ways and it's been a great honour to work under his guidance.

I am deeply thankful to **Dr. Amjad Ali**, Head, School of Chemistry and Biochemistry for offering me the opportunity to explore the research work and allowing me to use various facilities in respective departments. I would also like to thank **Dr. Susheel Mittal lab** research scholars who helped us whenever required.

I also want to thank my friends Ms. **Akanksha Katoch**, **Priya Kamboj, Chandana Bansal** and **Mandeep Kaur** for helping me whenever I required.

I express my deepest gratitude to my parents for their blessings, endless love, support, encouragement. Without them, this journey would not be completed. I would like to dedicate my achievement to them.

Above all, I express my indebtedness to **Almighty God** whose blessings and kindness helped to complete this work successfully.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

AcOH	Acetic acid
CAN	Acetonitrile
CV	Cyclic Voltammetry
DI water	Deionised water
DMF	Dimethlyformamide
GHG	Green house gases
HER	Hydrogen evolution reaction
MLTC	Metal to ligand charge transfer
NMR	Nuclear magnetic resonance
TLC	Thin layer chromatography
TBAHFP	Tertabutylammomiumhexafluorophosphate
TOF	Turn over frequency

SYMBOLS

A	Ampere
D_0	Diffusion coefficient
E_{cat}	Catalytic potential
i_{cat}	Catalytic current
i_{pa}	Anodic current
i_{pc}	Cathodic current
mM	Millimolar
mA	Milliampere
H	Overpotential
μA	Microampere
μL	Microlitre
V	Volt

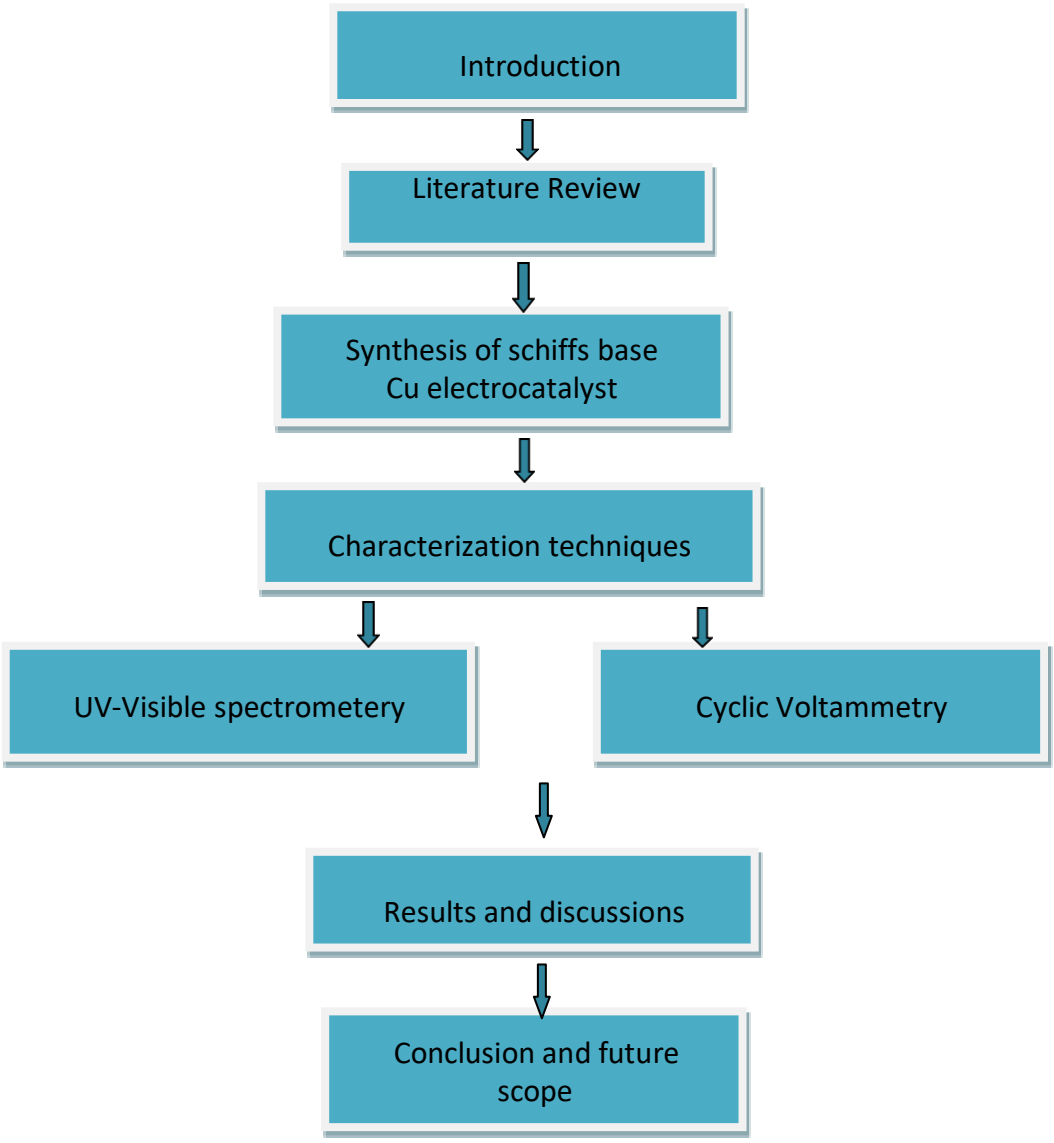
ABSTRACT

The greatest challenges that are faced by today's generation is shortage of energy sources Scientists has emphasized their efforts for the production of clean, environment friendly and sustainable sources of energy. There is concern that the emission of harmful gases will deplete the ozone layer and increase temperature which leads to global warming.

Hydrogen is a promising alternative energy carrier fuel since it is a renewable contains high energy content and do not show participation to the green house effect also, the most abundant element in the universe. There are various techniques for hydrogen production which includes various biological methods as there is formation of various side products numerous challenges are related with these techniques. It is essential to develop an appropriate electrocatalyst which can produce chemicals selectively with high faradic efficiency. Electrocatalysts based on Noble metals such as Pt, Pd, and Ru are good towards hydrogen evolution but are not in application because of their high cost. Recently, studies have been made using earth abundant metal complexes.

In the current studies, copper based complex are found to be attractive and it had been used for electrochemical reduction of protons to produce hydrogen. We have synthesized copper electrocatalyst and studied its electrochemical properties in presence of acids giving TOF $3.1s^{-1}$ at an overpotential of 90 mV. Also, the reaction is proved to be diffusion controlled at different scan rates all these studies showed the possibility of catalyst towards the hydrogen evolution. However, controlled potential coulometry (CPC) coupled with gas chromatography studies will confirm the hydrogen evolution.

THESIS OVERVIEW



CHAPTER 1 –INTRODUCTION

The major challenge of twenty first century is to meet the global demand for energy due to increasing population and rising standards of living. There is need of non fossil energy to solve this problem. Hydrogen has attracted the considerable attention and can be used as chemical fuel vector because of its following properties:

• Hydrogen has high quality to carry energy with high efficiency.

• Hydrogen shows good electrochemical properties due to which it can be used in fuel cell.

• Hydrogen can be stored in different forms for its applications.

Due to zero-emission fuel hydrogen has its widespread applications and can act as good fuel source.

Hydrogen production

There are various environmental concerns that are caused by the production and use of energy such as, acid rain depletion of ozone layer and several other climate changes to solve these environmental problems we need to produce hydrogen from environment friendly techniques. [1].With the increase of energy demand there is large amount of rise of greenhouse gases (GHG) in the atmosphere. Steam reformation of natural gas led to emissions of large amount GHG and about 50% of the globally hydrogen is produced by steam reformation of natural gas, 30% from chemical industries reformation, 18% from gasification of coal, and 0.1% from other sources [2].

Natural gas steam reforming

Almost, half amount of the hydrogen is produced in the world is obtained through reformation of natural gas. In this method the natural gas, methane, reacts with high temperature steam in a catalytic converter. Nickel catalyst and temperature above 1000 K is required for this reaction. Carbon monoxide and hydrogen is generated by steam methane reaction [3].

$$CH_4 + H_2O \xrightarrow[Ni]{1000\text{-}1100K} CO + 3H_2$$

Water reacts with carbon monoxide further to produce hydrogen

$$CO + H_2O \longrightarrow H_2 + CO_2$$

Coal gasification

Coal gasification is another method for hydrogen production. The process includes conversion of coal from a solid to natural gas which can be used to create different fertilizer, chemicals. Coal is oxidized in the presence of oxygen and steam and is combined to produce synthesis gas.

Partial oxidation

Partial oxidation of hydrocarbons is method for hydrogen production which is exothermic in nature. Heavy hydrocarbons are converted to mixture of H_2, CO, Co_2 by superheated steam and oxygen.

Electrolysis

Water electrolysis is one of the industrial hydrogen production processes which do not depend on fossil energy also. The method includes splitting of elements or compounds when electric current is passed through it. It is also called solid oxide steam electrolysis a method in which water gets splitted into oxygen and hydrogen by passing an electric current. Reactions carried out at various electrodes as follow:

Cathode: $4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$

Anode: $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$

Net: $2H_2O \rightarrow 2H_2 + O_2$

Electrolysis is considered as one of the cleanest method to produce hydrogen. Photo-electrolysis is another method, in which the photovoltaic cells act as electrodes that decompose water into hydrogen and oxygen gas.

Photocatalytic hydrogen production

Photocatalytic hydrogen production includes the production of hydrogen using solar energy. It is considered as an environmentally safe energy source also, low cost fuel production method. We can produce hydrogen from H_2S whose main source is waste of refining industries which contributes to acid rain. On the other hand, Photocatalytic hydrogen production using H_2S is environmental friendly method but coal as non-renewable energy source will be depleted and there will be no H_2S to produce hydrogen [4].Therefore, solar-light-dependent splitting of water using TiO_2 seems good for hydrogen production. Electrochemical cell construction consists of TiO_2 electrode which is connected to platinum electrode is active towards hydrogen evolution. The reactions occurring are as follow:

$TiO_2 + hv \rightarrow 2e^- + 2p^+$ (excitation of TiO_2 by light)

$2p^+ + H_2O \rightarrow 1/2O_2 + 2H^+$ (at TiO_2 electrode)

$2e^- + 2H^+ \rightarrow H_2$ (at platinum electrode)

$H_2O + 2hv \rightarrow 1/2O_2 + H_2$ (overall reaction)

Using nanomaterials is another effective way for photoelectric water splitting for generating hydrogen in an easy and sustainable way and by further improving these photocatalyst according to their band width increases its efficiency towards hydrogen production [5]. Hydrogen can be photochemicaly evolved from heterogenous environment in water from catalysts using nanorods as photosensitizer and a sacrificial donor for the complete reaction[6].

Biological process

Microorganisms such as bacteria and algae can produce hydrogen through biological processes in environment. Hydrogenase is an enzyme that actively participates in catalysis by reduction of proton to generate hydrogen molecule. The metalloenzyme that produce hydrogen is base for many anaerobic bacteria[7] which produces 0.3Gt hydrogen every year[8] Hydrogenases are of three type Fig. 1.1 [Fe-Fe] Fig. 1.2 [Ni-Fe] Fig. 1.3 [Fe] only. The [Ni-Fe] and [Fe-Fe] hydrogenase both contains an active site and Fe-S cluster. The Fe-only contains only one active site not Fe-S cluster. Hydrogenase enzyme produces hydrogen at organometallic Fe-Fe, Ni-Fe,

Fe active sites[9]. Cu metal fused with porphyrin ring has its great activity towards hydrogen production with maximum TOF which is biologically supported HER reaction[10].

[Fe-Fe] hydrogenase

Fe-Fe hydrogenase consists of Fe-S cluster in their active site. It is biological catalyst for active for hydrogen oxidation and reduction it is highly sensitive towards oxygen and gets inactivated in presence of aerobic environment.

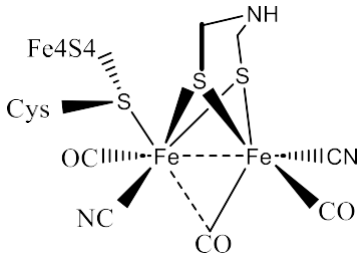


Fig. 1.1 Structure of [Fe-Fe] hydrogenase enzyme

[Ni-Fe] hydrogenase

Ni-Fe hydrogenase consists of Ni-S and Fe-S clusters. Like [Fe-Fe] hydrogenases, [Ni-Fe] hydrogenases are known to be usually deactivated by molecular oxygen[11]. Nickel metal participate in the redox reaction for catalytic process.

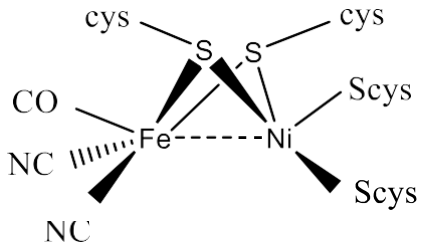


Fig .1.2 structure of [Ni-Fe] hydrogenase enzyme

Fe-only hydrogenase

Fe only hydrogenase catalyses the reduction of Methenyltetrahydromethanopterpin with hydrogen to Methylenetetrahydromethanopterin.

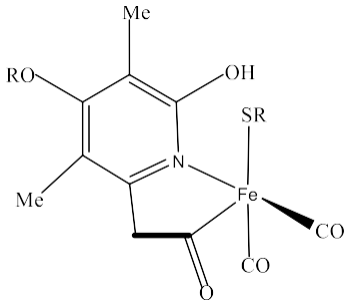


Fig. 1.3 structure of Fe hydrogenase enzyme.

Though, hydrogenase enzymes also uses earth abundand metals for oxidation and production of hydrogen but they are not capable of producing hydrogen in large amount as to meet the commercial demands also these enzymes are not stable under certain conditions so there was need of other catalyst that produce hydrogen in environment friendly way also should produce hydrogen to meet the global demand. These all considerations led to development molecular catalysts based on abundance of metals several complexes that produce hydrogen these contain nickel, iron cobalt and molybdenum electrocatalysts for the production of hydrogen.

Electrocatalytic hydrogen production

An electrocatalyst is defined as a catalyst that takes part in electrochemical reactions and increases the rate of chemical reactions without being used in the reaction. These are form of catalysts that itself work at electrode surfaces or can be the electrode surface itself. It can be heterogeneous or homogenous by nature.

Several efforts have been made for the development of the low cost and highly efficient catalysts. The metals based on first row transition metals found to be highly active for this availability as they are highly available and are less toxic also. Metals such as Pt and its alloys are expensive and are not used as much for this work but the complexes of iron[13] nickel[14-15] cobalt[16], copper, zinc, and molybdenum[17] are known as electrocatalyst for hydrogen production Cu based electrocatalysts acts as a good source for fuel production. Cu metal and its complexes have been used for the solar fuel production. Mainly this group metals are focused for hydrogen production application because they are abundant in nature and produce energy sources without causing any harm to environment. As much catalysts are not known for copper but

recently a mononuclear complex of copper is active towards HER reaction though it needs higher overpotential [18].

CHAPTER 2- LITERATURE REVIEW

This chapter provides the detailed literature survey made by various researchers in this field. In this chapter we will study about the literature of the metal assisted hydrogen evolution, ligand assisted hydrogen evolution.

Dempsey *et al.*[19] in their work reported that $Co(dmgBF_2)_2(L_2)$ ($dmgBF_2$= difluoroboryldimethylglyoxime) which catalyses the reduction of aqueous Hcl using Cr^{2+} as electron donor. Dissociation of an intermediate chloro-bridged complex was formed during inner-sphere electron transfer from Cr^{2+} to Co^{2+}, produces $[Co(dmgBF_2)_{2L}]^-$ in the acid presence Co^{1+} anion is protonated to form hydride which evolves hydrogen. Peters *et al.*[20] reported the water soluble molecular cobalt compexes with tetraaza macrocyclic ligands are capable of electrocatalytic hydrogen production at pH of 2.2 out of which two diimine-dioxime complexes were reported capable of catalytic hydrogen activity at lower overpotential as compared to other cobalt complexes in aqueous solutions.

Ligand centered hydrogen evolution

Haddad *et al.*[21]in their work they had showed the homogenous electrocatalytic hydrogen production and oxidation using metal free transition complexes. Diacetyl-bis(N-4-methyl-thiosemicarbazone) and zinc diacetyl-bis(N-4-methyl-3-thiosemicarbazone) displays highest TOF of any homogenous ligand centered hydrogen evolution electrocatalyst at $1320s^{-1}$ and $1170s^{-1}$also, turnover frequency for hydrogen oxidation is $72s^{-1}$. Haddad *et al.*[22] reported the complex of rhenium that is ReL_3(L is diphenylphosphinobenzenethiolate) which is acting as a good electrocatalyst for hydrogen evolution or hydrogen oxidation. In presence of acid and base shows different results with overpotential 380mV and turn over frequency of $32s^{-1}$ and in presence of base it gives value of TOF $4s^{-1}$ therefore it was reported as ligand dependent hydrogen evolution. Haddad *et al.*[23]reported Cu(II) complex of diacetyl-bis(N-4-methyl-3-thiosemicarbazonato) as an ligand dependent for hydrogen evolution under electrochemical studies displaying maximum turn over frequency in presence of acetonitrile as compared in dimethylformamide at different overpotential values. Also, the gas chromatography analysis confirms it as electrocatalyst for hydrogen evolution with faradic efficiency of 81%. Kinetic isotopic effect was 7.54 using deuterated acid.

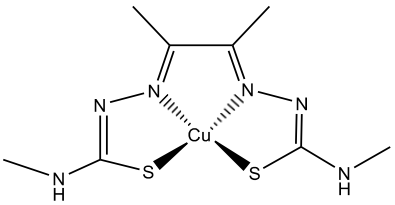
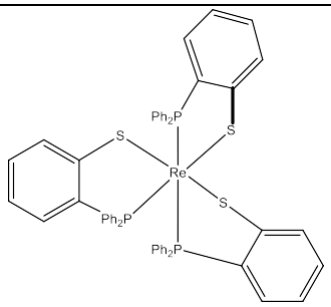
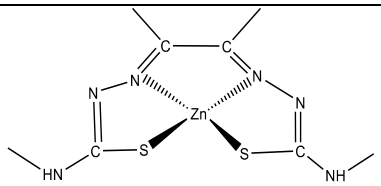
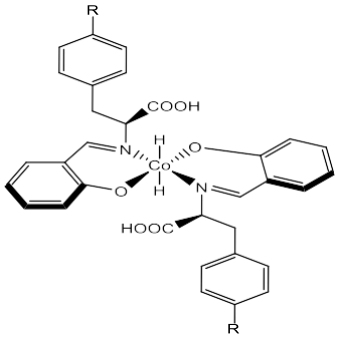
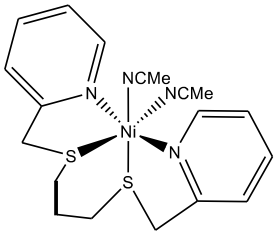
Metal-centered hydrogen production

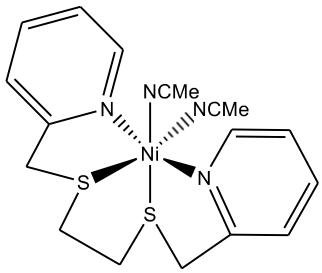
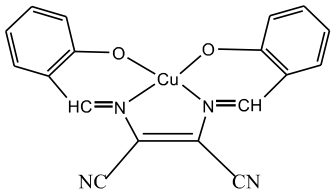
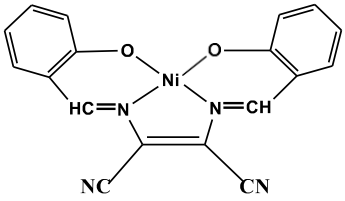
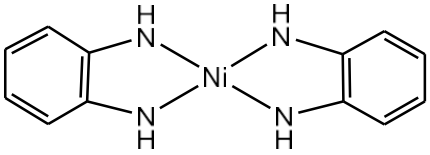
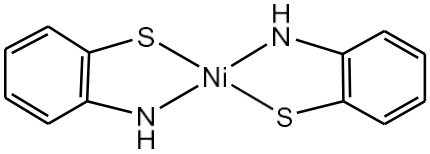
Khandekwal *et al.*[24] in their work they have studied the effect of protic functionalities on cobalt-salen groups towards the electrocatalytic hydrogen production. The complexes containing carboxylic group functionalities have their different activity towards hydrogen evolution.in their work have shown the dependence of pH of their complexes towards hydrogen evolution. And the cobalt complex shows posistive result at below pH 4. The NMR data shows that the presence of protic functionalities in water plays a vital role in hydrogen production even in inactive Co-salen complexes.

Cao *et al.*[25-26] schiff-base Cu and Ni complexes were synthesized by this group and Cu(II) species with TOF of 457(pH 7) and TON 817mV was reported for electrochemical hydrogen production from neutral water and faradic efficiency of 91.5% was observed with no decomposition of catalyst. also, electrochemical studies show that Ni complex evolved hydrogen from acetic acid or from water.TOF of 193 (in DMF) and 574 (in buffer, pH 6) moles of hydrogen per mole of catalyst per hour. GC analysis was performed and 42 h electrolysis was done with no observable decomposition of the catalyst.

Hong *et al.*[27]made studies on the electrocatalytic and photocatalytic hydrogen evolution ofNi(II) complexes using S_2N_2 type of tetradentate ligands of different sizes. Two complexes with five membered and six membered chelate ring out of which five membered chelated ring is more active towards Photocatalytic and electrocatalytic hydrogen production. In electrochemical measurements it was observed that first reduction was electron transfer reaction which forms Ni(I) complex and second one is proton-coupled electron transfer reaction. In photocatalytic hydrogen evolution the complex with five membered ring is more active. Liu *et al.*[28]in their work reported that Cu(II) complex can acts as good hydrogen evolution catalyst in neutral aqueous solution which could further be developed to form water reduction. Characterization carried by CV gave the value of TON equals to 5876 and TOF $734s^{-1}$ in film form also, it was estimated that due to presence of ligand the film becomes stable therefore, Cu catalyst is found to be more systematic and stable catalyst for proton reduction in aqueous medium.

Table2.1 List of electrocatalyst showing activity towards hydrogen evolution reaction.

S.No.	Metal	Catalyst	TON	TOF	Overpotential	Faradic efficiency
1.	Cu		-	$10000s^{-1}$ (ACN) $5100s^{-1}$ (DMF)	0.80V 0.76V	81%
2.	Re		-	$32s^{-1}$ (CH_2Cl_2) $4s^{-1}$ (base)	0.38V	-
3.	Zn		-	$1170s^{-1}$	-	-
4.	Co		-	$255s^{-1}$	0.67V	-
5.	Ni		19	3.6 h^{-1}		80%

6.	Ni		1100	$2.3\times10^{2}h^{-1}$		95%
7.	Cu		817	$457s^{-1}$	-	91.5%
8.	Ni		-	$193s^{-1}$ (DMF) $574s^{-1}$ (buffer)	-	-
9.	Ni		900	$57600s^{-1}$	-	-
10.	Ni		6190	$27000s^{-1}$	-	-

CHAPTER 3- MATERIALS AND METHODS

This chapter contains all the information on chemicals, glassware, labware, instruments and methodologies used for carrying out the research work described in this thesis.

MATERIALS

Chemicals used

Salicylaldehyde($C_7H_6O_2$), Aniline($C_6H_5NH_2$), Ethanol(CH_3CH_2OH), Triethylamine $N(CH_2CH_3)_3$, Copper nitrate$Cu(NO_3)_2$, Diethyl ether$(C_2H_5)_2O$, Acetonitrile(CH_3CN), Glacial acetic acid(CH_3COOH). All these chemicals were bought from Loba chemicals and were used without further purification.

Glassware and labware used

Beakers (100mL), round bottom flasks (250mL), measuring cylinder, magnetic bead, condenser, guard tube, spatula, dropper, oil bath, filter paper, glass vials, buchner funnel, thermometer, magnetic stirrer, micropipettes (2-20μL, 0.2-2 μL), quartz cuvettes (2.5mL).

Equipments and instruments used

Magnetic stirrer with hot-plate

In this research work, a magnetic stirrer with hot plate Tarsons Spinot digital was used. It is a laboratory device which is used to provide magnetic field which allows the magnetic stir bar to rotate when immersed in liquid also, it contains heat plate that heat the liquid when placed on it.

Rotary evaporation

In this research work, rotary evaporation was used. It is a device that is used in laboratories for efficient and proper removal of solvents from samples by evaporation method.

Vacuum filtration

Vacuum filtration is a technique mostly used dry out small amount of solutions to get the solid products that are generally crystals. This method needs a Buchner funnel filter paper and a rubber.

UV-Visible spectrophotometer

UV- Visible spectrometer (PerkinElmer Lambda 35) is used in this work. UV-Visible spectroscopy is type of absorption spectroscopy in which light of ultra-violet region (200-400nm) is absorbed by the molecule. Absorption of these radiations leads to excitation of molecules from ground to excited state and the energy absorbed by molecule is equal to the energy difference of ground and excited state. Mostly transitions occurs from highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) and possible transitions in their increasing order are $n\text{-}\pi^* < n\text{-}\sigma^* < \pi\text{–}\pi^* < \sigma\text{–}\pi^* < \sigma\text{–}\sigma^*$. The law followed during absorption of substance is beer- Lambert law which states that absorbance of light is directly proportional to the molar concentration of the sample and path length.

$A = \log_{10}(I_0/I) = \varepsilon.c.l$

Where, A- Absorbance, I_0- Intensity of incident light, I- Intensity of transmitted light c- Molar concentration of solute, l- path length, ε- molar absorptivity.

With increase in concentration the value of transmittance decreases. Detector gives us value of transmittance but the graph is plotted between absorbance and concentration as shown by formula which is useful for calculation of concentration of sample.

$\text{Log}_{10}(1/T) = \varepsilon.c.l$

When the graph is plotted between absorbance and wavelength then the value at which maximum absorbance occurs corresponds to λ_{max}. This technique is useful for calculation of concentration and wavelength of the unknown compound.

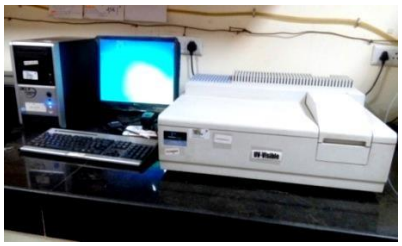


Fig. 3.1UV-Visible spectrophotometer

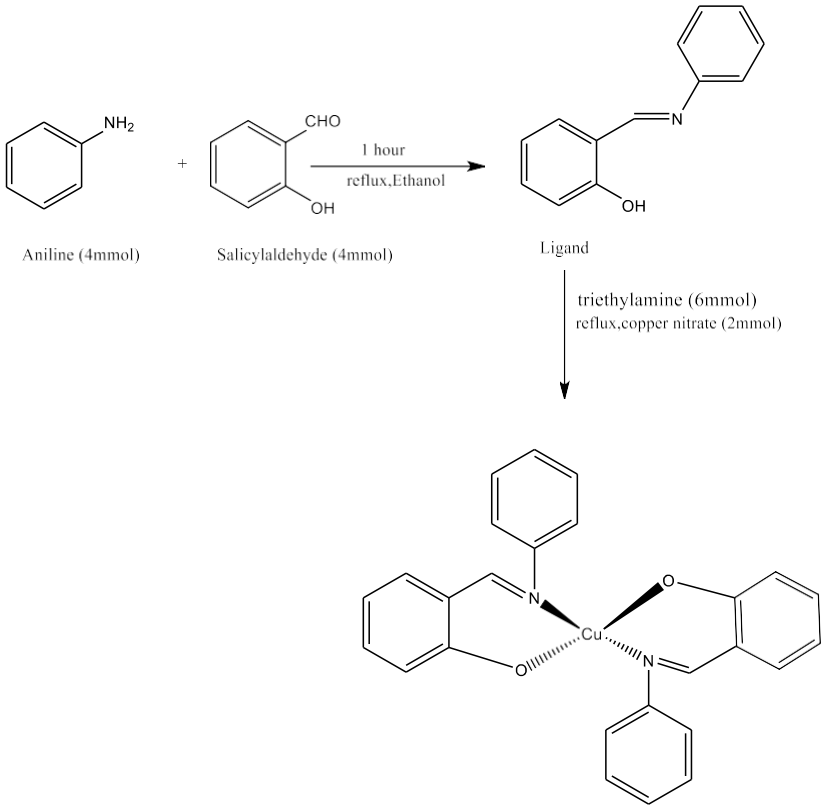
Cyclic voltammetry

In this work cyclic voltammetry instrument is used to carry out the electrochemical studies. It is a potentiodyanamic electrochemical measurement technique used for electrochemical studies and also useful for studying the electrode reactions. The working electrode potential is varied linearly with time. In this technique initial current obtained is capacitive current which is formed by double charge layer formed at the surface of electrode. As the as experiment progressed we get peak current and as moving towards positive current value we get anodic peak potential (Ep_a) and anodic peak current (ip_a) and, towards negative current anodic peak potential (Ep_c) and anodic peak current (ip_c) is obtained. In forward potential value oxidation peak and in reverse potential reduction peak is formed. To verify whether the reaction is reversible or not the difference in cathodic and anodic peak potential should be equal to 59 mV also, the ratio of anodic peak current value to cathodic peak current should be equal to one.

Methodology

Synthesis of Schiff-base Cu complex

Salicylaldehyde (488.88 mg, 4mM) and aniline (372.52 mg, 4mM) was dissolved in 10mL of ethanol and was set up for refluxing for one hour at 50 $^{\circ}$C as the setup shown below (Fig. 3.2). After one hour TLC of the reaction was checked and reaction mixture was brought to room temperature after that triethylamine (607.14 mg, 6mM) and copper nitrate (375.12 mg, 2mM) dissolved in 5 mL of ethanol was added drop wise to it. Solution was concentrated followed by dissolving of diethylether to it and product was vacuum filtered and washed with DI water (5 mL) and diethylether (2×5 mL) and further was air dried to afford brown crystals with 82% yield.



Scheme. 3.1 Synthesis of Schiff- base metal complex.

Fig.3.2 Set up for synthesis of schiffs base Cu complex .

Fig.3.3 Synthesized Cu complex

Sample prepration for UV-Visible spectroscopy

0.1 mM of Cu solutions were prepared in 10mL of ethanol and were taken 2mL for UV-Visible spectroscopy.

3.5 Set up and sample prepration for Cyclic Voltammetry

The first step is cleaning of electrodes so that there is good electron transfer. Cleaning process includes sonication of working electrode (glassy carbon with 0.071cm^2 area) and counter electrode (platinum wire) in acetonitrile for 2-3 minutes and and reference electrode (Ag/AgCl) was rinsed properly first with water and then with acetonitrile. Reference electrode, working electrode, counter electrode were dipped in solution of (0.1M ACN/TBAHFP) and connections are made in such a way that black clip is connected to working, red to counter and white to reference electrode and all three electrodes should be dipped such that they are equidistant from the bottom. Firstly voltammogram was run for 5mL blank solution (0.1M ACN/TBAHFP). after that for solution with Cu catalyst [Cu(2mM) in 5ml of Acetonitrile] with potential -1.5V to +1.5V with varying scan rates (1V,0.5V, 0.2V, 0.1V, .05V) followed by voltammograms with varying glacial acetic acid concentrations (30 mM, 60 mM, 90 mM).

Fig.3.4 Set up for cyclic voltammetry

CHAPTER-4 RESULTS AND DISCUSSIONS

The studies of prepared catalyst using various spectroscopic techniques have been discussed in this chapter with include the study of catalyst by cyclic voltammetry and UV-Visible spectroscopy.

Electronic spectroscopy:

The catalyst dissolved in acetonitrile shows the absorption peak at 274nm corresponding to π-π* transitions Showing the progress from ligand to complex formation with metal. Also first two bands in spectra are due to Cu(II) to ligand charge transfer (MLCT) transitions. The presence of this band indicates the complex formation of ligand with Cu metal whereas third band is due to d-d transition.

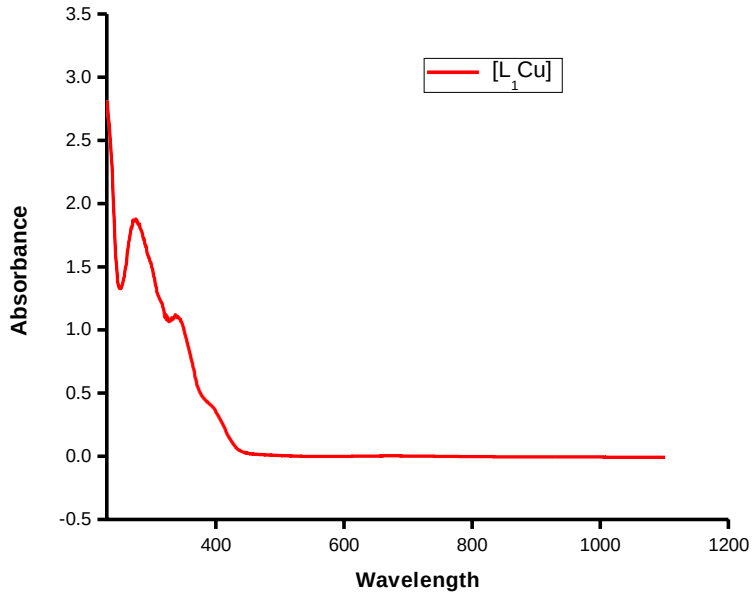


Fig4.1: UV-Visible spectra of 0.1Mm solution of [L_1Cu] in acetonitrile

Cyclic voltammetry:

The cyclic voltammetry of CuL^1 in acetonitrile containing 0.1M TBAHFP used as a supporting electrolyte displays the value of irreversible reduction at 1.35 V. Additional data obtained by scanning at various scans from 0.05 to 1V/s in acetonitrile (Fig. 4.2).

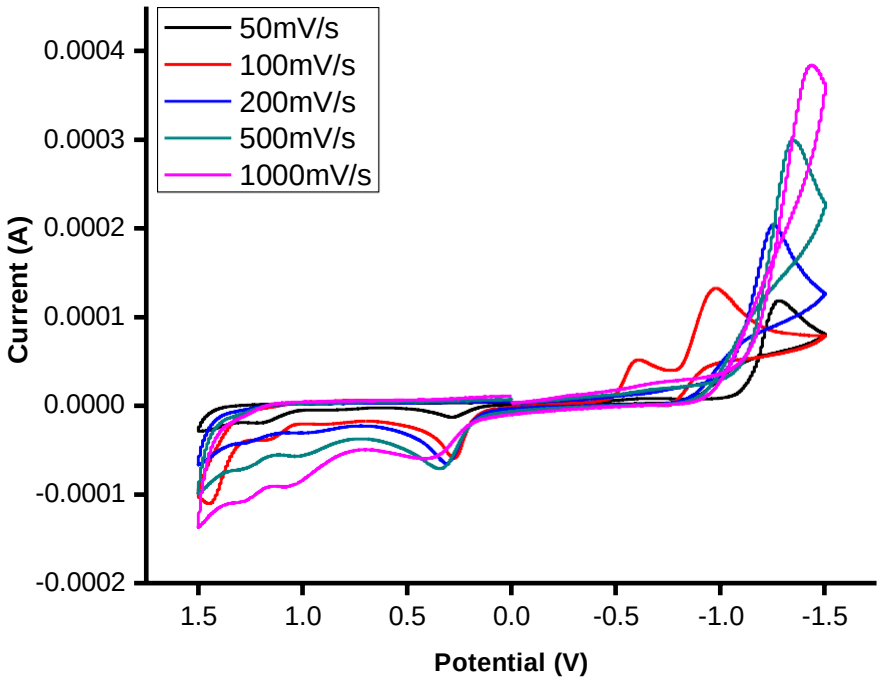


Fig.4.2 CVs for CuL^1 in 0.1M TBAHFP in acetonitrile at various scan rates

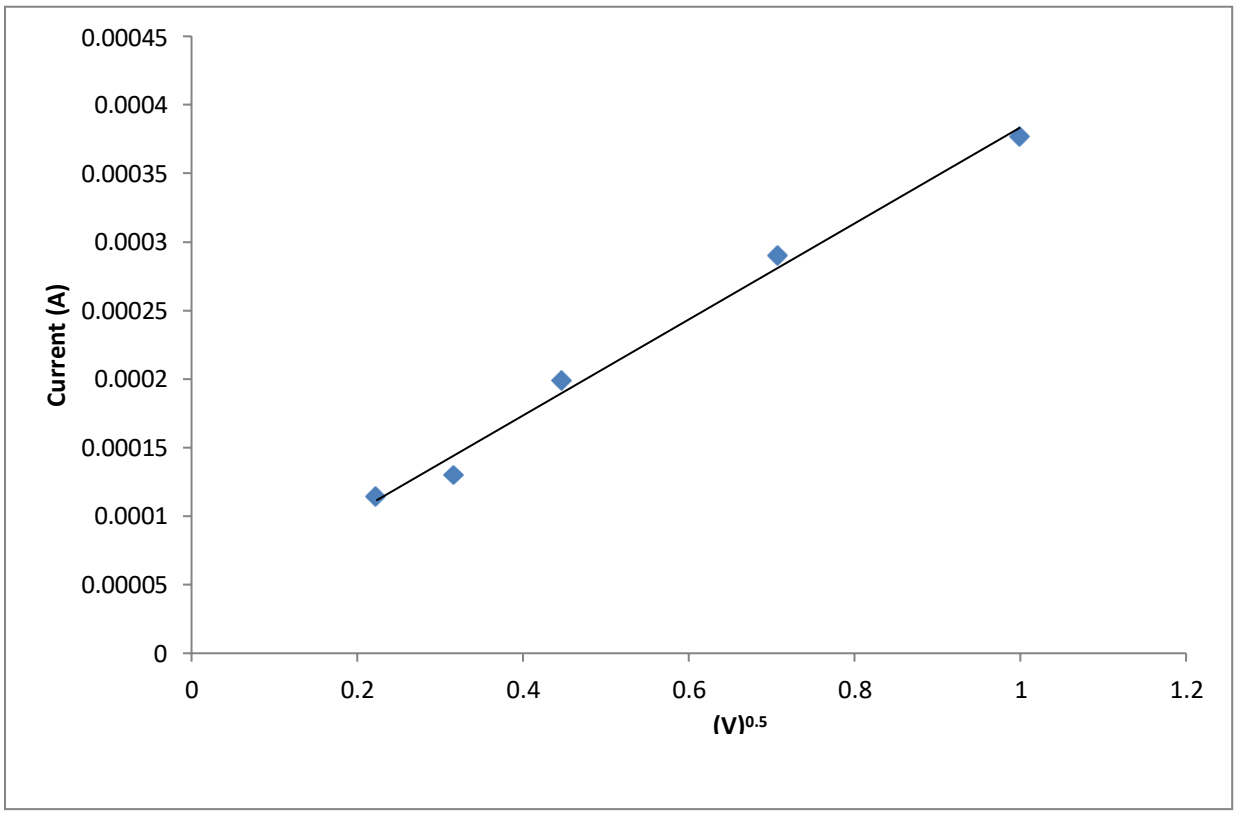


Fig. 4.3 Plot of peak current v/s square root of scan rate

The value of slope calculated from this graph gives the value of diffusion coefficient equals to $9.4 \times 10^{-5} cm^2/s$ calculated from Randles Sevcik equation[29] which shows that the reaction is diffusion controlled reaction with above value of diffusion coefficient.

Slope = $3.4 \times 10^{-4} = 0.4463FA\ [cat][(FD_0/RT)]^{0.5}$

$A=0.072\ cm^2$

$[cat] = 2 \times 10^{-6}$ moles/L

R = ideal gas constant

F = 96485 C/mole e-

T = 298 K

Electrochemical studies using acid concentrations:

On addition of 20mM of acid in CuL^1 in 0.1M TBAHFP in acetonitrile solution gives the value of cathodic current at 0.9V indicating the reduction of catalyst in presence of acid as compared to blank solution on acid addition (Fig. 4.4). Also, rise in current shows the reduction occuring at metal centre and due to addition of metal complex the current rises highly with potential shifting to less negative value [30].

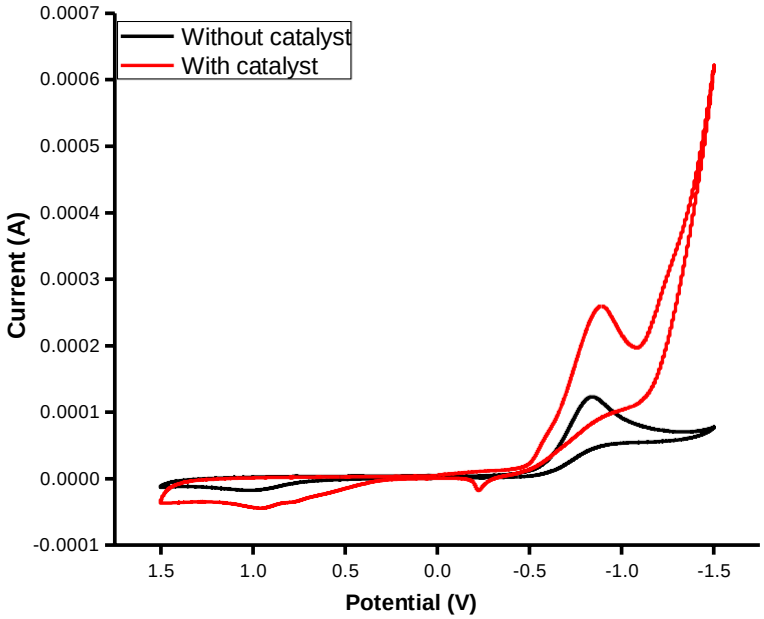


Fig. 4.4 increase in current on acid addition with catalyst(red) and without catalyst(black) 0.1M TBAHFP/ACN

Addition of acetic acid at various concentrations shifts the reduction potential of $Cu^{II/I}$ from -0.69 to 0.99V and there is generation of catalytic cathodic current at -1.3V with shift of potential of 1.6V.with increase in concentration of acid the current increases continuously and at 90mM it shows saturation and current starts decreasing means reaction becomes acid independent at this concentration. The values for $Cu^{II/I}$ i_p is 2.6×10^{-4}A at i_{cat} 10.53×10^{-4}A calculated from the acid independent region. The maximum value of i_{cat}/ip is 4.05 giving TOF $3.15s^{-1}$

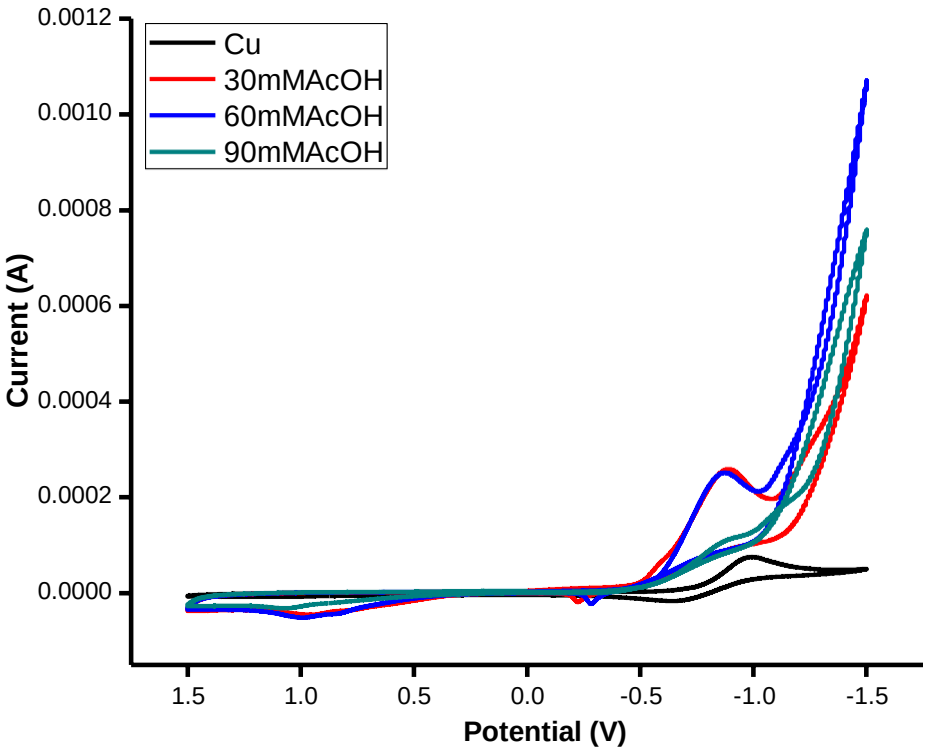


Fig.4.5 Change in cathodic current with increasing acetic acid concentration

NOTE

The current polarity of above all voltammograms are opposite than as shown.

4.2.3 Parameters Calculated:

1. Diffusion coefficient (D_0)

Slope ≡ $3.4\times10^{-4} = 0.4463FA[cat][(FD_0/RT)]^{0.5}$

A=0.071 cm^2

[cat] = 2×10^{-6} moles/L

F = 96485 C/mole e-

R = ideal gas constant

T = 298 K

$D_0 = 9.4018\times10^{-5}$ cm^2/s

2. **Catalytic current (i_{cat})** =10.53×10^{-4} A

3. **Peak current (i_p)** = 2.6×10^{-4} A

4. i_{cat}/ip = 4.05

5. TOF = $1.94\times\nu\times(i_{cat}/i_p)^2$ ν = 0.1V

= 3.15 s^{-1}

6. Overpotential

The value of overpotential is calculated by using reference of Aaron M Appel [31-32]

$(\eta) = E_{H^+} - E_{cat/2}$

E_{H^+} v/s Fe = -0.028-(0.0591 × 23.51) = -1.41V

Here 23.51 is p_{ka} of acetic acid

Now, $E_{cat/2}$ vs Fc^+/Fc = -1.28-0.04 = -1.32V

Overpotential = $E_{H^+} - E_{cat/2}$ = -1.41-(-1.32) = 0.09 V

CHAPTER 5- CONCLUSION AND FUTURE RECOMMENDATIONS

Conclusion

We have successfully synthesized Schiff-base copper based electrocatalyst as an earth-abundant electrocatalyst. The synthesized complex was characterized by UV-Visible spectroscopy and cyclic voltammetry. UV-Visible spectroscopy confirmed the formation of ligand metal copper complex with maximum absorption at 274 nm and electrochemical studies in the presence of acetic acid showed the complex activity towards hydrogen production in the presence of acid. giving current at lower overpotential of 90mV with TOF of $3.15s^{-1}$. The TOF achieved is low because of metal-ligand interaction as compare to good overpotential value which is due to surrounding environment. This is good approach towards the hydrogen production in environment friendly way without emissions of any harmful pollutants.

Future recommendations

We can confirm the hydrogen production by Cu catalyst by performing GC and can further faradic efficiency can be calculated. Kinetic isotopic effect can also be calculated by using deuterium source and photochemical studies towards hydrogen evolution can be performed by using this catalyst and we can see the efficiency by this method to. By attaching different functional groups to our complex we can study electrochemical properties which will differ efficiency, TOF, overpotential and current according to its selectivity with different groups.

REFERENCES

1. Dincer, I.; Balta, M. T. Potential thermochemical and hybrid cycles for nuclear based hydrogen production. *International Journal of Energy Reseacrch* **2011**, *35*, 123-137.
2. Dincer, I. Green methods of hydrogen production. *International Journal of Hydrogen Energy* **2017**, *37*, 1954-1971.
3. Kudo, A.; Miseki, Y. Heterogenous photocatalyst material for water splitting. *Chemical Society Reviews* **2009**, *38*, 253-278.
4. Kanmani, S.; Preethi, V. Photocatalytic hydrogen production. *Materials Science in Semiconductor Processing* **2013**, *16*, 561-575.
5. Joy, J.; Mathew, J.; George, S. C. Nanomaterials for photoelectrochemical water splitting. *International Journal of Hydrogen Energy* **2018**, *43*, 4804-4817.
6. Lei, J. M.; Luo, S. P.; Zhan, S. Z.; Wu, S. P. A nickel(II) complex of S,S bis(2-pyridylmethyl)-1,2-thioethane a cocatalyst for photochemical driven hydrogen evolution from water under visible light. *Inorganic Chemistry Communications* **2018**, *95*, 158-162.
7. Binobaid, A.; Iglesias, M.; Beetsta, D. J.; Karuiki, B.; Dervisi, A.; Fallis, I. A.; Cavell, K. J. Expanded ring and functionalized expanded ring N heterocyclic carbenes as ligands in catalysis. *Dalton Transactions* **2009**, *35*, 7009-7112.
8. Thauer, R. K. Hydrogenases and the global hydrogen cycle. *European Jourrnal of Inorganic Chemistry* **2014**, *114*, 4081-4148.
9. Schilter, D.; Camara, J. M.; Huynh, M. T.; Hammes-Schiffer, S.; Rauchfuss, T. B. Hydrogenase enzymes and their synthetic models: the role of metal hydrides. *Chemical Review* **2016**, *116*, 8693-8749.
10. Khusnutdinova, D.; Wadsword, B. L.; Flores, M.; Beiler, A. M.; Cruz, E. A. R.; Zenkov, Y.; Moore, G. F. Electrocatalytic properties of binuclear Cu(II) fused pophyrins for hydrogen evolution. *ACS Catalysis* **2018**, *8*, 9888-9898.
11. Jugder, B. E.; Welch, J.; Aguey. Zinsou, K. F.; Marquis, C. P. Fundamental and electrochemical applications of [Ni-Fe] uptake hydrogenases. *RSC Advances* **2013**, *3*, 8142.

12. Acar, C.; Dincer, I. Science direct comparative assessment of hydrogen production methods for renewable and non-renewable sources. *International Journal of Hydrogen Energy* **2013**, *39*, 1-12.
13. Lv, H.; Ruberu, T. P. A.; Fleischauer, V. E.; Brennessel, W. W.; Neidig, M. L.; Eisenberg, R. Catalytic light driven generation of hydrogen from water and iron dithiolene complexes. *Journal of American Chemical Society* **2016**, *38*, 11654-11663.
14. Das, A.; Han, Z.; Brennessel, W. W; Holland, P. L.; Eisenberg, R. Nickel complex for robust light driven and electrocatalytic hydrogen production from water. *ACS Catalysis* **2015**, *5*, 1397-1406.
15. Inoue, S.; Mitsuhashi, M.; Ono, T.; Yan, Y. N.; Kataoka, Y.; Handa, M.; Kawamoto, T. Photo and electrocatalytic hydrogen production using valence isomers of N_2S_2 type nickel complex. *ACS Inorganic Chemistry* **2017**, *56*, 12129-12138.
16. Peng, Q. X.; Xue, D.; Yang, L. F.; Zhan, S. Z. A coordinatively saturated cobalt complex as a new kind catalyst for efficient electro- and photo-catalytic hydrogen production in purely aqueous media. *International Journal of Hydrogen Energy* **2017**, *42*, 16428-16435.
17. Thoi, V. S.; Karunadasa, H. I.; Surendranath, Y.; Long, J. R.; Chang, C. J.; Electrochemical generation of hydrogen from acetic acid using molecular molybdenum. *Journal of Energy and Environment Science* **2012**, *5*, 7762-7770.
18. Du, J.; Wang, J.; Ji, L.; Xu, X.; Chen, Z. A highly and robust copper based electrocatalyst towards hydrogen evolution reaction with low overpotential in neutral solution. *ACS Application of Material Interfaces* **2016**, *8*, 30205-30211.
19. Dempsey, J. L.; Brunschwig, B. S.; Winkler, J. R; Gray, H. B. Hydrogen evolution catalyzed by cobaloximes. *Accounts of Chemical Research* **2009**, *42*, 1995-2004.
20. McCrory, C. C. L.; Uyeda, C.; Peters, J. C. Electrocatalytic hydrogen evolution in acidic water with molecular cobalt tetraazamacrocycles. *Journal of American Chemical Society* **2012**, *134*, 3164-3170.
21. Haddad, A. Z.; Garabato, B. D.; Kozlowski, P. M.; Buchanan, R. M.; Grapperhaus, C. A. Beyond metal-hydrides non transition metal and metal free ligand centered electrocatalytic hydrogen evolution and hydrogen oxidation. *Journal of the American Chemical Society* **2016**, *138*, 7844-7847.

22. Haddad, A. Z.; Kumar, D.; Sampson, K. O.; Matzner, A. M.; Mashuta, M. S.; Grapperhaus, C. A. Proposed ligand centered electrocatalytic hydrogen evolution and hydrogen oxidation at a noninnocent mononuclear metal thiolate. *Journal of American Chemical Society* **2015**, *137*, 9238-9241.
23. Haddad, A. Z.; Cronin, S. P.; Mashuta, S. P.; Buchanan, R. M.; Grapperhaus, C. A. Metal assisted ligand centered electrocatalytic hydrogen evolution upon reduction of a bis(thiosemicarbazonato) Cu(II) complex. *Inorganic Chemistry* **2017**, *56*, 11254-11265.
24. Cao, J. P.; Fang, T.; Fu, L. Z.; Zhou, L. L.; Zhan, S. Z. First mononuclear copper(II) electrocatalyst for catalyzing hydrogen evolution from acetic acid and water. *International Journal of Hydrogen Energy* **2014**, *39*, 13972-13978.
25. Cao, J. P.; Fang, T.; Fu, L. Z.; Zhou, L. L.; Zhan, S. Z. A nickel molecular electrocatalyst for generating hydrogen from acetic acid and water. *International Journal of Hydrogen Energy* **2014**, *39*, 10980-10986.
26. Hong, D.; Tsukakoshi, Y.; Kotani, H.; Ishizuka, T.; Ohkubo, K.; Shiota, Y.; Yoshizawa, K.; Fukuzumi, S.; Kojima, T. Mechanistic insights into homogeneous electrocatalytic and Photocatalytic hydrogen evolution catalyzed by high spin high spin Ni(II) complexes with S_2N_2 type tetradentate ligands. *Inorganic Chemistry* **2018**, *87*, 7180-7190.
27. Khandelwal, S.; Zamader, A.; Nagayach, V.; Dolui, D.; Mir, A. Q.; Dutta, A. Inclusion of peripheral basic groups activates dormant cobalt based molecular complexes for catalytic hydrogen evolution in water. *ACS Catalysis* **2019**, *9*, 2334-2344.
28. Liu, S.; Xin, Z. J.; Lei, Y. J.; Yang, Y.; Yan, X. Y.; Lu, Y. B.; Li, C. B.; Wang, H. Y. Thin copper based film for efficient electrochemical hydrogen production from neutral aqueous solutions. *ACS Sustainable Chemistry and Engineering* **2017**, *5*, 7496-7501.
29. Wilson, A. D.; Newell, R. H.; McNevin, M. J.; Muckerman, J. T.; DuBois, M. R.; Dubois, D. L. Hydrogen oxidation and production using Nickel-based molecular catalysts with positioned proton relays. *Journal of American Chemical Society* **2006**, *128*, 358−366.

30. Karunadasa, H. I.; Chang, C. J.; Long, J. R. A molecular molybdenum oxo catalyst for generating hydrogen from water. *International Journal of Science* **2010**, *464*, 1329-1333.
31. Kutt, A.; Leito, I.; Kaljurand, I.; Soovali, L.; Vlasov, V. M.; Yagupolskii, L. M.; Koppel, I. A. Extension of the self-consistent spectrophotometric basicity scale in acetonitrile to a full span of 28 pKa units: unification of different basicity scales. *Journal of Organic Chemistry* **2006**, *71*, 2829-2833.
32. Appel, A. M.; Helm, M. L. Determination of overpotential of molecular catalyst. *ACS Catalysis* **2014**, *4*, 630-633.

M.Sc. Thesis

ORIGINALITY REPORT

15%	6%	6%	8%
SIMILARITY INDEX	INTERNET SOURCES	PUBLICATIONS	STUDENT PAPERS

PRIMARY SOURCES

1	www.biotecharticles.com Internet Source	2%
2	Jie-Ping Cao, Ting Fang, Ling-Zhi Fu, Ling-Ling Zhou, Shuzhong Zhan. "A nickel molecular electro-catalyst for generating hydrogen from acetic acid or water", International Journal of Hydrogen Energy, 2014 Publication	1%
3	Submitted to Higher Education Commission Pakistan Student Paper	1%
4	patents.justia.com Internet Source	1%
5	Submitted to The University of Manchester Student Paper	1%
6	Submitted to Savitribai Phule Pune University Student Paper	1%
7	Jillian L. Dempsey, Bruce S. Brunschwig, Jay R. Winkler, Harry B. Gray. "Hydrogen Evolution	1%

Jemini

Davinder Kumar